PYROLYSIS PRODUCT COMPOSITION COMPRISING CHAR PARTICLES

FIELD OF THE INVENTION

The present invention relates to a pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles dispersed therein, to a process for the production of a solid pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles dispersed therein and to a pyrolysis system configured to convert a mixture of char particles and hydrocarbons resulting from pyrolysis of plastic waste material into a product in the form of solid particles.

BACKGROUND OF THE INVENTION

Large quantities of waste plastics are generated in the present society. While recycling of plastics is becoming ever more efficient and effective, it is still the case that much of the waste plastic cannot be effectively or efficiently recycled and is disposed to landfill sites where it takes many years to degrade, or it is incinerated. Even worse, it may be lost to the environment where it can be damaging to ecosystems.

Plastic materials can however be converted for reuse. For example, fuels such as diesel may be derived from waste plastics, or waste plastics may be converted to raw materials suitable for synthesis of new materials, such as new plastics, other hydrocarbon materials, or similar. Materials recovered from waste plastics may be useful to at least partially replace hydrocarbons obtained from fossil sources.

In plastic-to-chemical plants, waste plastics, typically mostly comprising polyethylene and polypropylene from domestic sources, form the input. These waste plastics that are made up of very long chain hydrocarbons are then cracked into shorter chains forming a wide spectrum of molecules with a variety of chain lengths. The resulting mixtures can be distilled into various fractions, typically including light hydrocarbons (LHC), heavy hydrocarbons (HHC), char particles and non-condensables (gases). Currently, LHC, HHC, or mixtures thereof, are the most desirable products, however, this is market dependent.

As used herein, the term '*char particles*' refers to the solid carbonaceous material remaining after a plastic feed stream has been pyrolyzed. It is known that certain plastic compositions yield char in higher amounts than others. Rigid plastics and aromatic-molecule-containing plastics, such as PVC, PET, PS and acrylonitrile butadiene styrene for example, tend to result in more char than polyethylene and polypropylene at comparable processing conditions. Moreover, non-plastic contaminants that may be present in plastic waste streams, such as food, wood and paper, and additives typically present in plastics, such as fillers, flame retardants and colorants, all have an influence on the amount of the char formed during pyrolysis and can be part of this char. As is generally known to the skilled person, no matter how efficient the pyrolysis process is performed and irrespective of the composition of the feedstock, always some char particles are formed. These char particles are typically considered a

byproduct of less value than the pyrolysis liquids (LHC and HHC) which are the target products. Nevertheless, commercial applications for char particles resulting from pyrolysis have been found.

A known process in the art for converting waste plastic to, among other things, diesel, is the thermochemical breakdown process of pyrolysis. Pyrolysis is the thermal decomposition of material in an inert atmosphere, i.e. in the absence of oxygen. In effect, the long polymer chains of the plastic's polymers are cracked through heating, resulting in shorter hydrocarbon chains, which are generally more useful as a product. Various attempts to provide technically and cost-effective processes for pyrolysis of waste plastic have been attempted previously.

Batch-type pyrolysis processes are typically performed to such extent that only char particles are remaining in the reactor at the end of the pyrolysis reaction. At the end of the pyrolysis reaction, these char particles can then be removed from the reactor as a powder. In this respect, reference is made to WO2011/077419A1. In a batch process, char particles are removed from the bottom of the reactor after each reaction cycle. Batch operation is in many circumstances undesired. Operators require multiple reaction trains to avoid production interruption, and schedules become complex. Batch operation can also contribute to variations in product quality over time unless a large number of parallel trains are used in a staggered schedule. Operating in this way adds both capital and operating cost.

In continuous pyrolysis processes, it is not possible to proceed with the pyrolysis reaction until only char particles are remaining in the pyrolysis reactor. In a continuous pyrolysis process, fresh feed to be pyrolysed is continuously supplied to the pyrolysis reactor and pyrolysis products, including condensable and non-condensable gases and char particles, are continuously removed from the pyrolysis reactor. This means that during a continuous pyrolysis process, materials which are cracked to a variety of degrees and char particles with a variety of sizes are simultaneously present. It is therefore not possible to continuously discharge a bottom fraction of char particles without also discharging at least some liquid hydrocarbon material. Discharging a mixture of char particles and liquid hydrocarbon material results, without further work-up, in a process with a lower efficiency because the yield of the commercially most relevant streams, *i.e.* the liquid hydrocarbons, decreases. Hence, the current challenges in developing continuous pyrolysis processes include amongst others improving the yield of the process by minimizing char production and by efficiently separating char particles from liquid hydrocarbons.

Technically useful results have been achieved by the technologies discussed in patent publications US2018/0010050A1, WO2021/053139A1 and US2022/0204861A1, the contents of which publications are incorporated herein by reference.

US2018/0010050A1 discloses a method and system for recovering hydrocarbons from plastic waste with reduced caking and coke formation. The process involves melting the plastic waste in two heating devices **3** and **4** and mixing a recycle stream **10** derived from a cracking reactor **5** with the incoming molten plastic waste of the first heating device **3**. The heated, molten plastic from the second heating device **4** is passed to the cracking reactor **5** where the plastic materials are cracked. Subsequent

thereto, the resulting short-chain hydrocarbons are removed via the top side of the cracking reactor and are distilled into diesel and light boilers. A stream of high-energy pitch- and tar-like substances that have not assumed the gaseous state, non-meltable solid impurities and excess carbon that results during the cracking of polymers is collected in the sump of the cracking reactor **5**, is continuously discharged from the bottom part of the cracking reactor **5** by means of a high-temperature pump and is supplied to a separator system, such as a cyclone separator **8** connected to a sedimentation tank **9**, wherein bigger particles are separated off. The residual stream **10** comprising high-energy pitch- and tar-like substances that have not assumed the gaseous state and optionally smaller particles is returned to the cracking reactor **5** via the second heating device **4**. Recycle stream **10** is described to bring about continuous intermixing in the cracking reactor **5**, making additional agitation unnecessary. It is described that the separator system results in a separated higher-density phase containing the solids that is removed and may be used as high-energy fuel.

US2022/0204861A1 discloses a process and a reactor system for pyrolysis of a mixed plastic stream that contains PVC. The reactor system comprises a melting reactor and a pyrolysis reactor having a cylindrical geometry and comprising an internal cylinder, such that an annular space is formed between the reactor wall and the internal cylinder. The pyrolysis reactor has a conical bottom part. It is described that the process using the reactor system provides a continuous pyrolysis operation and solid separation. The melting reactor melts the waste plastics and produces a first vapor stream **2** and a first liquid stream **3**. The first liquid stream **3** is fed to the pyrolysis reactor where it is cracked, resulting in a second vapor, a second liquid and solid particles. It is described that a portion **8** of the pyrolysis reactor liquid is circulated and that part **10/11** of it is heated in a heater system where all heat needed to sustain the main cracking reaction is provided and that the remaining part **9** is directly sent to the melting reactor to sustain melting reaction needs. Heated recirculated stream **11** is fed back into the pyrolysis reactor in a tangential direction in the annular space resulting in a swirl-like movement of the reactor contents along the cylindrical reactor wall. The reactor system does not apply a physical mixer. During the pyrolysis reaction, char particles are produced that settle along the circular wall area down to the bottom of the pyrolysis reactor together with metal particles. Metal and large char particles are collected and discharged as a residue, which residue amounts to 2-15 % of the weight of the first liquid stream fed from the melting reactor to the pyrolysis reactor. It is described that this residue is discharged '*as a mix of liquid and solid that may not have high profit such as it is considered a byproduct*'.

WO2021/053139A1 discloses a method for breaking down long-chain hydrocarbons from plastic-containing waste with limited carbonization of the hydrocarbons, said method comprising providing material containing long-chain hydrocarbons, subjecting the material to heating in a heating structure **11** followed by separation in a separation structure **12**. The heating structure **11** typically comprises more than one serial heating zones with increasing temperatures in the downstream direction. The material leaving the last heating zone and entering separation structure **12** contains both long-chain hydrocarbons and cracked hydrocarbons. The separation structure **12** comprises a cylinder-shaped

intermediate portion containing a separation zone, and a funnel shaped bottom portion containing a settling zone with the funnel ending in an outlet for heavy hydrocarbons and/or solid carbons. Part of the hydrocarbon liquid formed in separation structure **12** is discharged from and recycled to the separation structure **12** via a reheating zone **6**. It is disclosed in WO2021/053139A1 that the reheated hydrocarbon liquid can be mixed with the material exiting the last heating zone before feeding it to the separation structure **12**. The heavy hydrocarbons and/or solid carbons are released via a valve structure **13** and can enter a lock chamber **34**. The heavy hydrocarbons and/or solid carbons in lock chamber **34** are above their ignition temperature and need to be cooled prior to contacting air. It is therefore suggested to feed the heavy hydrocarbons and/or solid carbons into a cooling chamber to be cooled prior to being released.

J. Baena-González *et al.*, *Waste Management*, 118 (2020), pp 139-149, disclose pyrolysis of plastic waste, resulting in a (a) volatile fraction that is partly condensed to obtain pyrolysis oil and non-condensable gas and (b) an undefined solid fraction. The pyrolysis oil - not the solid fraction - was treated using distillation to determine its composition, resulting in a distillate and a bitumen which solidified upon cooling. It is described that the composition of the bitumen was determined by S.A.R.A. analysis resulting in 55.05 wt% saturated compounds, 33.41 wt% aromatic compounds, 4.62 wt% resins and 6.91 wt% asphaltenes. J. Baena-González *et al.* do not disclose a bituminous hydrocarbon fraction comprising char particles, let alone a bituminous hydrocarbon fraction and char particles dispersed within said bituminous hydrocarbon fraction, wherein the weight ratio of the bituminous hydrocarbon fraction to the char particles is defined.

Y. Yang *et al.*, *Journal of Cleaner Production*, 187 (2018), pp 390-399, disclose pyrolysis of the organic fraction of municipal solid waste, resulting in a char fraction and a pyrolysis liquid that is obtained after condensing the condensable part of the pyrolysis vapour. Figure 1 of Y. Yang *et al.* discloses a pyrolysis system (1) comprising a pyrolysis vapour outlet (7) in fluid connection with a condenser (11) and a char outlet/char pot (9). The pyrolysis liquid is described to have a solids content (> 1 μm particles) of 19.3 wt%. The authors state that there are two sources that can contribute to the solids content in the pyrolysis oil: (a) fine char and ash particles flowing with the hot pyrolysis vapour to the downstream process and (b) heavy organics that tend to agglomerate when condensed. Y. Yang *et al.* provide contradictory statements concerning the rheological properties of the pyrolysis oil. Figure 5 of Yang *et al.* discloses the viscosity of the pyrolysis oil as a function of temperature and at different undefined shear rates. The units of the viscosities appear to be Pa·s. Figure 7 discloses the viscosity of the pyrolysis oil as a function of shear rate at different temperatures. The units of the viscosities appear to be cP (=mPa·s). A comparison between the data presented in Figures 5 and 7 reveals that the curves match, meaning that either the units Pa·s in Figure 5 are incorrect or the units cP in Figure 7. Given the fact that the fraction is called a pyrolysis '*liquid*' or pyrolysis '*oil*' and that its liquid fraction concerns a condensed vapour, the correct units are cP, meaning that the pyrolysis oil has a viscosity at 40 °C and

a shear rate of 20 s^{-1} of 2000 cP (mPa.s) and a viscosity at 40 °C and a shear rate of 1 s^{-1} of ~10000 mPa.s. Accordingly, the pyrolysis oil is not a solid at temperatures up to 35 °C.

None of US2018/0010050A1, WO2021/053139A1 and US2022/0204861A1 discloses the composition of the mixture of char particles, non-meltable solid impurities and liquid hydrocarbons that is discharged from the pyrolysis reactor. As will be appreciated by those skilled in the art, this mixture of char particles, non-meltable solid impurities and liquid hydrocarbons is typically disposed of and incinerated. Since this mixture is typically fluid-like and sticky, it is often difficult to handle and its disposal, including transportation to the incineration site, involves significant costs.

It is therefore an object of the invention to provide a process and a corresponding system for converting a mixture of char particles and hydrocarbons resulting from pyrolysis of plastic waste into a product with improved handleability and/or processability.

It is a further object of the invention to provide mixtures of char particles and hydrocarbons resulting from pyrolysis of plastic waste with improved handleability and/or processability.

SUMMARY OF THE INVENTION

The inventors have unexpectedly found that only specific pyrolysis product compositions provide a transition between liquid and solid character at advantageous temperatures. More in particular, it was found that if the '*liquid*' pyrolysis product composition accumulated in the bottom part of the pyrolysis reactor comprises too much char particles, e.g. 90 wt% or more, based on the weight of the pyrolysis product composition, continuous discharging from the pyrolysis reactor and subsequent cooling under agitation to provide a cooled '*liquid*' pyrolysis product composition is not or hardly feasible because of the high viscosity. On the other hand, it was found that if the pyrolysis product composition accumulated in the bottom part of the pyrolysis reactor comprises a too low amount of char particles, e.g. 5 wt% or less, based on the weight of the pyrolysis product composition, the pyrolysis product composition does not result in a product that is sufficiently solid up to temperatures of 35 °C.

Accordingly, in a first aspect, a pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles dispersed within said bituminous hydrocarbon fraction is provided, wherein the bituminous hydrocarbon fraction and the char particles together constitute at least 70 wt% of the pyrolysis product composition, wherein the bituminous hydrocarbon fraction and the char particles are present in a weight ratio of between 1 : 1 and 9 : 1, and wherein said composition is a liquid at a temperature between 120 and 230 °C and is a solid at temperatures up to 35 °C.

In a second aspect, the invention provides a process for the production of a pyrolysis product composition according to the first aspect in the form of a solid, said process comprising the steps of:

(a) providing a stream (1a) of, preferably liquid, plastic waste material to a pyrolysis reactor (1);

(b) pyrolyzing the, preferably liquid, plastic waste material at a temperature of between 350 and 600 °C in the pyrolysis reactor (1) resulting in gaseous hydrocarbon material, liquid hydrocarbon material and char particles, said liquid hydrocarbon material comprising a bituminous hydrocarbon fraction;

(c) discharging a liquid pyrolysis product composition (1b) having a temperature of between 350 and 600 °C and comprising a bituminous hydrocarbon fraction and char particles dispersed within said bituminous hydrocarbon fraction from a bottom outlet of the pyrolysis reactor (1) to a cooling section (2); and

(d) cooling the liquid pyrolysis product composition (1b) in the cooling section (2) to obtain a solid pyrolysis product composition (2b), wherein said bituminous hydrocarbon fraction and the char particles together constitute at least 70 wt% of the pyrolysis product composition, wherein the bituminous hydrocarbon fraction and the char particles are present in a weight ratio of between 1 : 1 and 9 : 1, and wherein said composition is a liquid at a temperature between 120 and 230 °C and is a solid at temperatures up to 35 °C.

In a third aspect, the invention provides a pyrolysis system configured to convert a mixture of char particles and hydrocarbons, the mixture resulting from pyrolysis of plastic waste material into a product in the form of solid particles, said system comprising:

(i) a pyrolysis reactor (1) with an inlet (1a) configured to receive, preferably liquid, plastic waste material, a bottom outlet (1b) configured to discharge a liquid pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles dispersed therein and a top outlet (1c) configured to discharge pyrolysis gases; and

(ii) a cooling section (2) having an inlet (2a) in fluid communication with the bottom outlet (1b) of the pyrolysis reactor (1) via a valve or pump (5a), wherein said cooling section (2) comprises a cooling vessel (2A) and a cooling device (2B) downstream thereof, wherein said cooling device (2B) is in fluid communication with cooling vessel (2A) via a pump (5e), wherein said cooling vessel (2A) comprises means to agitate its contents and is configured to be operated under an inert atmosphere, and wherein said cooling device (2B) is a device configured to produce solid particles from a melt.

DEFINITIONS

The terms '*char (particles)*' and '*coke (particles)*' as used herein are used interchangeably and concern the solid mostly carbonaceous material remaining after a plastic waste feed stream has been pyrolyzed. In addition to carbonaceous material, these particles can also contain non-combustible components (ash).

The term '*autoignition temperature*' as used herein in the context of a composition refers to the minimum temperature at which self-sustaining combustion in air, independent of the heating source,

takes place. The autoignition temperature as used herein is measured in accordance with ASTM E659-15:2023.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 depicts flow schemes of the process according to the second aspect. Figures 2-5 depict flow schemes of embodiments of the process according to the second aspect. Figures 3-5 depict embodiments of the pyrolysis system according to the third aspect.

The reference numerals in the figures have the meanings indicated below:

(1) pyrolysis reactor; (2) cooling section; (2A) cooling vessel; (2B) cooling device; (3) equalization vessel; (4) heating section, (4A, 4B, ...) heating units; (5a), (5b), (5f) and (5i) valves or pumps; (5c) and (5d) valves; (5e) and (5g) pumps; and (5h) heater.

In the context of the process according to the second aspect, the additional numerals in the figures have the following meanings:

(1a) stream of, preferably liquid, plastic waste material supplied to the pyrolysis reactor (1);

(1b) liquid pyrolysis product composition discharged from the bottom outlet of the pyrolysis reactor (1);

(1b') part of the liquid pyrolysis product composition (1b) discharged from the bottom outlet of the pyrolysis reactor (1) that is fed to the cooling section (2);

(1b'') part of the liquid pyrolysis product composition (1b) discharged from the bottom outlet of the pyrolysis reactor (1) that is recycled to the pyrolysis reactor (1);

(1c) stream of pyrolysis gases (1c) discharged via a top outlet of the pyrolysis reactor (1);

(1d) recycle stream of volatile parts to the top of the pyrolysis reactor (1);

(1e) part of the hydrocarbon liquid formed in the pyrolysis reactor (1) that is discharged from the pyrolysis reactor (1);

(1e') part of (1e) that is heated and directly recycled to the pyrolysis reactor (1);

(1e'') part of (1e) that is heated and recycled to the pyrolysis reactor (1) after combination with stream (4b);

(2a) feed of the liquid pyrolysis product composition to the cooling system (2), in particular to the cooling vessel (2A);

(2b) solid pyrolysis product composition formed in the cooling section (2), in particular in the cooling device (2B);

(2c) stream of volatile parts discharged from the cooling system (2), in particular from the cooling vessel (2A);

(2d) cooled liquid pyrolysis product composition discharged from cooling vessel (2A);

(2d') part of (2d) fed to cooling device (2B);

(2d'') part of (2d) recycled to cooling vessel (2A);

(3a) liquid pyrolysis product composition discharged from the bottom outlet of the pyrolysis reactor (1) and fed to equalization vessel (3);

(3b) liquid pyrolysis product composition discharged from the bottom outlet of the equalization vessel (3);

(3c,3c') pressure compensation line, stream of volatile parts to the top of the pyrolysis reactor (1);

(4a) plastic waste material; and

(4b) degassed and molten plastic waste material;

In the context of the pyrolysis system according to the third aspect, some additional numerals in the figures have the following meanings:

(1a) inlet configured to receive a, preferably liquid, plastic waste material;

(1b) bottom outlet configured to discharge a liquid pyrolysis product composition from the pyrolysis reactor (1);

(1c) top outlet configured to discharge pyrolysis gases from the pyrolysis reactor (1);

(1d) top inlet of the pyrolysis reactor (1);

(2a) inlet of the cooling system (2), in particular of the cooling vessel (2A);

(2b) outlet of the cooling system (2), in particular of the cooling device (2B);

(3a) inlet of equalization vessel (3);

(3b) bottom outlet of equalization vessel (3);

(3c) top outlet of equalization vessel (3), pressure compensation line;

(4a) inlet heating section (4); and

(4b) outlet heating section (4).

DETAILED DESCRIPTION

Pyrolysis product composition comprising char particles

In a first aspect, the invention concerns a pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles dispersed within said bituminous hydrocarbon fraction, wherein the bituminous hydrocarbon fraction and the char particles together constitute at least 70 wt% of the pyrolysis product composition, wherein the bituminous hydrocarbon fraction and the char particles are present in a weight ratio of between 1 : 1 and 9 : 1, and wherein said composition is a liquid at a temperature between 120 and 230 °C and is a solid at temperatures up to 35 °C.

The weight ratio of the bituminous hydrocarbon fraction and the char particles in the pyrolysis product composition can be determined by subjecting the pyrolysis product composition to batchwise pyrolysis at 440 °C until no vapor is obtained anymore. During this batchwise pyrolysis at 440 °C, the absolute weight of the char particles remains rather constant, whereas the volatile pyrolysis products of the bituminous fraction are separately collected. Based on the initial weight of the pyrolysis product

composition and the weight of the fraction remaining after batchwise pyrolysis at 440 °C until no vapor is obtained anymore, the weight ratio of the bituminous hydrocarbon fraction and the char particles in the pyrolysis product composition can be calculated.

The first aspect concerns a pyrolysis product composition. The wording '*pyrolysis product composition*' indicates that it concerns a product of a pyrolysis process instead of a composition that is (yet) to be subjected to pyrolysis. In a preferred embodiment, the pyrolysis product composition is a product resulting from pyrolysis of a plastic waste stream, more preferably a product resulting from pyrolysis of a plastic waste stream comprising polyethylene (PE) and/or polypropylene (PP) plastics. Preferably, the sum of polyethylene and polypropylene in the plastic waste stream is at least 50 wt% by weight of the plastic waste stream, more preferably at least 60 wt%, still more preferably at least 75 wt%, most preferably at least 90 wt%. The preferred plastic for the plastic waste stream is polyethylene or polypropylene. The plastic waste stream may also comprise polyvinylchloride (PVC) plastics, however, the level of PVC is preferably limited to less than 10 wt% by weight of the plastic waste stream, preferably less than 5 wt%. The plastic waste stream may also comprise polyethylene terephthalate (PET) plastics, preferably in an amount greater than 3 wt% by weight of the plastic waste stream, more preferably greater than 4 wt%. The plastic waste stream preferably comprises less than 20 wt% PET plastic. The plastic waste stream may comprise up to 100 wt% polystyrene (PS) plastics by weight of the plastic waste stream. In embodiments, the plastic waste stream may comprise at least 5 wt%, more preferably 20 wt%, more preferably 50 wt% polystyrene by weight of the plastic waste stream.

In pyrolysis processes wherein additional sources of hydrogen are not provided, or are not provided in adequate quantities, a substantial portion of solid carbonaceous material is produced, also called char or coke particles. This is at least partly because of a shortage of available hydrogen atoms to complete the newly generated shorter unsaturated hydrocarbon chains. This generation of char or coke particles is common to pyrolysis.

As described hereinbefore, in continuous pyrolysis processes, it is not possible to proceed with the pyrolysis reaction until only solid char particles are remaining in the pyrolysis reactor. During a continuous pyrolysis process, materials which are cracked to a variety of degrees and char particles with a variety of sizes are simultaneously present in the pyrolysis reactor. It is therefore not possible to continuously discharge a bottom fraction of char particles from the pyrolysis reactor without also discharging at least some liquid hydrocarbon material. Since condensable and non-condensable pyrolysis gases produced during the pyrolysis reaction are continuously removed from the pyrolysis reactor, the hydrocarbon fraction in the bottom fraction is typically enriched in a heavier fraction of organic compounds (e.g. complexes of hydrocarbons or very large hydrocarbons) and inorganic compounds that cannot or can hardly be pyrolyzed. These compounds are not removable or very

difficult to remove from the pyrolysis process as condensable or non-condensable pyrolysis gases and thus accumulate within the pyrolysis reactor if not removed continuously or at regular time intervals. The density of the char particles is typically higher than that of the pyrolyzing plastic, and so a dense mixture of char particles may tend to accumulate, *i.e.* in the bottom part of the pyrolysis reactor, due to settling and/or separation based on an imposed liquid flow pattern of the reactor contents. Although being enriched in non-pyrolysable materials, the hydrocarbon fraction in the bottom fraction also comprises pyrolysable material, such as partly pyrolyzed liquid hydrocarbons. Since the hydrocarbon fraction in the bottom fraction is enriched in a heavier fraction of organic compounds (e.g. complexes of hydrocarbons or very large hydrocarbons), this hydrocarbon fraction is called the bituminous hydrocarbon fraction in the context of the invention.

As will be appreciated by those skilled in the art, the bituminous hydrocarbon fraction is to a large extent responsible for the transition between liquid and solid character of the pyrolysis product composition at advantageous temperatures, because the char particles remain solid at temperatures between 120 and 230 °C. Nevertheless, the inventors have found that the presence of too much char particles or too low an amount of char particles in the pyrolysis product composition adversely affects the transition between liquid and solid character of the pyrolysis product composition and/or the processability. More in particular, it was found that if the '*liquid*' pyrolysis product composition accumulated in the bottom part of the pyrolysis reactor comprises too much char particles, e.g. 90 wt% or more, based on the weight of the pyrolysis product composition, continuous discharging from the pyrolysis reactor and subsequent cooling under agitation to provide a cooled '*liquid*' pyrolysis product composition is not or hardly feasible because of the high viscosity. On the other hand, it was found that if the pyrolysis product composition accumulated in the bottom part of the pyrolysis reactor comprises a too low amount of char particles, e.g. 5 wt% or less, based on the weight of the pyrolysis product composition, the pyrolysis product composition does not result in a product that is sufficiently solid up to temperatures of 35 °C.

In a preferred embodiment, the bituminous hydrocarbon fraction and the char particles together constitute at least 90 wt% of the pyrolysis product composition, preferably at least 95 wt%, more preferably at least 98 wt%, most preferably at least 99 wt%.

As already indicated, it was found that the weight ratio of the bituminous hydrocarbon fraction to the char particles is important to maintain a sufficiently liquid character during cooling to temperatures of between 120 and 230 °C in a stirred vessel and to obtain sufficiently solid character at temperatures up to 35 °C such that the composition can be converted to solid particles, such as pellets or flakes.

In a preferred embodiment, the bituminous hydrocarbon fraction and the char particles are present in a weight ratio of between 1.5 : 1 and 3 : 1, more preferably in a weight ratio of between 1.7 : 1 and 2.3 : 1.

The pyrolysis product composition according to the first aspect is liquid at a temperature between 120 and 230 °C. In an embodiment, the pyrolysis product composition according to the first aspect is liquid at a temperature between 120 and 230 °C and at atmospheric pressure.

In a preferred embodiment, the pyrolysis product composition has a viscosity of between 1 and 2000 mPa·s at a temperature between 120 and 230 °C and at a shear rate of 100 s^{-1}, as measured with a coaxial cylinder geometry (CC10) and in accordance with ISO 3219-2:2021, preferably between 10 and 1000 mPa·s, more preferably between 15 and 500 mPa·s.

In another preferred embodiment, the pyrolysis product composition as defined hereinbefore has a viscosity of between 2 and 400 mPa·s at a temperature of 230 °C and at a shear rate of 100 s^{-1}, as measured with a coaxial cylinder geometry (CC10) and in accordance with ISO 3219-2:2021, preferably between 5 and 200 mPa·s, more preferably between 10 and 50 mPa·s.

In yet another preferred embodiment the pyrolysis product composition as defined hereinbefore has a viscosity of between 40 and 1800 mPa·s at a temperature of 120 °C and at a shear rate of 100 s^{-1}, as measured with a coaxial cylinder geometry (CC10) and in accordance with ISO 3219-2:2021, preferably between 60 and 1000 mPa·s, more preferably between 80 and 500 mPa·s.

In a very preferred embodiment, the pyrolysis product composition as defined hereinbefore has a viscosity of between 5 and 40 mPa·s at a temperature of 230 °C and at a shear rate of 100 s^{-1} and a viscosity of between 50 and 200 mPa·s at a temperature of 120 °C and at a shear rate of 100 s^{-1}, as measured with a coaxial cylinder geometry (CC10) and in accordance with ISO 3219-2:2021.

The pyrolysis product composition according to the first aspect is a solid at temperatures up to 35 °C. As will be appreciated by those skilled in the art, the wording '*a solid at temperatures up to A °C*' means that the pyrolysis product composition is solid at any temperature below *A* °C and up to *A* °C. In an embodiment, the pyrolysis product composition according to the first aspect is a solid at temperatures up to 35 °C and at atmospheric pressure.

In an embodiment, the solid character of the pyrolysis product composition at temperatures up to 35 °C is characterized by a solidification temperature range that is between 50 and 100 °C, as measured with differential scanning calorimetry (DSC), preferably between 60 and 80 °C.

A pure chemical component has a unique melting point, at a specific pressure such as atmospheric pressure, characterized by a single temperature. Mixtures of chemical components on the other hand typically have a melting point range at a specific pressure. As will be appreciated by those skilled in the art, the bituminous hydrocarbon fraction of the pyrolysis product composition is a complex mixture of many different chemical components.

The concept of melting point range is well known to those skilled in the art. Starting from a solid mixture of chemical components and upon increase of the temperature, the temperature at which melting begins is known as the '*solidus*' whereas the temperature where melting is complete is called the

'*liquidus*'. The range between the solidus and the liquidus is called the melting point range. The term '*solidification temperature range*' as used herein is the opposite of the melting point range. The wording '*a solidification temperature range that is between A and B °C*' as used herein not necessarily means that the solidification temperature range exactly coincides with the range of between *A* and *B* °C, although this is not excluded, but that the liquidus and solidus are within this range.

In a preferred embodiment, the pyrolysis product composition is a solid at temperatures up to 40 °C, more preferably at temperatures up to 45 °C.

Solid character of the pyrolysis product composition can also be defined in terms of '*tan(δ)-values*'. The term '*tan(δ)*', wherein δ is the phase shift, is defined by the ratio G''/G', as is commonly known in the field of rheology. G'' represents the loss modulus and characterizes the viscous character or the liquid-like behaviour of a composition. G' represents the storage modulus and characterizes the elastic character or the solid-like behaviour of a composition. If a composition shows purely viscous behaviour and there is no elastic behaviour, $\delta=90°$, $G'=0$ and $\tan(\delta)=\infty$. If a sample shows purely elastic behaviour and there is no viscous behaviour, $\delta=0°$, $G''=0$ and $\tan(\delta)=0$.

In an embodiment, the pyrolysis product composition is characterized by tan(δ)-values, measured with a rheometer with a plate-plate geometry and a gap distance of 0.5 mm at a temperature of 35 °C, that are lower than 0.3 at oscillatory frequencies between 10 and 0.1 Hz. In a preferred embodiment, the tan(δ)-values, measured with a rheometer with a plate-plate geometry and a gap distance of 0.5 mm at a temperature of 35 °C, are between 0.001 and 0.3, more preferably between 0.01 and 0.2, at oscillatory frequencies between 10 and 0.1 Hz.

In another embodiment, the pyrolysis product composition is characterized by tan(δ)-values, measured with a rheometer with a plate-plate geometry and a gap distance of 0.5 mm at a temperature of 40 °C, that are lower than 0.3 at oscillatory frequencies between 10 and 0.1 Hz. In another preferred embodiment, the tan(δ)-values, measured with a rheometer with a plate-plate geometry and a gap distance of 0.5 mm at a temperature of 40 °C, are between 0.001 and 0.3, more preferably between 0.01 and 0.2 at oscillatory frequencies between 10 and 0.1 Hz.

In yet another embodiment, the pyrolysis product composition is characterized by tan(δ)-values, measured with a rheometer with a plate-plate geometry and a gap distance of 0.5 mm at a temperature of 45 °C, that are lower than 0.3 at oscillatory frequencies between 10 and 0.1 Hz. In a further preferred embodiment, the tan(δ)-values, measured with a rheometer with a plate-plate geometry and a gap distance of 0.5 mm at a temperature of 45 °C, are between 0.001 and 0.3, more preferably between 0.01 and 0.2, at oscillatory frequencies between 10 and 0.1 Hz.

The pyrolysis product composition is characterized in that it contains in addition to char particles a relatively high weight percentage of hydrocarbon material, as part of the bituminous hydrocarbon fraction, that is not (yet) fully pyrolyzed. In other words, the atomic ratio of hydrogen to carbon atoms is relatively high. This relatively high weight percentage of hydrocarbon material that is not (yet) fully

pyrolyzed can be characterized by a calorific value related to full combustion. Hence, in an embodiment, the pyrolysis product composition has a calorific value between 10 and 50 MJ/kg, as measured in accordance with DIN 51900-3:2005, preferably between 20 and 45 MJ/kg.

In an embodiment, the pyrolysis product composition comprises between 40 and 85 wt% carbon and between 10 and 30 wt% hydrogen, based on the weight of the pyrolysis product composition, as determined in accordance with ASTM D5291:2021, and between 1 and 30 wt% ash, based on the weight of the pyrolysis product composition, as determined using thermogravimetric analysis (TGA) in an oxidative atmosphere, preferably between 50 and 82 wt% carbon, between 12 and 25 wt% hydrogen and between 3 and 25 wt% ash, more preferably between 60 and 80 wt% carbon, between 14 and 25 wt% hydrogen and between 5 and 20 wt% ash.

In an embodiment, the char particles in the pyrolysis product composition have a particle size distribution wherein at least 90% of the particles by number have a particle size of between 0.5 and 100 μm, preferably at least 95%, more preferably at least 98%, as determined by optical microscopy in accordance with ISO 4407:2002 and following NAS 1638.

In a preferred embodiment, the char particles in the pyrolysis product composition have a particle size distribution wherein at least 60% of the particles by number have a particle size of between 1 and 25 μm, more preferably at least 70%, even more preferably at least 80%, as determined by optical microscopy in accordance with ISO 4407:2002 and following NAS 1638.

In a preferred embodiment, the char particles in the pyrolysis product composition have a particle size distribution wherein at least 50% of the particles by number have a particle size of between 1.5 and 15 μm, more preferably at least 60%, even more preferably at least 70%, as determined by optical microscopy in accordance with ISO 4407:2002 and following NAS 1638.

In an embodiment, the pyrolysis product composition has a density at a temperature in the range of 180 to 230 °C, as determined in accordance with ASTM D4052:2022, between 750 kg/m^3 and 1300 kg/m^3, preferably between 780 and 1100 kg/m^3, more preferably between 800 and 900 kg/m^3.

In an embodiment, the pyrolysis product composition has a bulk density at 25 °C between 300 kg/m^3 and 750 kg/m^3, such as between 350 and 500 kg/m^3.

In an embodiment, the pyrolysis product composition according to the first aspect is provided in the form of a liquid, *i.e.* having a temperature (and pressure) at which the pyrolysis product composition is liquid. In a preferred embodiment, the pyrolysis product composition according to the first aspect is provided in the form of solid particles, preferably in the form of pellets or flakes.

The solid particles, preferably pellets or flakes, are stable at ambient temperature, are storable and can thus be easily processed and transported.

Process for the production of a solid pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles

In a second aspect, the invention concerns a process for the production of a pyrolysis product composition according to the first aspect in the form of a solid, said process comprising the steps of:

(a) providing a stream (1a) of, preferably liquid, plastic waste material to a pyrolysis reactor (1);

(b) pyrolyzing the, preferably liquid, plastic waste material at a temperature of between 350 and 600 °C in the pyrolysis reactor (1) resulting in gaseous hydrocarbon material, liquid hydrocarbon material and char particles, said liquid hydrocarbon material comprising a bituminous hydrocarbon fraction;

(c) discharging a liquid pyrolysis product composition (1b) having a temperature of between 350 and 600 °C and comprising a bituminous hydrocarbon fraction and char particles dispersed within said bituminous hydrocarbon fraction from a bottom outlet of the pyrolysis reactor (1) to a cooling section (2); and

(d) cooling the liquid pyrolysis product composition (1b) in the cooling section (2) to obtain a solid pyrolysis product composition (2b), wherein said bituminous hydrocarbon fraction and the char particles together constitute at least 70 wt% of the pyrolysis product composition, wherein the bituminous hydrocarbon fraction and the char particles are present in a weight ratio of between 1 : 1 and 9 : 1, and wherein said composition is a liquid at a temperature between 120 and 230 °C and is a solid at temperatures up to 35 °C.

See for example Figures 1 to 5, for process schemes wherein a stream (1a) of, preferably liquid, plastic waste material is pyrolyzed in a pyrolysis reactor (1), wherein a liquid pyrolysis product composition (1b) is discharged from a bottom outlet of the pyrolysis reactor (1), which is subsequently cooled in cooling section (2) to obtain a solid pyrolysis product composition (2b).

The process according to the second aspect is preferably performed in a continuous way. Discharging liquid pyrolysis product composition (1b) from the bottom outlet of the pyrolysis reactor (1) to the cooling section (2) is preferably performed with a valve or pump (5a) which can be operated via a control mechanism. See in this respect for example Figures 1A and 1B.

In a preferred embodiment, part (1b') of the liquid pyrolysis product composition (1b) is discharged to the cooling section (2) as feed (2a) and the remainder (1b'') is recycled to the pyrolysis reactor (1). See in this respect for example Figure 1B.

As will be appreciated by those skilled in the art, the stream discharged from a first device is typically fed to a downstream second device. Hence, in Figure 1A, the liquid pyrolysis product composition (1b) discharged from the bottom outlet of the pyrolysis reactor (1) is also stream (2a) fed to the cooling section (2). Likewise, in Figure 1B, part (1b') of the liquid pyrolysis product composition

(1b) discharged from the bottom outlet of the pyrolysis reactor (1) is also stream (2a) fed to the cooling section (2).

During step (b), a stream of pyrolysis gases (1c) is discharged via a top outlet of the pyrolysis reactor (1).

The pyrolysis temperature applied in step (b) is generally between 350 and 600 °C and may vary within this range dependent upon factors such as feedstock makeup and operating pressures. Preferably the pyrolysis temperature is between 370 and 550, more preferably, between 390 and 450 °C, such as about 410 °C.

The stream (1a) of, preferably liquid, plastic waste material provided to the pyrolysis reactor (1) in step (a) is preferably based on a feedstock comprising polyethylene (PE) and/or polypropylene (PP) plastics. Preferably, the sum of polyethylene and polypropylene in the feedstock is at least 50 wt% by weight of the feedstock, more preferably at least 60 wt%, still more preferably at least 75 wt%, most preferably at least 90 wt%. The preferred plastic for the feedstock is polyethylene or polypropylene. The feedstock on which stream (1a) of, preferably liquid, plastic waste material provided to the pyrolysis reactor (1) is based may also comprise polyvinylchloride (PVC) plastics, however, the level of PVC is preferably limited to less than 10 wt% by weight of the feedstock, preferably to less than 5 wt%. The feedstock on which stream (1a) of, preferably liquid, plastic waste material provided to the pyrolysis reactor (1) is based may also comprise polyethylene terephthalate (PET) plastics, preferably in an amount greater than 3 wt% by weight of the feedstock, more preferably greater than 4 wt%. The feedstock preferably comprises less than 20 wt% PET plastic. The feedstock may comprise up to 100 wt% polystyrene (PS) plastics by weight of the feedstock. In embodiments, the feedstock may comprise at least 5 wt%, more preferably 20 wt%, more preferably 50wt% polystyrene by weight of the feedstock.

The stream (1a) of, preferably liquid, plastic waste material provided to the pyrolysis reactor (1) in step (a) may further include impurities typically present in plastic waste material, such as food, wood, paper, metal particles, sand, fillers (e.g. inorganic additives and flame retardants), salts, and other detritus including for example organic matter. Such impurities will typically end up, to the extent that they concern non-pyrolysable materials, in the liquid pyrolysis product composition (1b) that is discharged from the bottom outlet of the pyrolysis reactor (1).

Since pyrolysis is performed in the absence of oxygen and at a temperature that is above the autoignition temperature of the liquid pyrolysis product composition (1b) discharged from the bottom outlet of the pyrolysis reactor (1) and since the solid pyrolysis product composition (2b) obtained in step (d) is to be applied under ambient conditions, it is preferred that the liquid pyrolysis product

composition (1b) discharged from the bottom outlet of the pyrolysis reactor (1) is cooled in the cooling section (2) to a temperature below the autoignition temperature in an inert atmosphere before it is subjected to ambient conditions.

In a very preferred embodiment, the cooling section (2) in step (d) comprises a cooling vessel (2A) and a downstream cooling device (2B), wherein the liquid pyrolysis product composition (1b, 1b', 2a) is cooled in the cooling vessel (2A) under agitation and under an inert atmosphere to a temperature below the autoignition temperature of the (liquid) pyrolysis product composition (1b, 1b', 2a), wherein the autoignition temperature of the composition is determined with ASTM E659-15:2023, to obtain a cooled liquid pyrolysis product composition (2d) and wherein at least part (2d') of the cooled liquid pyrolysis product composition (2d) is supplied to the downstream cooling device (2B) using a pump (5e) where it is further cooled to obtain the solid pyrolysis product composition (2b).

In an embodiment, the cooling vessel (2A) comprises a mechanical agitator, such as an impeller, to agitate the contents in vessel (2A) during cooling.

In a preferred embodiment, part (2d') of the cooled liquid pyrolysis product composition (2d) is supplied to the downstream cooling device (2B) and the remainder (2d'') is recycled to the cooling vessel (2A) using pump (5e). This recycling step provides agitation of the contents in cooling vessel (2A) during cooling. See in this respect Figures 3A, 3B, 4 and 5. A combination of mechanical agitation and agitation with the recycling step is also encompassed by the invention.

In an embodiment wherein the cooling section (2) in step (d) comprises the cooling vessel (2A) and the downstream cooling device (2B), the liquid pyrolysis product composition (1b, 1b', 2a) is cooled in the cooling vessel (2A) under agitation and under an inert atmosphere to a temperature that is at least 5 °C below the autoignition temperature of the (liquid) pyrolysis product composition (1b, 1b', 2a), preferably to a temperature that is at least 10 °C below the autoignition temperature of the (liquid) pyrolysis product composition (1b, 1b', 2a). In another embodiment, the liquid pyrolysis product composition (1b, 1b', 2a) is cooled in the cooling vessel (2A) under agitation and under an inert atmosphere to a temperature that is between 5 °C below the autoignition temperature of the (liquid) pyrolysis product composition (1b, 1b', 2a) and 120 °C, preferably to a temperature that is between 10 °C below the autoignition temperature of the (liquid) pyrolysis product composition (1b, 1b', 2a) and 120 °C. In yet another embodiment, the liquid pyrolysis product composition (1b, 1b', 2a) is cooled in the cooling vessel (2A) under agitation and under an inert atmosphere to a temperature that is between 180 and 120 °C.

The liquid pyrolysis product composition (1b) as discharged from the bottom outlet of the pyrolysis reactor (1) preferably already has the composition of the pyrolysis production composition according to the first aspect of the invention. To this purpose, properties of the liquid pyrolysis

production composition in the bottom part of the pyrolysis reactor (1) are preferably continuously measured during step (b), *e.g.* density, particle size of the char particles and concentration of char particles. Based on the measured properties, the rate of discharge of the liquid pyrolysis production composition can be adjusted.

It is however also possible to remove certain volatile parts from the bituminous hydrocarbon fraction in the downstream cooling section (2) before solidification and obtain the composition of the pyrolysis production composition according to the first aspect of the invention in the cooling vessel (2A). To this purpose, the liquid pyrolysis product composition (2a, 1b', 1b) can be heated, *e.g.* under vacuum, in the cooling section (2) before cooling takes place. Hence, in an embodiment, the cooling section (2), preferably the cooling vessel (2A), comprises an outlet and valve (5d) to discharge a stream of volatile parts (2c) from the bituminous hydrocarbon fraction in the cooling section (2), preferably the cooling vessel (2A), and feed it as stream (1d) to the pyrolysis reactor (1) via a top inlet. See in this respect for example Figures 2B, 3B and 5.

In a preferred embodiment wherein the cooling section (2) in step (d) comprises the cooling vessel (2A) and the downstream cooling device (2B), the downstream cooling device (2B) is a device wherein solid particles are produced. In a preferred embodiment, the downstream cooling device (2B) is a device wherein solid particles are produced chosen from the group consisting of a pelletizer or flaker to produce pellets or flakes, a spray hut wherein the cooled liquid pyrolysis product composition (2d') is sprayed with an excessive amount of water resulting in the formation of solid particles that can be separated off, or a spray tower cooled by forced air resulting in the formation of solid particles. Examples of flakers include belt flakers and drum flakers. Examples of pelletizers include belt pelletizer and cooling screws with knife cutters. In a very preferred embodiment, the downstream cooling device (2B) is a belt flaker or drum flaker.

In a preferred embodiment, a conventional rotary drum flaker is used as downstream cooling device (2B) to quench and solidify the cooled liquid pyrolysis product composition (2d'). The flakes can also be produced using any other known equipment or method such as a quench belt. The term '*quenching*' as used herein refers to a process in which the cooled liquid pyrolysis product composition (2d') is further cooled such that there is adequate solidification to change the nature of the flake on the flaker drum surface allowing a reduction in the adhesive force that holds the flake onto the drum metal surface and making it easier to break off. Solidified flakes can be chipped off from the drum using a stationary blade in the rotary drum flaker. The chipped off material is preferably in the form of flakes having a largest dimension in the range of from 3 to 150 mm, such as in the range of from 20 to 100 mm. These flakes then preferably drop by gravity from the rotary drum flaker onto a conveyor belt and are preferably allowed to further cool to a temperature of about 50 ° C to ambient temperature on the conveyor belt. At the end of the conveyor belt, the material is then preferably allowed to fall into a packing station for packaging into bags.

In an embodiment, the rotary drum flaker uses a cooling medium, preferably water, at a temperature in the range from 5 °C to 25 °C, such as from 8 °C to 22 °C.

The solid particles (2b) produced, preferably pellets or flakes, in downstream cooling device (2B) are stable at ambient temperature, are storable and can thus be easily processed and transported.

In an embodiment, the process according to the second aspect further comprises the additional step of discharging the liquid pyrolysis product composition (1b) from the bottom outlet of the pyrolysis reactor (1) as feed (3a) to an equalization vessel (3) where it can be stored before a batch (3b) of the liquid pyrolysis product composition (1b) is supplied as stream (2a) to the cooling section (2). See in this respect Figures 2A, 2B and 5. In an embodiment, the top part of the equalization vessel (3) is provided with a pressure compensation line (3c) that is in fluid connection with a top inlet of the pyrolysis reactor (1) via valve (5c). This pressure compensation line (3c) allows subjecting the pyrolysis reactor (1) and the equalization vessel (3) to the same fluid pressure at their top portions, allowing the equalization vessel (3) to fill under the pressure from the liquid inside the pyrolysis reactor (1). If the cooling section (2), preferably the cooling vessel (2A), comprises an outlet, conduit and valve (5d) to discharge a stream of volatile parts (2c) from the bituminous hydrocarbon fraction in the cooling section (2), the pressure compensation line (3c) and this conduit are preferably in fluid connection. See in this respect Figures 2B and 5.

As for example indicated in Figure 5, discharging liquid pyrolysis product composition (1b) from the bottom outlet of the pyrolysis reactor (1) to the equalization vessel (3) as feed (3a) and subsequently to the cooling section (2) as feed (3b, 2a), is preferably performed with valves (5c, 5d) and with pumps or valves (5a, 5b) that can be operated via a control mechanism. In this regard reference is made to WO2021/05139A1, the contents of which are incorporated herein by reference.

The stream (1a) of, preferably liquid, plastic waste material provided to the pyrolysis reactor (1) in step (a) of the process according to the second aspect preferably is a stream of plastic waste material (4a) that has been compacted and subjected to heat in a heating section (4), resulting in a degassed and molten plastic waste material (4b). The heat treatment in the heating section (4) not only melts the plastic waste material, but typically also results in some pyrolysis. In an embodiment, the plastic waste material is forwarded through the heating section (4) using a pump or an extruder such as a screw auger arranged before the heating section (4). The degassed and molten plastic waste material (4b) can then be supplied as stream (1a) to the pyrolysis reactor (1) via for example a pressure control valve (5f). In embodiments, the heating section (4) comprises more than one serial heating zones (4A, 4B, ..) with increasing temperatures in the downstream direction. See in this respect Figure 4.

In a preferred embodiment, part (1e) of the hydrocarbon liquid formed in the pyrolysis reactor (1) in step (b) is continuously discharged from and recycled as heated stream (1e') to the pyrolysis reactor (1) via a pump (5g) and a heating unit (5h).

In an embodiment, part (1e) of the hydrocarbon liquid formed in the pyrolysis reactor (1) in step (b) is continuously discharged from and recycled as heated stream (1e") to the pyrolysis reactor (1) via a pump (5g) and a heating unit (5h) after combining heated stream (1e") with degassed and molten plastic waste material (4b) via valves or pumps (5f) and (5i) to form stream (1a) of, preferably liquid, plastic waste material.

In another embodiment, part (1e) of the hydrocarbon liquid formed in the pyrolysis reactor (1) in step (b) is continuously discharged from and, after heating in a heating unit (5h), recycled to the pyrolysis reactor (1) using a pump (5g), wherein a fraction of (1e) is directly recycled as heated stream (1e') to the pyrolysis reactor (1) and the remainder of (1e) is recycled as heated stream (1e") to the pyrolysis reactor (1) after combining heated stream (1e") with degassed and molten plastic waste material (4b) via valves or pumps (5f) and (5i) to form stream (1a) of, preferably liquid, plastic waste material. See Figures 4 and 5 in this regard.

In a preferred embodiment, the process according to the second aspect is performed in a pyrolysis reactor (1) comprises a cylinder-shaped intermediate portion containing a separation zone and a funnel-shaped, preferably conical, bottom portion containing a settling zone with the funnel ending in the bottom outlet. In a preferred embodiment, the, preferably liquid, plastic waste material (1a) is provided to the pyrolysis reactor (1) through an inlet that is configured to forward the material tangentially into the separation zone. As a result, the liquid inside the pyrolysis reactor (1) is caused to spin. As a result of this spinning flow pattern, the bituminous fraction and char particles hit the wall, decelerate and sink towards the bottom or flow downwardly. In a preferred embodiment, the bituminous fraction and char particles accumulate in the settling zone. The funnel-shaped, preferably conical, bottom portion is intended to guide the bituminous fraction and char particles to the bottom outlet.

Pyrolysis system

In a third aspect, the invention concerns a pyrolysis system configured to convert a mixture of char particles and hydrocarbons, said mixture resulting from pyrolysis of plastic waste material into a product in the form of solid particles, said system comprising:

(i) a pyrolysis reactor (1) with an inlet (1a) configured to receive, preferably liquid, plastic waste material, a bottom outlet (1b) configured to discharge a liquid pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles dispersed therein and a top outlet (1c) configured to discharge pyrolysis gases; and

(ii) a cooling section (2) having an inlet (2a) in fluid communication with the bottom outlet (1b) of the pyrolysis reactor (1) via a valve or pump (5a), wherein said cooling section (2) comprises a

cooling vessel (2A) and a cooling device (2B) downstream thereof, wherein said cooling device (2B) is in fluid communication with cooling vessel (2A) via a pump (5e), wherein said cooling vessel (2A) comprises means to agitate its contents and is configured to be operated under an inert atmosphere, and wherein said cooling device (2B) is a device configured to produce solid particles from a melt.

See Figures 3A, 3B, 4 and 5 for a pyrolysis system according to the third aspect.

In a preferred embodiment, the cooling device (2B) is a device chosen from the group consisting of a pelletizer or flaker, a spray hut wherein solid particles can be formed by spraying a melt with an excessive amount of water, or a spray tower cooled by forced air.

In a preferred embodiment, the pyrolysis system according to the third aspect further comprises an equalization vessel (3) comprising an inlet (3a) that is in fluid communication with the bottom outlet (1b) of the pyrolysis reactor (1) via the valve or pump (5a), further comprising a bottom outlet (3b) that is in fluid communication with an inlet (2a) of the cooling section (2) via valve or pump (5b) and comprising a top outlet (3c) that is in fluid communication with a top inlet (1d) of the pyrolysis reactor (1) via a valve (5c) to be able to level out pressure differences between the equalization vessel (3) and the pyrolysis reactor (1). See Figure 5 for an embodiment of the pyrolysis system according to the third aspect comprising an equalization vessel (3).

In another preferred embodiment, the system comprises a heating section (4) upstream of and in fluid communication with the pyrolysis reactor (1), said heating section (4) having an inlet (4a) configured for receiving solid plastic waste material and an outlet (4b) configured for providing, preferably liquid, plastic waste material to the pyrolysis reactor (1) via a pressure control valve or pump (5f). See in this regard Figures 3A, 3B, 4 and 5.

In an embodiment, the heating section (4) comprises more than one serial heating zones (4A, 4B, ..) configured to be operated at increasing temperatures in the downstream direction. See in this respect Figure 4.

In a preferred embodiment, the pyrolysis reactor (1) comprises a cylinder-shaped intermediate portion containing a separation zone and a funnel-shaped, preferably conical, bottom portion containing a settling zone with the funnel ending in the bottom outlet. In a preferred embodiment, the inlet (1a) of the pyrolysis reactor which is configured to receive, preferably liquid, plastic waste material is further configured to forward this, preferably liquid, material tangentially into the separation zone.

In a preferred embodiment, the system according to the third aspect is configured to perform the process according to the second aspect.

Thus, the invention has been described by reference to certain embodiments discussed above. It will be recognized that these embodiments are susceptible to various modifications and alternative forms well known to those of skill in the art.

Furthermore, for a proper understanding of this document and its claims, it is to be understood that the verb '*to comprise*' and its conjugations are used in their non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. In addition, reference to an element by the indefinite article '*a*' or '*an*' does not exclude the possibility that more than one of the element is present, unless the context clearly requires that there be one and only one of the elements. The indefinite article '*a*' or '*an*' thus usually means '*at least one*'.

EXAMPLES

Example 1

Several streams of plastic waste material having roughly the polymer composition (dry matter) as indicated in Table 1 and having ash contents of between 1 and 5 wt%, based on the weight of the plastic waste material (dry matter) were pyrolyzed in a system as depicted in Figure 5 comprising a pyrolysis reactor, equalization vessel and cooling system, said cooling system comprising a stirred cooling vessel and a downstream cooling device being a belt flaker.

Table 1: polymer composition plastic waste material (dry matter)

Polymer compounds	**wt%**
PE	85-95
PP	3-12
Other polymers	0.5-3
Total	**100**

These plastic waste streams were continuously extruded and compacted and subjected to heat treatment in a heating zone to result in a degassed and liquid plastic waste stream. The pyrolysis reactor comprised a cylinder-shaped intermediate portion containing a separation zone and a funnel-shaped conical bottom portion containing a settling zone with the funnel ending in a bottom outlet. The inlet of the pyrolysis reactor was configured to supply the liquid material tangentially into the separation zone.

The degassed and liquid plastic waste stream was continuously supplied to the pyrolysis reactor and subjected to pyrolysis at temperatures between 390 and 450 °C to result in liquid hydrocarbons,

condensable gases and non-condensable gases and a further liquid pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles dispersed within said bituminous hydrocarbon fraction. Condensable and non-condensable gases were continuously discharged from the pyrolysis reactor via a top outlet. The further liquid pyrolysis product composition was also continuously discharged via the bottom outlet to the equalization vessel until a certain level was reached in the equalization vessel. The temperature of the pyrolysis product composition stored in the equalization vessel was always above 390 °C.

Characteristics of the liquid pyrolysis product compositions discharged via the bottom outlet of the pyrolysis reactor are indicated in Table 2.

The weight ratio of the bituminous hydrocarbon fraction and the char particles in the pyrolysis product composition was determined by subjecting the pyrolysis product composition to batchwise pyrolysis at 440 °C until no vapor is obtained anymore. During this batchwise pyrolysis at 440 °C, the absolute weight of the char particles remains rather constant, whereas the volatile pyrolysis products of the bituminous fraction are separately collected. Based on the initial weight of the pyrolysis product composition and the weight of the fraction remaining after batchwise pyrolysis at 440 °C until no vapor is obtained anymore, the weight ratio of the bituminous hydrocarbon fraction and the char particles in the pyrolysis product composition can be calculated.

Table 2: composition the pyrolysis product composition (dry matter)

Characteristics	**Value**	**Method**
Weight ratio bituminous hydrocarbon fraction to char particles	1.5 : 1 to 3 : 1	*Vide supra*
Content of combined bituminous hydrocarbon fraction and char particles based on pyrolysis product composition (wt%)	>99	
Carbon content (wt%)	50-82	ASTM D5291:2021
Hydrogen content (wt%)	13-25	ASTM D5291:2021
Ash content (wt%)	3-25	TGA

Certain properties of the (liquid) pyrolysis product compositions were determined, as indicated in Table 3. The viscosity was measured with an Anton Paar rheometer equipped with a coaxial cylinder geometry (CC10) and in accordance with ISO 3219-2:2021. Further specifications used are as follows. Measuring Bob diameter:9.995 mm, Measuring Bob gap length 14.989 mm, Measuring Cup diameter: 10.840 mm, Ratio of Radii: 1.084, Cone Angle: 120.000°, Measuring Gap: 0.422 mm, End Effect Correction Factor: 1.100, Active Length: 89.400 mm, Positioning Length: 72.500 mm.

The particle size distribution of the char particles dispersed in the bituminous hydrocarbon fractions were determined by optical microscopy in accordance with ISO 4407:2002 and following

NAS 1638. The bituminous hydrocarbon fraction was removed from the pyrolysis product compositions by dissolving the pyrolysis product composition in toluene or white spirits. More in particular, the percentages of the number of particles having a particle size of between 0.5 and 100 µm, between 1 and 25 µm and between 1.5 and 15 µm were determined.

In a further step of the process, the liquid pyrolysis product composition was discharged from the equalization vessel into a cooling vessel using a pump, wherein it was cooled under an inert atmosphere to a temperature of about 190 °C, which is well below the auto ignition temperature, under mechanical agitation to obtain a cooled liquid pyrolysis product composition.

Table 3: properties of the (liquid) pyrolysis product compositions

Properties	Value	Unit	Technique
Solidification temperature range	60-80	°C	DSC
Density at 180 to 230 °C	800-900	kg/m^3	ASTM D4052:2022
Autoignition temperature	300-350	°C	ASTM E659-15:2023
Viscosity at 120 °C and 100 s^{-1}	70-100	mPa·s	*Vide supra*
Viscosity at 230 °C and 100 s^{-1}	10-35	mPa·s	*Vide supra*
Particles with size 0.5-100 µm	>95	%	*Vide supra*
Particles with size 1-25 µm	>90	%	*Vide supra*
Particles with size 1.5-15 µm	>85	%	*Vide supra*
Calorific value	20-45	MJ/kg	DIN 51900-3:2005

In a first experiment of a subsequent stage of the process, the thus cooled liquid pyrolysis product compositions were discharged at a temperature of 190 °C from the cooling vessel and pumped to a cooling device being a belt flaker. The belt was cooled by spraying cooling water (15 °C) to the underside of the belt. The temperature of the char leaving the belt was about 28.5 °C. Solid dry and brittle char flakes were scraped off at the end of the belt.

In a second experiment of a subsequent stage of the process, the thus cooled liquid pyrolysis product compositions were discharged at a temperature of 190 °C from the cooling vessel and pumped to a cooling device being a drum flaker using cooling water temperatures of between 8 and 22 °C. Again, solid dry flakes were obtained. The flakes were thin and long shaped (20-100 mm long, 5-10 mm wide and about 1 mm thick).

Example 2

Similar as described in Example 1, pyrolysis was performed at a temperature of 440 °C and a pyrolysis product composition was retrieved from the bottom of the reactor. A volume fraction of around

20% of the ingoing molten plastic waste was retrieved as pyrolysis product composition. The pyrolysis product composition was cooled with water after retrieving it from the reactor. Prior to analysis of the amount of char particles, the cooling water included in the char was removed by means of heating at 100 - 150 °C in a pan such that the water evaporated. The composition of the pyrolysis product composition thus obtained is provided in Table 4.

Table 4: composition the pyrolysis product composition (dry matter)

Characteristics	Value	Method
Weight ratio bituminous hydrocarbon fraction to char particles	2:1	*Vide supra*
Content of combined bituminous hydrocarbon fraction and char particles based on pyrolysis product composition (wt%)	>99	
Carbon content (wt%)	69-73	ASTM D5291:2021
Hydrogen content (wt%)	13-17	ASTM D5291:2021
Ash content (wt%)	14-18	TGA

Certain properties of the (liquid) pyrolysis product compositions were determined, as indicated in Table 5.

Table 5: properties of the (liquid) pyrolysis product compositions

Properties	Value	Unit	Technique
Solidification temperature range	70-107	°C	DSC
Viscosity at 140 °C and 100 s^{-1}	300	mPa·s	*Vide supra*
Viscosity at 180 °C and 100 s^{-1}	200	mPa·s	*Vide supra*

Comparative example 3

The pyrolysis product composition from Example 2, was batchwise pyrolyzed for several hours at 440 °C until no vapor was formed anymore. The remaining product of about 100% char particles was a dry, powdery product at both room temperature and at higher temperatures up to at least 230 °C.

CLAIMS

1. A pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles dispersed within said bituminous hydrocarbon fraction,
wherein the bituminous hydrocarbon fraction and the char particles together constitute at least 70 wt% of the pyrolysis product composition,
wherein the bituminous hydrocarbon fraction and the char particles are present in a weight ratio of between 1 : 1 and 9 : 1, and
wherein said composition is a liquid at a temperature between 120 and 230 °C and is a solid at temperatures up to 35 °C.

2. Pyrolysis product composition according to claim 1, having a viscosity of between 1 and 2000 mPa·s at a temperature between 120 and 230 °C and at a shear rate of 100 s^{-1}, as measured with a coaxial cylinder geometry (CC10) and in accordance with ISO 3219-2:2021, preferably between 10 and 1000 mPa·s, more preferably between 15 and 500 mPa·s.

3. Pyrolysis product composition according to claim 1 or 2, having a viscosity of between 2 and 400 mPa·s at a temperature of 230 °C and at a shear rate of 100 s^{-1}, as measured with a coaxial cylinder geometry (CC10) and in accordance with ISO 3219-2:2021, preferably between 5 and 200 mPa·s, more preferably between 10 and 50 mPa·s.

4. Pyrolysis product composition according to any one of claims 1 to 3, having a viscosity of between 40 and 1800 mPa·s at a temperature of 120 °C and at a shear rate of 100 s^{-1}, as measured with a coaxial cylinder geometry (CC10) and in accordance with ISO 3219-2:2021, preferably between 60 and 1000 mPa·s, more preferably between 80 and 500 mPa·s.

5. Pyrolysis product composition according to any one of claims 1 to 4, having a solidification temperature range that is between 50 and 100 °C, as measured with DSC, preferably between 60 and 80 °C.

6. Pyrolysis product composition according to any one of claims 1 to 5, wherein said composition is a solid at temperatures up to 40 °C, preferably at temperatures up to 45 °C.

7. Pyrolysis product composition according to any one of claims 1 to 6, characterized by tan(δ)-values, measured with a rheometer with a plate-plate geometry and a gap distance of 0.5 mm at a temperature of 35 °C, that are lower than 0.3 at oscillatory frequencies between 10 and 0.1 Hz.

8. Pyrolysis product composition according to any one of claims 1 to 7, wherein the bituminous hydrocarbon fraction and the char particles together constitute at least 90 wt% of the pyrolysis product composition, preferably at least 95 wt%, more preferably at least 98 wt%, most preferably at least 99 wt%.

9. Pyrolysis product composition according to any one of claims 1 to 8, wherein the bituminous hydrocarbon fraction and the char particles are present in a weight ratio of between 1.5 : 1 and 3 : 1, preferably in a weight ratio of between 1.7 : 1 and 2.3 : 1.

10. Pyrolysis product composition according to any one of claims 1 to 9, having a calorific value between 10 and 50 MJ/kg, as measured in accordance with DIN 51900-3:2005.

11. Pyrolysis product composition according to any one of claims 1 to 10, comprising between 40 and 85 wt% carbon and between 10 and 30 wt% hydrogen, based on the weight of the pyrolysis product composition, as determined in accordance with ASTM D5291:2021, and between 1 and 30 wt% ash, based on the weight of the pyrolysis product composition, as determined using thermogravimetric analysis in an oxidative atmosphere, preferably between 50 and 82 wt% carbon, between 12 and 25 wt% hydrogen and between 3 and 25 wt% ash.

12. Pyrolysis product composition according to any one of claims 1 to 11, wherein the char particles have a particle size distribution wherein at least 90% of the particles by number have a particle size of between 0.5 and 100 μm, as determined by optical microscopy in accordance with ISO 4407:2002 and following NAS 1638.

13. Pyrolysis product composition according to claim 12, wherein at least 60% of the particles by number have a particle size of between 1 and 25 μm.

14. Pyrolysis product composition according to any one of claims 1 to 13, having a density at a temperature in the range of 180 to 230 °C, as determined in accordance with ASTM D4052:2022, between 750 kg/m^3 and 1300 kg/m^3, preferably between 780 and 1100 kg/m^3, more preferably between 800 and 900 kg/m^3.

15. Pyrolysis product composition according to any one of claims 1 to 14, in the form of solid particles, preferably in the form of pellets or flakes.

16. Pyrolysis product composition according to any one of claims 1 to 14, in the form of a liquid.

17. A process for the production of a pyrolysis product composition according to any one of claims 1 to 14 in the form of a solid, said process comprising the steps of:
    (a) providing a stream (1a) of, preferably liquid, plastic waste material to a pyrolysis reactor (1);
    (b) pyrolyzing the, preferably liquid, plastic waste material at a temperature of between 350 and 600 °C in the pyrolysis reactor (1) resulting in gaseous hydrocarbon material, liquid hydrocarbon material and char particles, said liquid hydrocarbon material comprising a bituminous hydrocarbon fraction;
    (c) discharging a liquid pyrolysis product composition (1b) having a temperature of between 350 and 600 °C and comprising a bituminous hydrocarbon fraction and char particles dispersed within said bituminous hydrocarbon fraction from a bottom outlet of the pyrolysis reactor (1) to a cooling section (2); and
    (d) cooling the liquid pyrolysis product composition (1b) in the cooling section (2) to obtain a solid pyrolysis product composition (2b), wherein said bituminous hydrocarbon fraction and the char particles together constitute at least 70 wt% of the pyrolysis product composition, wherein the bituminous hydrocarbon fraction and the char particles are present in a weight ratio of between 1 : 1 and 9 : 1, and wherein said composition is a liquid at a temperature between 120 and 230 °C and is a solid at temperatures up to 35 °C.

18. Process according to claim 17, wherein the cooling section (2) in step (d) comprises a cooling vessel (2A) and a downstream cooling device (2B), and wherein the liquid pyrolysis product composition (1b) is cooled in the cooling vessel (2A) under agitation and under an inert atmosphere to a temperature below the autoignition temperature of the pyrolysis product composition (1b), wherein the autoignition temperature of the composition is determined with ASTM E659-15:2023, to obtain a cooled liquid pyrolysis product composition (2d) and wherein at least part (2d') of the cooled liquid pyrolysis product composition (2d) is supplied to the downstream cooling device (2B) using a pump (5e) where it is further cooled to obtain the solid pyrolysis product composition (2b).

19. Process according to claim 18, wherein the cooling device (2B) is a device wherein solid particles are produced, chosen from the group consisting of a pelletizer or flaker, a spray hut wherein the cooled liquid pyrolysis product composition (2d') is sprayed with an excessive amount of water resulting in the formation of solid particles that can be separated off, or a spray tower cooled by forced air resulting in the formation of solid particles.

20. A pyrolysis system configured to convert a mixture of char particles and hydrocarbons, said mixture resulting from pyrolysis of plastic waste material into a product in the form of solid particles, said system comprising:

(i) a pyrolysis reactor (1) with an inlet (1a) configured to receive, preferably liquid, plastic waste material (1a), a bottom outlet (1b) configured to discharge a liquid pyrolysis product composition comprising a bituminous hydrocarbon fraction and char particles dispersed therein and a top outlet (1c) configured to discharge pyrolysis gases; and

(ii) a cooling section (2) having an inlet (2a) in fluid communication with the bottom outlet (1b) of the pyrolysis reactor (1) via a valve or pump (5a), wherein said cooling section (2) comprises a cooling vessel (2A) and a cooling device (2B) downstream thereof, wherein said cooling device (2B) is in fluid communication with cooling vessel (2A) via pump (5e), wherein said cooling vessel (2A) comprises means to agitate its contents and is configured to be operated under an inert atmosphere, and wherein said cooling device (2B) is a device configured to produce solid particles from a melt.

21. Pyrolysis system according to claim 20, wherein the cooling device (2B) is a device chosen from the group consisting of a pelletizer or flaker, a spray hut wherein solid particles can be formed by spraying a melt with an excessive amount of water, or a spray tower cooled by forced air.