(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
25 March 2021 (25.03.2021)

WIPO | PCT

(10) **International Publication Number**
WO 2021/054897 A1

(51) **International Patent Classification:**
C01B 32/162 (2017.01) *C10J 3/66* (2006.01)
C01B 32/184 (2017.01) *C01B 3/32* (2006.01)
C01B 32/186 (2017.01) *C01B 3/34* (2006.01)
B09B 3/00 (2006.01) *C01B 3/38* (2006.01)
B29B 17/04 (2006.01) *C10B 49/02* (2006.01)
C08J 11/12 (2006.01) *C10B 49/04* (2006.01)
C10B 53/02 (2006.01) *B82Y 30/00* (2011.01)
C10J 3/60 (2006.01) *B82Y 40/00* (2011.01)

(21) **International Application Number:**
PCT/SG2020/050531

(22) **International Filing Date:**
17 September 2020 (17.09.2020)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
10201908635T 17 September 2019 (17.09.2019) SG

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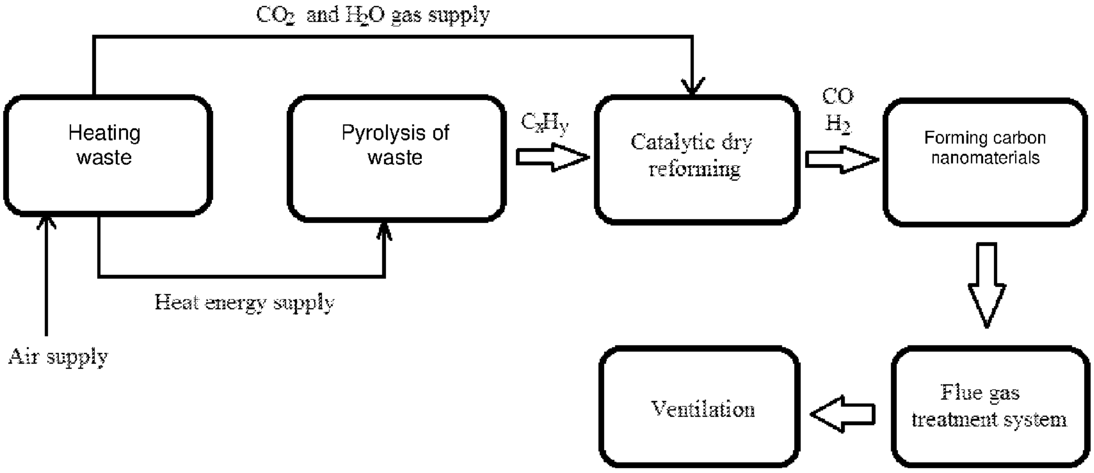
(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW,

(54) **Title:** WASTE TREATMENT SYSTEM

Figure 1(a)



(57) **Abstract:** There is provided a method of treating waste comprising: heating waste to generate inert gases and carbon dioxide; pyrolysing the waste in the presence of the inert gases and carbon dioxide to form a mixture of hydrocarbons; catalytically dry reforming the mixture of hydrocarbons to form at least carbon monoxide and hydrogen; and forming carbon nanomaterials from the carbon monoxide and hydrogen. There is also provided a system for treating waste.

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SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

Waste treatment system

Technical Field

The present invention relates to a method of treating waste and a waste treatment system.

Background

Global plastics production has steadily increased in recent years. However, with increased use, there is also an increase in the amount of plastic disposed as waste after its first use. Some plastics are reused and recycled. However, the majority is disposed as waste.

Waste plastic may be treated by several methods. An example of one such method includes incineration which is environmentally unfriendly since it generates a large carbon footprint and results in high emissions of harmful gases. Some waste treatment methods involve melting and powdering for a second use. However, these pose issues of contamination from the first use. Other methods include pyrolysis to produce biodiesel. However, the pyrolysis results in high energy consumption.

There is therefore a need for an improved waste treatment process.

Summary of the invention

The present invention seeks to address these problems, and/or provides an improved method and system for treating waste.

According to a first aspect of the present invention, there is provided a method of treating waste, the method comprising:

- heating waste to generate inert gases and carbon dioxide;
- pyrolysing the waste in the presence of the inert gases and carbon dioxide to form a mixture of hydrocarbons;
- catalytically dry reforming the mixture of hydrocarbons to form at least carbon monoxide and hydrogen; and
- forming carbon nanomaterials from the carbon monoxide and hydrogen.

The waste may be any suitable waste. According to a particular aspect, the waste may be plastic waste, biomass or a combination thereof.

According to a particular aspect, the heating may comprise combusting the waste.

According to another particular aspect, the pyrolysing may comprise catalytic or non-catalytic pyrolysing the waste. In particular, the pyrolysing may comprise catalytic pyrolysing the waste in the presence of a pyrolysis catalyst. The catalyst may be any suitable catalyst.

The pyrolysing may be performed under suitable conditions. For example, the pyrolysing may be performed at a temperature of 400-1000°C.

According to a particular aspect, the dry reforming may comprise dry reforming of the hydrocarbons with carbon dioxide to produce carbon monoxide and hydrogen gas. For example, the carbon dioxide may be from the heating and pyrolysing.

The dry reforming may be performed under suitable conditions. For example, the dry reforming may be performed at a temperature of 400-1000°C.

The forming carbon nanomaterials may comprise chemical vapour deposition of carbon nanomaterials from the carbon monoxide and hydrogen. According to a particular aspect, the chemical vapour deposition may be in the presence of a catalyst. The catalyst may be any suitable catalyst.

The forming carbon nanomaterials may be performed under suitable conditions. For example, the forming carbon nanomaterials may be performed at a temperature of 450-1000°C.

The carbon nanomaterials formed in the forming carbon nanomaterials may comprise, but is not limited to: carbon nanotubes, carbon spheres, carbon fibres, amorphous carbon, graphene-based nanomaterials, or a combination thereof. The carbon nanotubes may be single-walled carbon nanotubes, multi-walled carbon nanotubes, or a combination thereof.

The method may further comprise treating any flue gas produced during the heating, pyrolysing, dry reforming, and/or forming.

According to a second aspect, there is provided a waste treatment system comprising:

- an inlet for receiving waste;
- a heating chamber coupled to the inlet for heating the waste;
- a pyrolysis chamber for pyrolysing the waste, the pyrolysis chamber fluidically connected to the heating chamber;
- a dry reforming chamber fluidically connected to the pyrolysis chamber for dry reforming hydrocarbons formed in the pyrolysis chamber; and
- a chemical vapour deposition (CVD) chamber connected to the dry reforming chamber for forming carbon nanomaterials.

The system may further comprise an air inlet, wherein the heating chamber may be fluidically connected to the air inlet.

The system may further comprise a condensation system for condensing exhaust gases. The system may further comprise a flue gas treatment system in fluid communication with the condensation system and/or CVD chamber for treating exhaust gases.

The system may further comprise a gas outlet for venting exhaust gases.

<u>Brief Description of the Drawings</u>

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1(a) shows a schematic representation of a method of treating waste according to one embodiment of the present invention and Figure 1(b) shows a schematic representation of a method of treating waste according to another embodiment of the present invention;

Figure 2 shows a schematic representation of the waste treatment system according to one embodiment of the present invention; and

Figure 3 shows a schematic representation of the waste treatment system according to one embodiment of the present invention.

Detailed Description

As explained above, there is a need for an improved method and system for treating waste.

The present invention relates to a method for treating waste. The method is a green method with a low carbon footprint as the by-products from the method may be recycled in the method, thereby resulting in lower energy consumption. In general terms, the invention relates to a method and system for conversion of waste in a fast, efficient and green manner. In particular, the energy consumption is relatively low as the method and system are configured to use energy and gases generated from one part of the system and method for other parts/steps of the system/method. In this way, the amount of external energy and input required to run the system/method is reduced.

Further, the method enables the waste to be converted into carbon nanomaterials, thereby providing a high value output, which is a useful and environmentally friendly end product. The method of the present invention is also a green method since the energy consumption is low and because it enables a reduction in waste volume.

The method sequentially involves: combustion of waste to generate carbon dioxide and heat, pyrolysis of waste, dry reforming of pyrolysed hydrocarbons, formation of carbon nanomaterials, and optionally condensation and flue gas treatment.

According to a first aspect of the present invention, there is provided a method of treating waste, the method comprising:

- heating waste to generate inert gases and carbon dioxide;
- pyrolysing the waste in the presence of the inert gases and carbon dioxide to form a mixture of hydrocarbons;
- catalytically dry reforming the mixture of hydrocarbons to form at least carbon monoxide and hydrogen; and
- forming carbon nanomaterials from the carbon monoxide and hydrogen.

Figure 1(a) provides a schematic representation of the method according to the present invention. In particular, Figure 1(a) illustrates: combustion of waste to produce carbon dioxide and heat for next steps; pyrolysis of waste to produce hydrocarbons C_xH_y; catalytic dry reforming of C_xH_y with the CO_2 from the previous steps to produce carbon monoxide and hydrogen; generation of carbon nanomaterials by utilising syngas; optional condensation of the exhaust gas to retain any hydrocarbons not reacted; and optional treatment of flue gas before release to air.

Figure 1(b) illustrates one embodiment of the method according to the present invention in which plastic waste is subjected to the method to form single walled carbon nanotubes.

The waste may be any suitable waste for the purposes of the present invention. According to a particular aspect, the waste may be, but not limited to, plastic waste, biomass or a combination thereof. For example, the plastic waste may comprise municipal plastic waste, which can include one or more of but not limited to, low-density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), or a combination thereof. For example, the biomass may be, but not limited to, energy crops such as miscanthus, switchgrass, wood or forest residues, waste from food crops, horticulture and processed food such as wheat straw, bagasse, yard waste, corn cobs.

The method may comprise heating the waste. The heating may be any form of heating. According to a particular aspect, the heating may comprise combusting the waste. The heating may be under suitable conditions. For example, the heating may comprise heating the waste under suitable conditions to enable the waste to be heated and/or combusted to produce carbon dioxide and water. Heat may also be generated from the heating. In particular, the heating may be at a temperature of ≤ 1000°C. For example, the heating may be at a temperature of 30-1000°C, 50-950°C, 100-900°C, 150-850°C, 200-800°C, 250-750°C, 300-700°C, 350-650°C, 400-600°C, 450-550°C. Even more in particular, the heating may be at a temperature of 400-750°C.

The method also includes pyrolysing the waste to form hydrocarbons. In particular, the pyrolysing results in the formation of smaller hydrocarbons from the waste. In the method of the present invention, the pyrolysing is performed after the heating. This is because during the heating, the oxygen in the air provided enables carbon dioxide and nitrogen gas to be formed. The nitrogen gas and carbon dioxide gas from the heating step are inert gases and may therefore be suitable for the subsequent pyrolysing without requiring any further inert gas to be supplied during the pyrolysing. In this way, the method avoids the use of inert gas cylinders and/or generators, thereby making the method safer and cheaper.

The heat energy generated from the heating may be subsequently utilised for the pyrolysing. In this way, the method may not require any external energy source for supplying heat energy to continue the method of the present invention.

According to another particular aspect, the pyrolysing may comprise catalytic or non-catalytic pyrolysing the waste. In particular, the pyrolysing may comprise catalytic pyrolysing the waste in the presence of a pyrolysis catalyst. The catalyst may be any suitable catalyst. For example, the catalyst may be, but not limited to, acidic TiO_2, zeolites such as zeolite Y, HZSM-5, or a combination thereof.

The pyrolysing may be performed under suitable conditions. For example, the pyrolysing may be performed for a pre-determined period of time and at a pre-determined temperature. The pre-determined temperature may be 400-1000°C. In particular, the pre-determined temperature may be 400-900°C, 450-850°C, 500-800°C, 550-750°C, 600-700°C. Even more in particular, the pre-determined temperature may be 550-750°C.

The pre-determined period of time for the pyrolysing may be $\leq$ 180 minutes. In particular, the pre-determined period of time may be 5-180 min, 10-150 min, 20-100 min, 25-75 min, 30-70 min, 35-65 min, 40-60 min, 45-55 min. Even more in particular, the pre-determined period of time may be 25-45 minutes.

Following pyrolysing, the hydrocarbons formed from the pyrolysing may be subjected to dry reforming. Dry reforming may comprise a method of producing synthesis gas (syngas) from the reaction of carbon dioxide with hydrocarbons. According to a particular aspect, the dry reforming may comprise dry reforming of the hydrocarbons with carbon dioxide to produce carbon monoxide and hydrogen gas. The carbon dioxide formed from the heating may be used in the dry reforming. According to another particular aspect, the carbon dioxide may be from the previous steps of heating and pyrolysing or from an external source, such as flue gas containing carbon dioxide.

The dry reforming may be in the presence of a dry reforming catalyst. The dry reforming catalyst may be any suitable catalyst. For example, the dry reforming catalyst may be a transition metal-based catalyst. The dry reforming catalyst may be, but is not limited to, iron (Fe)-based, cobalt (Co)-based, nickel (Ni)-based, ruthenium (Ru)-based, rhodium (Rh)-based catalyst. The transition metal may be supported on a suitable support. For example, the transition metal may be supported on, but not limited to, aluminium oxide, silicon dioxide (SiO_2), zirconium oxide (ZrO_2), titanium oxide (TiO_2), manganese oxide (MgO), zeolite, mineral clay, or a combination thereof. The aluminium oxide support may comprise, but is not limited to, α-Al_2O_3, γ-Al_2O_3, or a combination thereof. According to a particular aspect, the dry reforming catalyst may comprise, but is not limited to, Ni-Co-Al, Ni-Co-Al-Mg, Co-Al-Mg, Co-Al-Zr, or a combination thereof.

The dry reforming may be performed under suitable conditions. For example, the dry reforming may be performed at a temperature of 400-1000°C. In particular, the dry reforming may be performed at a temperature of 500-950°C, 600-900°C, 650-850°C, 700-800°C, 725-750°C. Even more in particular, the temperature may be 500-850°C.

The dry reforming may be performed for a suitable period of time. For example, the dry reforming may be carried out for ≤ 180minutes. In particular, the dry reforming may be carried out for 5-180 min, 10-150 min, 20-100 min, 25-75 min, 30-70 min, 35-65 min, 40-60 min, 45-55 min. Even more in particular, the dry reforming may be carried out for 25-45 minutes.

The dry reforming may be represented by the following equations:

$$CO_2 + C_xH_y \rightarrow CO + H_2 \qquad \text{(Eq. 1)}$$

$$H_2O + C_xH_y \rightarrow CO + H_2 \qquad \text{(Eq. 2).}$$

In particular, the dry reforming comprises use of the carbon dioxide and water from the heating and reacts with hydrocarbons formed from the pyrolysing, as shown in equations 1 and 2.

The carbon monoxide and the hydrogen formed in the dry reforming are then used in forming carbon nanomaterials. The forming carbon nanomaterials may be by any suitable means. The forming carbon nanomaterials may be in the presence of a catalyst. The forming may be represented by the following equation:

$$CO + H_2 \rightarrow C + H_2O \qquad \text{(Eq. 3).}$$

According to a particular aspect, the forming carbon nanomaterials may comprise chemical vapour deposition (CVD) of the carbon monoxide and hydrogen to form the carbon nanomaterials. The CVD may be in the presence of a CVD catalyst. The catalyst may be any suitable catalyst. The CVD catalyst may be in the form of nanoparticles. In particular, the CVD catalyst may be in the form of nanocrystals. For example, the CVD catalyst may be transition metal-based catalysts. The catalysts may be such so as to minimise amorphous carbon production and control the conditions to favour the formation of the carbon nanomaterials.

The transition metal comprised in the transition metal-based catalysts may include, but is not limited to, Co, Fe, Mo, Cu, Ni, Au, Pt, Pd, or alloys thereof. In particular, the CVD catalysts may be Co-MgO, Fe-Mo/MgO, Fe-Cu/MgO, (Fe, Co)Ni/CeO_2, (Ni, Co)Fe/α- or γ-Al_2O_3, monolithic Fe, Co/γ-Al_2O_3, MoO_3/Al_2O_3, Ni-Co/Al_2O_3, (Fe, Co)Ni/zeolites, Ni-Co/Si, (Pt, Au)Pd/Al_2O_3, W/Co, or alloys thereof. Even more in particular, the CVD catalyst may be, but not limited to, Co-zeolite, Co-Fe-zeolite, Co-Ni-zeolite, Co-Mg, or alloys thereof.

The forming carbon nanomaterials may be performed under suitable conditions. For example, the forming carbon nanomaterials may be performed at a temperature of 450-1000°C. In particular, the forming carbon nanomaterials may be performed at a temperature of 450-950°C, 500-900°C, 550-850°C, 600-800°C, 650-750°C, 700-725°C. Even more in particular, the temperature may be 500-850°C.

The forming carbon nanomaterials may be performed for a suitable period of time. For example, the forming carbon nanomaterials may be carried out for $\leq$ 180 minutes. In particular, the forming carbon nanomaterials may be carried out for 5-180 min, 10-150 min, 20-100 min, 25-75 min, 30-70 min, 35-65 min, 40-60 min, 45-55 min. Even more in particular, the forming carbon nanomaterials may be carried out for 25-45 minutes.

The carbon nanomaterials may be formed on the surface of the dry reforming catalyst and/or the CVD catalyst.

The carbon nanomaterials formed in the forming carbon nanomaterials may be any suitable carbon nanomaterials. For the purposes of the present invention, carbon nanomaterial is defined as any carbon-based material which comprises at least one dimension in the nanoscale.

The carbon nanomaterials may comprise, but is not limited to: carbon nanotubes, carbon spheres, carbon fibres, amorphous carbon, graphene-based nanomaterials, or a combination thereof. In particular, the carbon nanotubes may be single-walled carbon nanotubes, multi-walled carbon nanotubes, or a combination thereof. Even more in particular, the carbon nanomaterials may be single-walled carbon nanotubes. The single-walled carbon nanotubes may comprise single chirality.

For the purposes of the present invention, a carbon nanotube may be defined as a nanoscale graphene cylinder (formed by rolled up one atom-thick sheets of graphite called graphene) that are closed at each end by half of a fullerene molecule. A carbon nanotube comprising only one cylinder is termed a single-walled carbon nanotube and carbon nanotubes comprising two or more graphene cylinders is termed a multi-walled carbon nanotube.

The single-walled carbon nanotubes may be metallic or semiconducting and may have bandgap in the range of 0.4 to about 2 eV while the multi-walled carbon nanotubes may be zero bandgap metals. The single-walled carbon nanotube may have a diameter in the range of 0.4-3 nm.

The carbon nanomaterials formed may be used in several applications including, but not limited to: electromagnetic and microwave absorbing coatings, thermal interface materials, ionic and electronic transport devices such as actuators, super capacitors, batteries, fibres, sensors, energy storage and energy conversion devices, radiation sources and nanometre-sized semiconductor devices, field emission tips for applications such as field emission displays, X-ray tubes, electron sources for microscopy and lithography, gas discharge tubes, vacuum microwave amplifiers, scanning probe tips, interconnect applications, and the like. The carbon nanomaterials formed may be further doped in order to tune their electronic response for use as a transistor or logic element. The carbon nanomaterials may also be used as membranes for water purification and gas separation.

The carbon nanomaterial formed may have an average size of 0.5-100 nm. In particular, the carbon nanomaterial may have an average size of 1-90 nm, 5-85 nm, 10-80 nm, 15-75 nm, 20-70 nm, 25-65 nm, 30-60 nm, 35-55 nm, 40-50 nm. Even more in particular, the carbon nanomaterial may have an average size range of 1-5 nm.

According to a particular aspect, the dry reforming and the forming the carbon nanomaterials may be simultaneous. In particular, the dry reforming step may utilise two greenhouse gases (carbon dioxide and hydrocarbon gases which may be produced from the pyrolysing) and may produce hydrogen and carbon monoxide. The forming carbon nanomaterials step may also produce carbon dioxide, which in turn may be utilized as a reactant in the dry reforming step. Further, the hydrogen produced in the dry reforming step may react with carbon dioxide, resulting in formation of carbon monoxide, which is advantageous as the carbon monoxide may be used for the forming of the carbon nanomaterials.

The dry reforming may comprise a by-reaction between carbon dioxide and hydrogen. This may be due to low activation energy, as shown in Equation 4. In particular, when the carbon monoxide content is high and hydrogen content is low due to the by-reaction during the dry reforming, a by-reaction may also happen in the forming carbon nanomaterials step. This by-reaction and disproportionation of carbon monoxide may form carbon nanomaterials and carbon dioxide, as shown in Equation 5.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \text{(Eq. 4)}$$

$$CO \rightarrow C + CO_2 \qquad \text{(Eq. 5).}$$

The method may further comprise condensing the hydrocarbon gases to retain and redirect the hydrocarbon gases for further use in the method of the invention. For example, the redirected hydrocarbon gas may be subjected to further dry reforming. The condensing may be by any suitable means. For example, the condensing may be carried out in a condensing system.

The method may further comprise treating any flue gas produced during the heating, pyrolysing, dry reforming, and/or forming. The treating may be in a flue gas treatment system. For example, the method may comprise treating any excess carbon monoxide, carbon dioxide, or hydrocarbon gas before being discharged. The treating may minimise odorous and/or environmentally harmful gas emissions.

Overall, the method of the present invention provides an exothermic reaction with a negative entropy value. Accordingly, the method does not require any external energy supply and may be self-sustainable. The heat generated during the heating may be utilised for the subsequent steps in the method. Any excess heat generated may also be harnessed and used for other applications. Another advantage of the method is that the carbon dioxide produced during the various steps may be utilised by other steps in the method, and accordingly, the overall carbon dioxide emission may be reduced.

The method of the present invention therefore allows heat energy to be recycled, cutting down on the amount of heat to be supplied by an external heat source, making the method more environmentally friendly.

The combination of the various steps described above is important for the purposes of the present invention. In particular, in the method of the present invention, the dry reforming comprises dry reforming mixed hydrocarbon gases. The hydrocarbon gases comprise methane as well as other higher molecular weight gases. Further, the sequence of the various steps in the method of the present invention ensures the self-sustainability of the method. For example, since the heating is the first step, it enables its product to be utilised in the subsequent dry reforming step. Further, the subsequently generated reducing gases from the pyrolysing and dry reforming enable a reducing atmosphere to be maintained. If, on the other hand, the heating was set as a second step following pyrolysing, all hydrocarbons produced from the pyrolysing may be burnt producing an oxidizing atmosphere (carbon dioxide) and no hydrocarbons would be available for subsequent dry reforming.

According to a second aspect, there is provided a waste treatment system comprising:

- an inlet for receiving waste;
- a heating chamber coupled to the inlet for heating the waste;
- a pyrolysis chamber for pyrolysing the waste, the pyrolysis chamber fluidically connected to the heating chamber;
- a dry reforming chamber fluidically connected to the pyrolysis chamber for dry reforming hydrocarbons formed in the pyrolysis chamber; and

- a chemical vapour deposition (CVD) chamber connected to the dry reforming chamber for forming carbon nanomaterials.

The waste treatment system may further comprise an air inlet, wherein the heating chamber may be fluidically connected to the air inlet. The air inlet may be configured to supply air to the heating chamber when the system is in use.

The heating chamber may be any chamber suitable for heating waste. For example, the heating chamber may be a combustion chamber.

The waste treatment system may further comprise a condensation system for condensing exhaust hydrocarbon gases. The condensation system may be any suitable condensation system. In particular, the condensation system may comprise an adsorbent suitable for adsorbing hydrocarbon gases. For example, the condensation system may comprise metallic, quartz, or ceramic tube/pipes, optionally with a heat sink.

According to a particular aspect, the waste treatment system may further comprise a flue gas treatment system in fluid communication with the condensation system and/or CVD chamber for treating exhaust gases. In use, the heating chamber, the pyrolysis chamber, dry reforming chamber and CVD chamber may emit flue gas which may therefore be treated before being discharged into the atmosphere. In this way, the system of the present invention does not emit any harmful and/or odourful gas into the atmosphere, making the system an environmentally friendly system. The flue gas treatment system may be any suitable system for the purposes of the present invention. In particular, the flue gas treatment system may comprise adsorbing solutions and/or solid cartridges for odour removal.

The system may further comprise a gas outlet for venting exhaust gases. In particular, the gas outlet may be fluidically connected to the flue gas treatment system for venting treated flue gas.

The waste treatment system may also comprise a temperature controller configured to measure temperatures of the heating chamber, pyrolysis chamber, dry reforming chamber and CVD chamber. In particular, the temperature controller may be configured to adjust the heating carried out in the heating chamber to ensure that sufficient heat is generated in the waste treatment system such that sufficient temperature is maintained in each of the pyrolysis chamber, dry reforming chamber and CVD chamber depending on the temperature of each of the chambers. The temperature controller may comprise an alarm to alert a user if the temperatures of the pyrolysis chamber, dry reforming chamber and/or CVD chamber falls below a certain pre-determined temperature. The temperature controller may be further connected to an external heat source to adjust the amount of heat being supplied to the waste treatment system in the event additional heat is required.

The waste treatment system may be for performing the method as described above in relation to the first aspect of the present invention.

Figure 2 shows a waste treatment system 100 according to one embodiment of the present invention. The system 100 comprises an inlet (not shown) into which the waste to be treated is fed. The inlet may be connected to a heating chamber 113 and a pyrolysis chamber 106. The waste 105 supplied to the heating chamber 113 and the pyrolysis chamber 106 may be placed in a container 104 within the respective chambers 113 and 106. The system 100 may further comprise an air inlet 112 for supplying air to the heating chamber 113.

The heating chamber 113 and the pyrolysis chamber 106 may be fluidically connected to each other. In this way, any gases and heat produced in the heating chamber 113 may flow to the pyrolysis chamber 106.

The system 100 may further comprise a dry reforming chamber 114 and a CVD chamber 119. The dry reforming chamber 114 is connected to the pyrolysis chamber 106 which in turn is connected to the CVD chamber 229. According to a particular aspect, the dry reforming chamber 114 and the CVD chamber 119 may be separated by a filter 117. The filter 117 may be any suitable filter. For example, the filter 117 may be a sintered filter.

The dry reforming chamber 114 may comprise dry reforming catalyst 116. The dry reforming catalyst 116 may be any suitable catalyst. For example, the dry reforming catalyst 116 may be as described above in relation to the method of treating waste.

The CVD chamber 119 may comprise CVD catalyst 118. The CVD catalyst 118 may be any suitable catalyst. For example, the CVD catalyst 118 may be as described above in relation to the method of treating waste.

The dry reforming chamber 114 and the CVD chamber 119 may further comprise heat insulation material 115 to retain the temperature within the chambers 114 and 119. Any suitable heat insulation material may be used. For example, the heat insulation material 115 may be, but not limited to, glass wool.

The system 100 may further comprise a condensation system 120. The CVD chamber 119 may be in fluid communication with the condensation system 120. In particular, the condensation system 120 may enable hydrocarbon gases produced within the system 100 to be retained and reused. Accordingly, the condensation system 120 may comprise a hydrocarbon adsorbent.

The condensation system 120 may be further connected to a flue gas system 109. In particular, pipes may enable flue gases from the condensation system 120 to be channelled to the flue gas treatment system 109 before being vented out from outlet 108. The flue gas treatment system 109 may be any suitable system for treating flue gas such as, but not limited to, excess CO, excess CO_2, SO_2, SO_3, H_2S, HCl.

Figure 3 shows a waste treatment system 200 according to another embodiment of the present invention. The components of the system 200 are similar to the components of the system 100. The difference between the systems 200 and 100 is in the arrangement of the components. The advantage of the system 200 over the system 100 is that there would be more contact time of the reactants within the dry reforming chamber 114 and the CVD chamber 119 with the dry reforming catalyst 116 and the CVD catalyst 118, thereby improving yield of the carbon nanomaterials formed within the system.

The method of the present invention will now be described in relation to the waste treatment system 100. Waste 105 is fed through an inlet of the heating chamber 113 and the pyrolysis chamber 106. Air is supplied to the heating chamber 113 via an air inlet 112. At the heating chamber 113, combustion of the waste 105 takes place. The combustion of the waste 105 results in the production of carbon dioxide and heat. The heated carbon dioxide gas is channelled to the pyrolysis chamber 106.

Subsequently, pyrolysis of waste 105 is carried out in the pyrolysis chamber 106. The pyrolysis may be carried out at a temperature of about 400-700°C. The heat for the pyrolysis is provided by the heat from the combustion of the waste 105 in the heating chamber 113. After a pre-determined period of time, the pyrolysis of the waste 105 results in the formation of hydrocarbon gases.

The hydrocarbon gases are then channelled to the dry reforming chamber 114 which in turn is connected to the CVD chamber 119. The carbon dioxide and hydrocarbon gases channelled into the dry reforming chamber 114 may undergo dry reforming in which carbon monoxide and hydrogen may be produced. The dry reforming within the dry reforming chamber may be at a temperature of 600-900°C in the presence of dry reforming catalysts 116. The carbon monoxide formed may further react with the hydrogen gas in the CVD chamber 119 to form carbon nanomaterials. The carbon nanomaterials may be formed within the CVD chamber 119 at a temperature of 450-700°C in the presence of CVD catalysts 118. The carbon nanomaterials may be formed on the surface of the dry reforming catalysts 116 and the CVD catalysts 118.

Any unreacted gases and/or flue gases from the heating chamber 113, pyrolysis chamber 106, dry reforming chamber 114, and CVD chamber 119 are routed to a condensation system 120 followed by a flue gas treatment system 109 via pipes. After the gases undergo treatment in the flue gas treatment system 109, the cleaned gases are vented out of the system 100 or 200 via outlet 108.

The present invention provides several advantages. In particular, the waste treatment system and method for treating waste have a low carbon footprint since the system and method utilise minimal external energy in view of the using the heat energy generated during the waste treatment process, as well as utilising the products from previous steps of the method. The system and method enable waste to be formed into a useful form. The system and method also enable any flue gases to be suitably handled, thereby eliminating release of unpleasant process related gases and odours.

Having now generally described the invention, the same will be more readily understood through reference to the following examples, which are provided by way of illustration, and are not intended to be limiting.

EXAMPLE

In the following example, all chemicals used are from Sigma-Aldrich.

Pyrolysis

10.0 grams of plastic waste comprising 42% LDPE, 20% HDPE, 16% PS, 12% PET, 10% PP (all by weight) was provided in a pyrolysis reactor and heated at a heating rate of 10°C/min and pyrolysed at 600°C with 200 ml/min of CO_2 as carrier gas. It was observed that at 530°C, methane started to be generated. Pyrolysis products mainly comprised 97.9% v/v of methane and 21,000 ppm of other hydrocarbons (C_xH_y). The pyrolysis was continued for 30 minutes. The final solid residue was 0.14 g, containing mainly carbon spheres, with a narrow diameter distribution 100-250 nm.

Dry reforming catalysts

Dry reforming catalysts Ni-Co-Al, Ni-Co-Al-Mg, Co-Al-Mg and Co-Al-Zr were synthesized as follows.

To synthesize Ni-Co-Al catalyst, firstly, 24.9 g of $Co(CH_3COO)_2{\cdot}4H_2O$, 1.17 g $Ni(NO_3)_2{\cdot}6H_2O$ of and 0.27 g of $Al_2(SO_4)_3{\cdot}18H_2O$ were added to 150 ml of deionized water, and the mixture was heated and stirred at 40°C for two hours until completely dissolved. Subsequently, 1.0 M of ammonia was slowly added to the mixed solution with agitation until at pH of 8.3, a large amount of precipitate appeared. About 10 minutes later, the precipitate was filtered, washed (with DI water) and dried overnight at 50°C before calcination in a reaction furnace at 750°C for about 3 hours. Finally, the obtained solid was ground into fine powder.

Ni-Co-Al-Mg, Co-Al-Mg and Co-Al-Zr catalysts were prepared in a similar manner with synthesis conditions summarized in Table 1.

Catalyst	Atomic ratio					pH value	Calcination temperature
	Ni	Co	Mg	Al	Zr		
Ni-Co-Al	5	125	-	1	-	8.3	750°C
Ni-Co-Al-Mg	1	1	1	1	-	8.3	750°C
Co-Mg-Al	-	1	20	20	-	10.0	750°C
Co-Al-Zr	-	2	-	1	20	9.5	800°C

Table 1: Preparation conditions of dry reforming catalysts

CVD catalysts

CVD catalysts Co-zeolite, Co-Fe-zeolite, Co-Ni-zeolite, and Co-Mg were prepared through ion exchange as follows. To prepare Co-zeolite catalyst, 0.46 g of $Co(CH_3COO)_2 \cdot 4H_2O$ and 5 g of zeolite were dissolved or dispersed in 200 ml of deionized water with stirring at 40°C for two hours. Subsequently the solution was filtered, washed and dried overnight before calcination at 500°C for 6 hours. Finally, it was ground into very fine powder.

Co-Fe-zeolite and Co-Ni-zeolite were prepared in a similar manner.

To synthesize Co-Mg catalyst, precursors (cobalt acetate, magnesium chloride) were mixed uniformly and 1.0 M of ammonia was added until a pH value 9.6 was reached to form a precipitate. The synthesis conditions of the CVD catalysts are summarized in Table 2.

Catalyst	**Atomic ratio**					**pH value**	**Calcination temperature**
	Co	**Ni**	**Fe**	**Mg**	**zeolite**		
Co-zeolite	1	-	-	-	50	-	500°C
Co-Ni-zeolite	1	1	-	-	33	-	750°C
Co-Fe-zeolite	1	-	1	-	33	-	500°C
Co-Mg	1	-	-	9	-	9.6	750°C

Table 2: Preparation conditions of CVD catalysts

Formation of carbon nanomaterials

2.0 grams of plastic waste (comprising by weight 42% LDPE, 20% HDPE, 16% PS, 12% PET, 10% PP) was placed in a pyrolysis chamber. 0.4 g of Ni-Co-Al as dry reforming catalyst and each of the CVD catalyst as shown in Table 2 were provided and heated at a heating rate 40°C/min. The waste was pyrolysed and catalytically dry reformed at 600°C for 60 minutes with 100 ml/min of CO_2 as a carrier gas. CO_2 carrier gas was used to replace the combustion step to simplify the experiments. CO, CO_2, CH_4, C_2H_2 and C_2H_4 were detected after CVD reaction using all the respective CVD catalysts.

Following the CVD, both single-walled carbon nanotubes and multi-walled carbon nanotubes were found on the surface of the CVD catalysts.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Claims

1. A method of treating waste, the method comprising:
   - heating waste to generate inert gases and carbon dioxide;
   - pyrolysing the waste in the presence of the inert gases and carbon dioxide to form a mixture of hydrocarbons;
   - catalytically dry reforming the mixture of hydrocarbons to form at least carbon monoxide and hydrogen; and
   - forming carbon nanomaterials from the carbon monoxide and hydrogen.

2. The method according to claim 1, wherein the waste is plastic waste, biomass, or a combination thereof.

3. The method according to claim 1 or 2, wherein the heating comprises combusting the waste.

4. The method according to any preceding claim, wherein the pyrolysing comprises catalytic or non-catalytic pyrolysing the waste.

5. The method according to any preceding claim, wherein the pyrolysing comprises catalytic pyrolysing the waste in the presence of a pyrolysis catalyst.

6. The method according to any preceding claim, wherein the pyrolysing is performed at a temperature of 400-1000°C.

7. The method according to any preceding claim, wherein the dry reforming comprises dry reforming of the hydrocarbons with carbon dioxide to produce carbon monoxide and hydrogen gas.

8. The method according to claim 7, wherein the carbon dioxide is from the heating and pyrolysing.

9. The method according to any preceding claim, wherein the dry reforming is performed at a temperature of 400-1000°C.

10. The method according to any preceding claim, wherein the forming carbon nanomaterials comprises chemical vapour deposition of carbon nanomaterials from the carbon monoxide and hydrogen.

11. The method according to claim 10, wherein the chemical vapour deposition is in the presence of a catalyst.

12. The method according to any preceding claim, wherein the forming carbon nanomaterial is performed at a temperature of 450-1000°C.

13. The method according to any preceding claim, wherein the carbon nanomaterials formed in the forming carbon nanomaterials comprises: carbon nanotubes, carbon spheres, carbon fibres, amorphous carbon, graphene-based nanomaterials, or a combination thereof.

14. The method according to claim 13, wherein the carbon nanotubes are single-walled carbon nanotubes, multi-walled carbon nanotubes, or a combination thereof.

15. The method according to any preceding claim, further comprising treating any flue gas produced during the heating, pyrolysing, dry reforming, and/or forming.

16. A waste treatment system comprising:

- an inlet for receiving waste;
- a heating chamber coupled to the inlet for heating the waste;
- a pyrolysis chamber for pyrolysing the waste, the pyrolysis chamber fluidically connected to the heating chamber;
- a dry reforming chamber fluidically connected to the pyrolysis chamber for dry reforming hydrocarbons formed in the pyrolysis chamber; and
- a chemical vapour deposition (CVD) chamber connected to the dry reforming chamber for forming carbon nanomaterials.

17. The system according to claim 16, further comprising a condensation system for condensing exhaust gases.

18. The system according to 16 or 17, further comprising a flue gas treatment system in fluid communication with the condensation system and/or CVD chamber for treating exhaust gases.

19. The system according to any of claims 16 to 18, further comprising a gas outlet for venting exhaust gases.

20. The system according to any of claims 16 to 19, wherein the heating chamber is fluidically connected to an air inlet.

Figure 1(a)

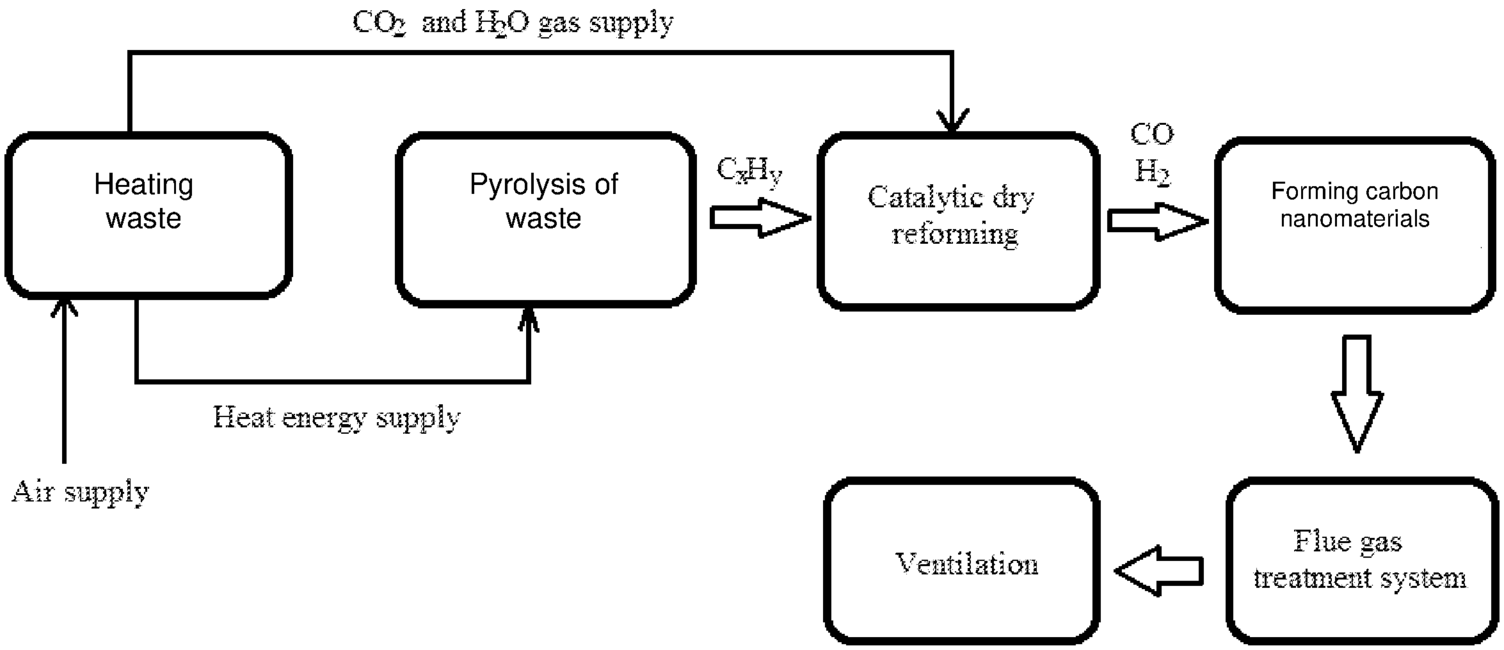
CO$_2$ and H$_2$O gas supply
Heating waste
Pyrolysis of waste
C$_x$H$_y$
Catalytic dry reforming
CO
H$_2$
Forming carbon nanomaterials
Heat energy supply
Air supply
Flue gas treatment system
Ventilation

Figure 1(b)

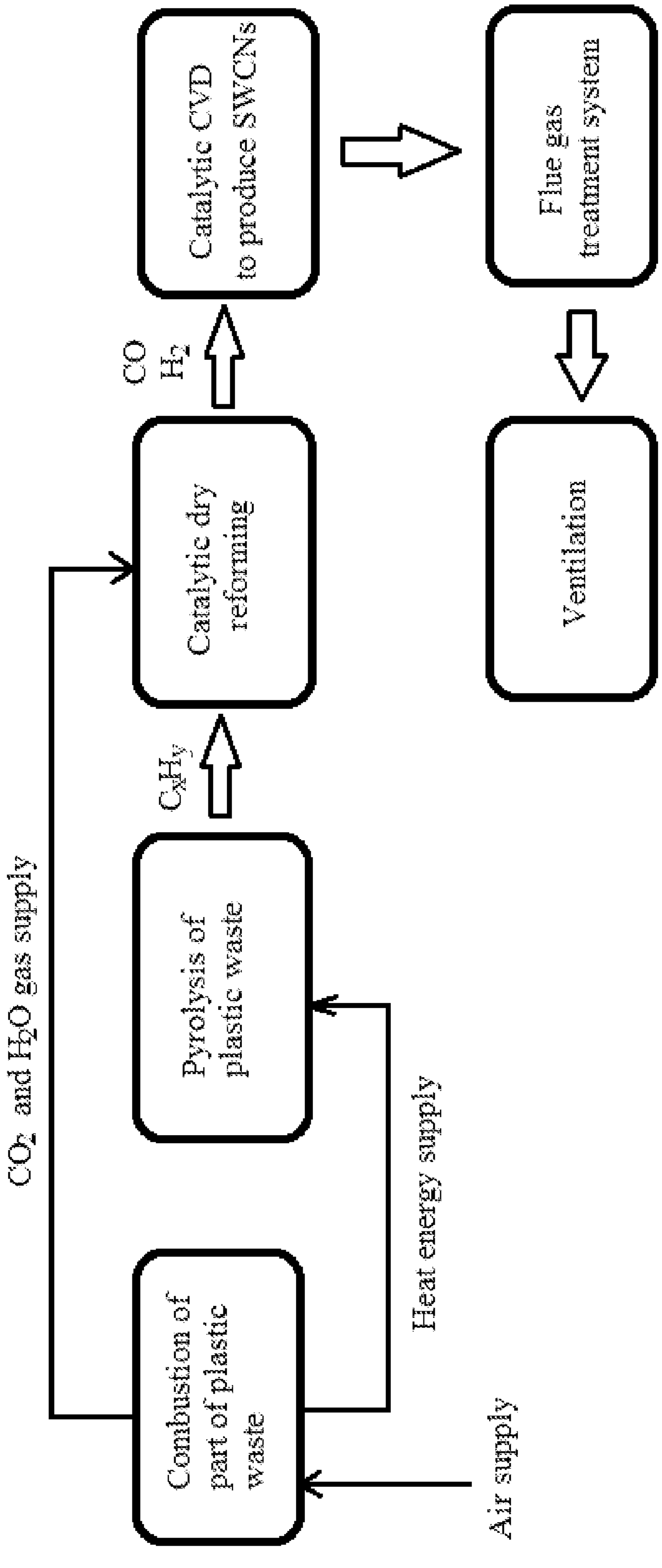
Combustion of part of plastic waste
Air supply
Heat energy supply
CO_2 and H_2O gas supply
Pyrolysis of plastic waste
C_xH_y
Catalytic dry reforming
CO
H_2
Catalytic CVD to produce SWCNs
Flue gas treatment system
Ventilation

Figure 2

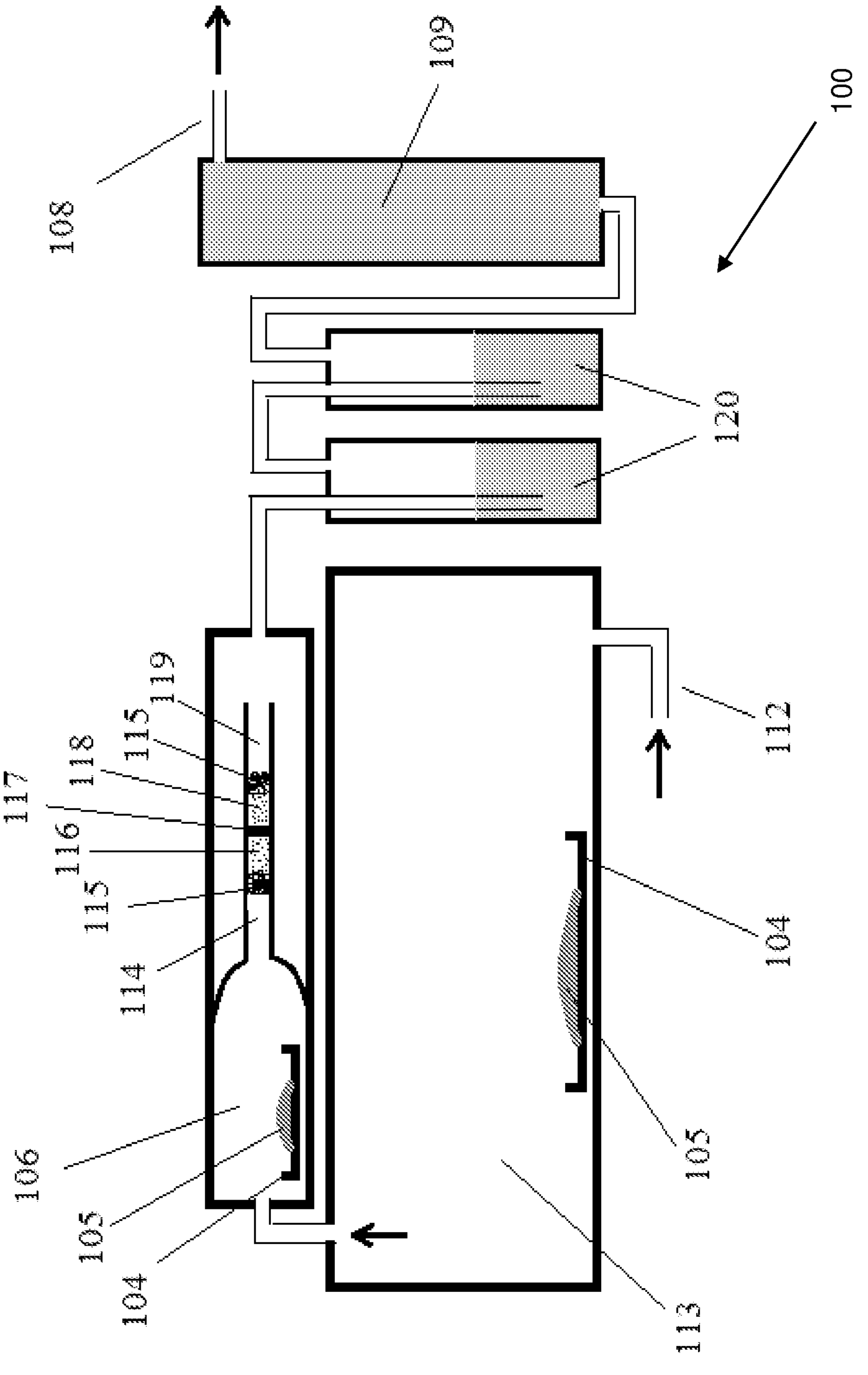
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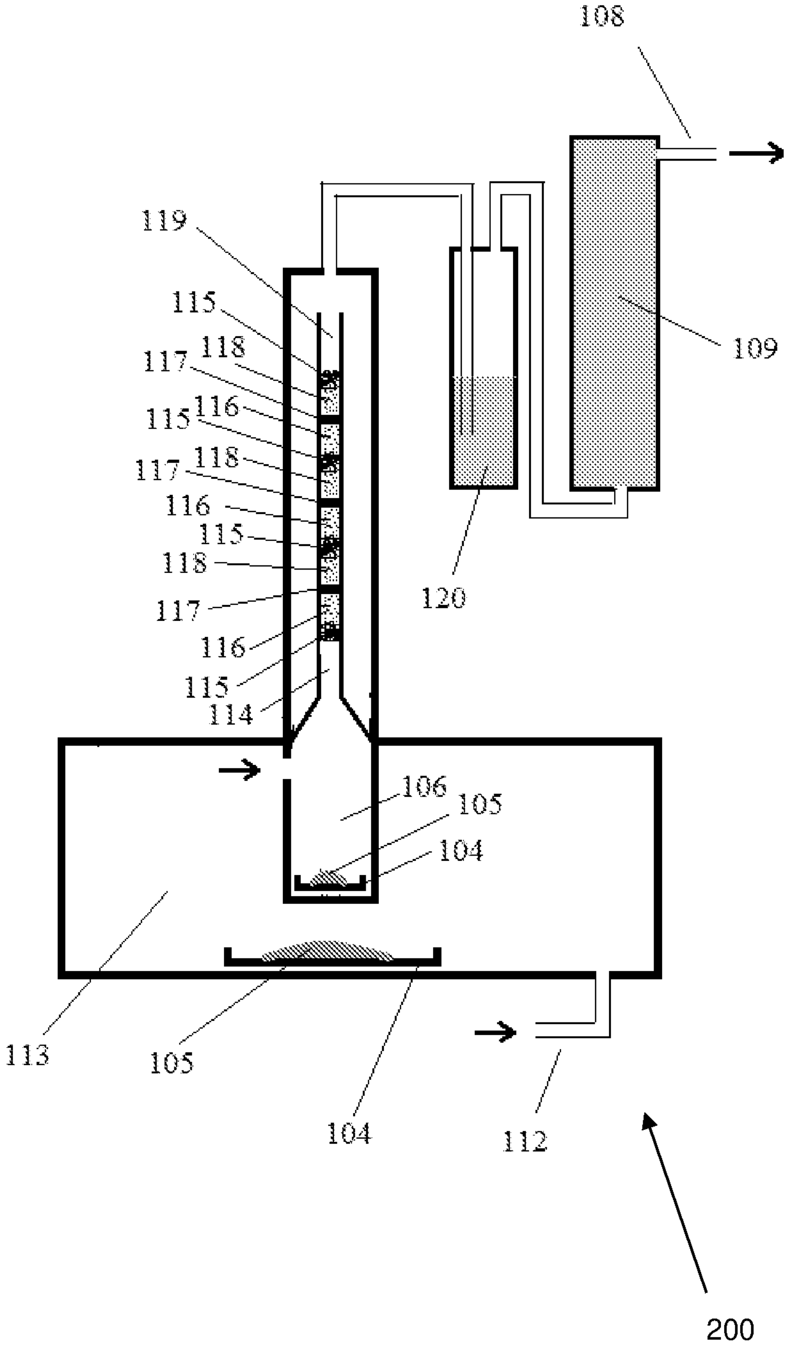
Figure 3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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2020/050531

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01B B09B B29B C08J C10B C10J B82Y

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)

Databases: FAMPAT, COMPENDEX, INSPEC

Keywords: plastics, polymer, biomass, tyres, coal, combustion, burning, partial oxidation, exothermic, pyrolysis, thermal decomposition, dry distillation, air, heat carrier, carrier gas, inert gas, dry performing, gasification, syngas, Bosch, Boudouard, chemical vapour deposition, carbon nanotubes, MWCNT, SWCNT, graphene and similar terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012/0219489 A1 (LEVENDIS, Y. ET AL.) 30 August 2012 See whole document, in particular Fig. 1-2, [0010], [0056], [0058]-[0067], [0071]-[0073], [0079]-[0080], [0084], [0086], [0088], [0092] and [0117]	1-20
Y	CN 102491308 A (ZHUO, X.K.) 13 June 2012 See whole document, in particular [0022], [0031]-[0035], [0044]-[0045] and [0049]- [0050] and examples 2 and 3 of the machine translation	1-20
Y	US 7794690 B2 (ABATZOGLOU N. ET AL.) 14 September 2010 See whole document, in particular Fig. 2, 5-7 and 12 and Example 1, 2 and 4-7	1-20

☒ 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 29/12/2020 *(day/month/year)*	Date of mailing of the international search report *30/12/2020* *(day/month/year)*
Name and mailing address of the ISA/SG **Intellectual Property Office of Singapore** 1 Paya Lebar Link, #11-03 PLQ 1, Paya Lebar Quarter Singapore 408533 Email: pct@ipos.gov.sg	Authorized officer Zhao Yan (Dr) IPOS Customer Service Tel. No.: (+65) 6339 8616

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2020/050531

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2014/0202073 A1 (LEONHARDT M.A.) 24 July 2014 See whole document, in particular Fig. 1, [0013], [0020]-[0022], [0025]-[0027], [0034], [0037], [0055] and [0068]	1-5, 7-14, 16-20
Y	CN 103224802 A (SHANGHAI INST TECHNOLOGY) 31 July 2013 See whole document, in particular Fig. 1, [0039], [0048]-[0049], [0054], [0060] and [0066] of the machine translation	1-5, 7-14, 16, 20
Y	US 2002/0159929 A1 (KANEKO S. ET AL.) 31 October 2002 See whole document, in particular Fig. 1 and 34, First and Twenty-Sixth Embodiment, [0171]-[0190], [0194], [0444], [0448], [0453]-[0456], [0463], [0466] and [0471]	1-16, 20
A	US 2011/0041388 A1 (SIPILA K. ET AL.) 24 February 2011 See whole document	
A	US 2012/0034150 A1 (NOYES, D.B.) 9 February 2012 See whole document	

Supplemental Box
(Classification of Subject Matter)

Int. Cl.

C01B 32/162 (2017.01)
C01B 32/184 (2017.01)
C01B 32/186 (2017.01)
B09B 3/00 (2006.01)
B29B 17/04 (2006.01)
C08J 11/12 (2006.01)
C10B 53/02 (2006.01)
C10J 3/60 (2006.01)
C10J 3/66 (2006.01)
C01B 3/32 (2006.01)
C01B 3/34 (2006.01)
C01B 3/38 (2006.01)
C10B 49/02 (2006.01)
C10B 49/04 (2006.01)
B82Y 30/00 (2011.01)
B82Y 40/00 (2011.01)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2020/050531

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

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