

METHOD OF FORMING CARBONACEOUS AND MINERAL NANOSTRUCTURED MATERIALS FROM PLASTICS

Cross-Reference to Related Application

[001] This application claims the benefit of priority of United States of America Provisional Patent Application No. 61/868,207, filed August 21, 2013, the contents of which being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[002] The invention relates to a non-combustible method of forming carbonaceous and mineral nanostructured materials from plastics. In particular, present method involves step annealing of the plastics.

Background

[003] Plastics by definition are formed through monomers creating long chains of polymers through polymerization processes. However, for practical uses, plastics are often molded or extruded into desired shapes and sizes with the help of additives such as antioxidants, stabilizers, plasticizers/softeners, blowing agents, flame retardants, and pigments. Plastics could then be classified through two categories, thermoset and thermoplastics while most common types of plastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC).

[004] The world production of plastics for the year 2010 is more than 200 millions tons with China, Japan, and the rest of Asia taking 23%, 5% and 16%, respectively, with the top three widely used plastics types being PE, PP, and PVC having the share of 29%, 19% and 11%, respectively.

[005] With the ever-increasing demand for plastic products, waste plastics which are not easily degradable received greater attention for recycling. To-date, most recycling efforts are

geared towards recycling of high density PE (HDPE) or low density PE (LDPE), PS, and PP, which are widely used and consumed worldwide. Major types of waste polymer/plastic recycling processes are mechanical and chemical recycling, of which chemical tertiary recycling converts these monomers into valuable chemicals. Thus, tertiary recycling of waste polymer/plastics are churning carbon nanotubes using various ways to recover monomers into these valuable products.

[006] Many plastic recycling processes are targeting at the formation of only carbon nanotubes/fibers or to produce coke and carbon black. However, most of the plastics that are used and consumed nowadays are made with expensive fillers and additives. Existing methodologies of converting waste polymers/plastics therefore do not fully utilize and recover these filler and additive materials.

Summary

[007] The ability to convert waste polymer/plastics into interwoven bamboo shaped crystalline nano mineral fibers (e.g. calcium carbonate nanowires) and carbon nanostructures is explored herein. Present disclosure emphasizes on the simplicity of thermal conversion which recovers not only carbonaceous material but also one of the widely used basic filler (e.g. calcium carbonate) while improving properties through morphology (nano fibers). This methodology of conversion has the potential of converting waste polymer/plastics almost completely to nanostructured materials while addressing the issue of clean and green environment. The resultant products are carbon nanotubes, carbon nanofibers, and mineral fibers which give complementary properties with ranges from <40 nm in diameter and ~400 nm in length.

[008] Thus, in accordance with one aspect of the disclosure, there is provided a method of forming carbonaceous and mineral nanostructured materials from plastics. The method comprises:

annealing the plastics in an inert or vacuum environment comprised in an enclosed reactor to form mineral nanostructured materials and carbonaceous gaseous products; and

feeding the carbonaceous gaseous products to a chemical vapour deposition reactor and heating the carbonaceous gaseous products therein to form carbonaceous nanostructured materials,

wherein the annealing comprises a first annealing stage and a second annealing stage,

wherein the first annealing stage comprises constant heating at a temperature range of between 100 °C and 150 °C for a period of 1 h to 4 h; and

wherein the second annealing stage comprises constant heating at a temperature range of between 400 °C and 1,500 °C for a period of 3 h to 11 h.

[009] In various embodiments, prior to feeding the carbonaceous gaseous products to the chemical vapour deposition reactor, the carbonaceous gaseous products are first fed to a distillation column for separation into a low octane gas stream and a high octane gas stream.

[010] In various embodiments, a portion of the carbonaceous gaseous products after passing through the distillation column is condensed to form a fuel.

Brief Description of the Drawings

[011] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

[012] Fig. 1 shows an overall process of present method of forming carbonaceous and mineral nanostructured materials from plastics.

[013] Fig. 2 shows a flow chart indicating various dwell times and temperatures at a constant ramp rate for the step annealing process of present methodology.

[014] **Fig. 3** shows transmission electron images of (a) and (b) carbon nanotubes obtained in one example.

[015] **Fig. 4** shows transmission electron images of (a) amorphous carbon fiber, and (b) crystalline mineral nanofibers (e.g. calcium carbonate) obtained in one example.

[016] **Fig. 5** shows EDX analysis (a) indication portions of amorphous carbon with detection of some calcium content, and (b) rich phases of calcium content forming crystalline calcium carbonate obtained in the example of **Fig. 4**.

[017] **Fig. 6** shows Rietveld refinement indication major phase of CaCO_3 content of **Fig. 5**.

[018] **Fig. 7** shows transmission electron images of (a) and (b) crystalline calcium carbonate obtained in one example.

[019] **Fig. 8** shows transmission electron images of crystalline calcium carbonate obtained in one example.

[020] **Fig. 9** shows transmission electron images of (a) and (b) crystalline calcium carbonate obtained in one example.

[021] **Fig. 10** shows transmission electron images of crystalline calcium carbonate obtained in one example.

[022] **Fig. 11** shows transmission electron images of crystalline calcium carbonate obtained in one example.

[023] **Fig. 12** shows transmission electron images of (a), (c) crystalline calcium carbonate and (b) amorphous carbon interwoven with crystalline calcium carbonate, enlargement of image 'a', obtained in one example.

[024] **Fig. 13** shows transmission electron image of crystalline calcium carbonate obtained in one example.

[025] **Fig. 14** shows transmission electron images of (a) crystalline calcium carbonate (b) crystalline calcium carbonate and amorphous carbon obtained in one example.

[026] Fig. 15 shows transmission electron images of crystalline nano calcium carbonate dispersed in graphite sheet obtained in one example.

Description

[027] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[028] Present disclosure relates to the conversion of various waste polymeric/plastic materials to tertiary products using a simple thermal conversion. These tertiary products are herein described as interwoven crystalline mineral fibers (e.g. calcium carbonate) and/or carbonaceous nanostructured materials. Advantageously, present disclosure enables recovery of a major plastics resin filler, particularly calcium carbonate, together with the formation of carbonaceous nanostructures, such as but not limited to carbon nanotubes, thus increasing the amount of recycle-able wastes.

[029] In particular, present disclosure describes a process for non-combustive thermal conversion of waste polymer/plastics into nanostructured materials by placing the waste polymer/plastics into designated reactors under inert/vacuum condition at various dwell times and at various annealing temperatures, after which the waste polymer/plastics are converted or pyrolysed into the desired nanostructured materials. The nanostructured materials are then oven-cooled to ambient temperature and are collected therefrom. The thus-formed nanostructured materials comprise crystalline mineral nanofibers (e.g. calcium carbonate) and/or carbonaceous nanostructures whereby these crystalline mineral nanofibers and/or

carbonaceous nanostructures can be in the form of nanoparticle, nanotube, nanofiber, nanobead, and/or graphitic sheet.

[030] Suitable waste polymers/plastics include, but not limited to, thermoplastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polycarbonate (PC).

[031] The carbonaceous nanostructured materials may be obtained in a form of nanotube, nanofiber, nanobead, nano/micro-diamonds, or graphitic structures such as graphene and graphitic rolls.

[032] Fig. 1 shows an overall process of present method of forming carbonaceous and mineral nanostructured materials from plastics in accordance with one embodiment.

[033] Waste plastics or polymers are placed in an enclosed reactor for pyrolysis of the plastics. In various embodiments, the plastics are placed in an enclosed bomb, quartz tube, or alumina crucible, which is purged with inert gases such as argon or nitrogen. Alternatively, ambient gas is pumped out from the reactor to vacuum which is then sealed to prevent oxygen from coming into contact with the plastics, and hence present thermal conversion method is a non-combustive method.

[034] In the enclosed reactor, the plastics are annealed or pyrolyzed to form mineral nanostructured materials and carbonaceous gaseous products. During the conversion process, the bonds C-C or C-H of the plastics break under thermal decomposing and form nanostructures. In various embodiments, the conversion process is performed in the absence of a catalyst. Alternatively, the conversion process is performed in the presence of a catalyst. While the conversion is taking place, care has to be taken to ensure that the enclosed reactor remains in vacuum or inert condition, thereby preventing any occurrence of combustion.

[035] As mentioned in earlier paragraphs, plastics frequently contain fillers or additives. During the conversion process, fillers, such as but not limited to calcium carbonate fillers,

present in the plastics are recovered. In particular, the fillers, which may originally be present in the plastics in various forms, such as nanosphere or powder, are now recovered in crystalline fiber forms (see **Fig. 4**, **Fig. 7**, for example).

[036] To recover the crystalline minerals in fiber forms, step annealing is performed, whereby the annealing comprises a first annealing stage and a second annealing stage.

[037] The first annealing stage comprises constant heating at a temperature range of between 100 °C and 200 °C for a period of 1 h to 4 h. For example, the first annealing stage comprises constant heating at 100 °C, 105 °C, 110 °C, 115 °C, 120 °C, 125 °C, 130 °C, 135 °C, 140 °C, 145 °C, 150 °C, 155 °C, 160 °C, 165 °C, 170 °C, 175 °C, 180 °C, 185 °C, 190 °C, 195 °C, or 200 °C. The dwell time may be 1 h, 1.5 h, 2 h, 2.5 h, 3 h, 3.5 h, or 4 h.

[038] In various embodiments, the first annealing stage comprises constant heating at a temperature range of between 100 °C and 120 °C for a period of 1 h to 4 h.

[039] In one embodiment, the first annealing stage comprises constant heating at 100 °C for 3 h.

[040] In another embodiment, the first annealing stage comprises constant heating at 120 °C for 3 h.

[041] In certain embodiments, the first annealing stage is repeated once but at different heating temperatures. For example, the waste plastics may first be constantly heated at 100 °C for 3 h, followed by constantly heating at 200 °C for another 3 h before proceeding to the second annealing stage.

[042] The second annealing stage comprises constant heating at a temperature range of between 400 °C and 1,500 °C for a period of 3 h to 11 h. For example, the second annealing stage comprises constant heating at 400 °C, 425 °C, 450 °C, 475 °C, 500 °C, 525 °C, 550 °C, 575 °C, 600 °C, 625 °C, 650 °C, 675 °C, 700 °C, 725 °C, 750 °C, 775 °C, 800 °C, 825 °C, 850 °C, 875 °C, 900 °C, 925 °C, 950 °C, 975 °C, 1,000 °C, 1,025 °C, 1,050 °C, 1,075 °C, 1,100 °C,

1,125 °C, 1,150 °C, 1,175 °C, 1,200 °C, 1,225 °C, 1,250 °C, 1,275 °C, 1,300 °C, 1,325 °C, 1,350 °C, 1,375 °C, 1,400 °C, 1,425 °C, 1,450 °C, 1,475 °C, or 1,500 °C. The dwell time may be 3 h, 3.5 h, 4 h, 4.5 h, 5 h, 5.5 h, 6 h, 6.5 h, 7 h, 7.5 h, 8 h, 8.5 h, 9 h, 9.5 h, 10 h, 10.5 h, or 11 h.

[043] In various embodiments, the second annealing stage comprises constant heating at a temperature range of between 400 °C and 1,200 °C for a period of 3 h to 11 h.

[044] In one embodiment, the second annealing stage comprises constant heating at 500 °C for a period of 3 h.

[045] In another embodiment, the second annealing stage comprises constant heating at 600 °C for a period of 3 h.

[046] In yet another embodiment, the second annealing stage comprises constant heating at 700 °C for a period of 3 h.

[047] In a further embodiment, the second annealing stage comprises constant heating at 800 °C for a period of 3 h.

[048] Fig. 2 shows an embodiment of the step annealing process. As illustrated, the waste plastics are heated from room temperature of 30 °C to the first annealing stage temperature of between 100 °C and 120 °C at a constant ramp rate of 5 °C/min to 20 °C/min. When the desired annealing temperature is reached, the annealing temperature is kept constant for a period of 1 h to 4 h. Thereafter, the waste plastics are then heated to the second annealing stage temperature of between 400 °C and 1,200 °C at a constant ramp rate of 5 °C/min to 20 °C/min. When the desired annealing temperature is reached, the annealing temperature is kept constant for a period of 3 h to 11 h. At the end of the second annealing stage, the pyrolyzed products may be cooled to room temperature.

[049] During the annealing or pyrolysis step, mineral nanostructured materials and carbonaceous gaseous products are formed. The carbonaceous gaseous products are then fed to and heated in a chemical vapour deposition reactor to form carbonaceous nanostructured

materials. Care has to be taken to ensure that the chemical vapour deposition reactor remains in vacuum or inert condition by purging the reactor with inert gases such as argon or nitrogen, or pumping ambient gas from the reactor to vacuum.

[050] In various embodiments, the heating of the carbonaceous gaseous products in the chemical vapour deposition reactor comprises heating at a temperature range of between 200 °C and 1,600 °C. For example, the carbonaceous gaseous products may be heated at 200 °C, 225 °C, 250 °C, 275 °C, 300 °C, 325 °C, 350 °C, 375 °C, 400 °C, 425 °C, 450 °C, 475 °C, 500 °C, 525 °C, 550 °C, 575 °C, 600 °C, 625 °C, 650 °C, 675 °C, 700 °C, 725 °C, 750 °C, 775 °C, 800 °C, 825 °C, 850 °C, 875 °C, 900 °C, 925 °C, 950 °C, 975 °C, 1,000 °C, 1,025 °C, 1,050 °C, 1,075 °C, 1,100 °C, 1,125 °C, 1,150 °C, 1,175 °C, 1,200 °C, 1,225 °C, 1,250 °C, 1,275 °C, 1,300 °C, 1,325 °C, 1,350 °C, 1,375 °C, 1,400 °C, 1,425 °C, 1,450 °C, 1,475 °C, 1,500 °C, 1,525 °C, 1,550 °C, 1,575 °C, or 1,600 °C.

[051] Generally, longer carbonaceous nanostructured materials are obtained from higher heating temperatures. For example, at heating temperatures of above 500 °C, longer carbon nanotubes can be obtained compared to heating temperatures below 500 °C.

[052] In various embodiments, the heating of the carbonaceous gaseous products in the chemical vapour deposition reactor is carried out in the presence of a catalyst. The catalyst may be selected from the group consisting of an organo-metallic material, a metal, a metal oxide, a transition metal, and a derivative thereof.

[053] In various embodiments, the catalyst for the conversion of the carbonaceous gaseous products to carbonaceous nanostructured materials is selected from the group consisting of ferrocene, iron oxide, cobaltocene, nickelocene, copper oxide, tungsten, titanium, platinum, nickel, vanadium, chromium, manganese, cobalt, zinc, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, and a mixture thereof.

[054] In one embodiment, the catalyst for the conversion of the carbonaceous gaseous products to carbonaceous nanostructured materials is ferrocene.

[055] Turning back to **Fig. 1**, prior to feeding the carbonaceous gaseous products to the chemical vapour deposition reactor, the carbonaceous gaseous products may be optionally fed to a distillation column. The distillation column separates the carbonaceous gaseous products into a high octane gas stream (i.e. C_1 - C_5) and a low octane gas stream (i.e. $\geq C_6$), whereby the low octane gas stream of the carbonaceous gaseous products is then fed to the chemical vapour deposition reactor and the high octane gas stream of the carbonaceous gaseous products is condensed in a condenser to form a fuel. Therefore, one advantage of distilling the carbonaceous gaseous products after pyrolysis and before conversion into carbonaceous nanostructured materials is that high octane fuel as a side-product may be obtained, thereby increasing the value of the recycling process since all possible components of the waste plastics can be recycled or recovered. Another advantage of performing the distillation prior to feeding the gaseous carbonaceous products to the chemical vapour deposition reactor is that the converted carbonaceous nanostructured materials, such as carbon nanotubes, obtained therefrom are of better quality compared to carbonaceous nanostructured materials obtained without the distillation step. Hence, depending on the desired quality of the carbonaceous nanostructured materials, the distillation step may or may not be needed.

[056] After heating and converting the carbonaceous gaseous products in the chemical vapour deposition reactor to carbonaceous nanostructured materials, the thus-obtained carbonaceous nanostructured materials may be subjected to a purification process.

[057] As illustrated in **Fig. 1**, the carbonaceous nanostructured materials may be purified and blended with a polymer to form a composite containing the polymer reinforced with the carbonaceous nanostructured materials, such as carbon nanotubes, carbon nanofibers, or carbon nanowires.

[058] Alternatively or additionally, the carbonaceous nanostructured materials may be purified and blended with a polymer and the crystalline minerals nanofibers to form a composite containing the polymer reinforced with the carbonaceous nanostructured materials and crystalline minerals nanofibers.

[059] Yet alternatively or additionally, the crystalline minerals nanofibers may be purified and blended with a polymer to form a composite containing the polymer reinforced with the crystalline minerals nanofibers.

[060] In summary, presently disclosed method of thermal non-combustible conversion using an enclosed environment in an inert condition has successfully enabled the formation of interwoven crystalline minerals (such as calcium carbonate) and carbonaceous nanostructures. The method affords an easy and safe conversion of waste plastics into high performance products (i.e. crystalline nano calcium carbonate and amorphous nanostructures of carbon) for the composite industry. The method is cost-efficient most materials of the waste plastics (and not just carbon/resins) are recovered and re-applied for high end applications. Large-scale production is also possible with a simple enclosed and inert condition.

[061] These products could have large potential market in the composite industries using existing technology which is cost efficient and could be sold at cheaper costs to companies incorporating carbon nanostructures into products for aerospace and aviation, automotive, composites and coatings, energy, environmental, information technology, manufacturing, medical, MEMS and NEMS, military and defense, advanced polymers, sensor, as well as sports and textile applications replacing aluminium, plastic, steel and wood materials from daily products.

[062] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[063] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[064] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[065] By "about" in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

[066] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[067] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups,

those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[068] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

Examples

[069] Synthesis of crystalline nano calcium carbonate and carbon nanostructures in inert/vacuum condition

[070] Waste polymers/plastics are placed into an enclosed bomb, quartz tube, or alumina crucible, which is purged with inert gases such as argon or nitrogen, or the ambient gas is pumped out from these reactors to vacuum which is then sealed to prevent oxygen from coming in contact with the waste materials. During conversion process, the bond C-C or C-H break under thermal decomposing and formed nanostructures either with or without the assistance of catalysts. In addition, calcium carbonate fillers in various forms (i.e. nano spheres, powders) are forming crystalline fibers. While the conversion is taking place, all reactors remain in vacuum or inert condition preventing any occurrence of combustion during the upcycling process. These conversions utilizes addition of catalysts or used without pre-treatment.

[071] Characterization of synthesized nanostructured materials

[072] Morphological studies were conducted using transmission electron microscopy (TEM, JEOL 2100F) in high resolution mode operating at an accelerating voltage of 200 kV with EDX analysis. Phase purity and crystal structure of crystalline nano calcium carbonate and amorphous nano carbon structures were examined by Bruker X-ray diffractometer D8 Powder (Cu-K α radiation, with step scanning (0.01°, 0.6 s dwell time, 40 kV). The obtained X-ray diffraction (XRD) patterns were analyzed by Rietveld refinement within the Topas V3 (Bruker-AXS), using the fundamental parameters approach.

[073] Morphology of synthesized materials under various conditions

[074] (i) Step annealing at 100 °C for 3 h and 600 °C for 3 h in Ar gas with ferrocene (waste plastic:ferrocene=6:1, w/w) at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (opaque LDPE in enclosed stainless steel bomb), **Fig. 3**.

[075] (ii) Step annealing at 100 °C for 3 h, 200 °C for 3 h, and 800 °C for 3 h in Ar gas with at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (opaque LDPE in alumina crucible/enclosed stainless steel bomb), **Fig. 4**.

[076] **Fig. 5** shows EDX analysis (a) indication portions of amorphous carbon with detection of some calcium content, and (b) rich phases of calcium content forming crystalline calcium carbonate obtained in the example of **Fig. 4**.

[077] **Fig. 6** shows Rietveld refinement indication major phase of CaCO_3 content of **Fig. 5**.

[078] (iii) Step annealing at 100 °C for 3 h, and 800 °C for 3 h in Ar gas platinum plate at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (opaque LDPE), **Fig. 7**.

[079] (iv) Step annealing at 120 °C for 6 h, and 500 °C for 3 h in Ar gas at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (opaque LDPE in alumina crucible), **Fig. 8**.

[080] (v) Step annealing at 120 °C for 3 h, and 500 °C for 6 h in Ar gas at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (opaque LDPE in alumina crucible), **Fig 9**.

[081] (vi) Step annealing at 120 °C for 3 h, and 500 °C for 6 h in Ar gas at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (opaque LDPE in alumina crucible), **Fig. 10**.

[082] (vii) Step annealing at 700 °C for 3 h in ambient at ramp rate of 5 °C/min (opaque LDPE in enclosed bomb), **Fig. 11**.

[083] (viii) Step annealing at 120 °C for 3 h, and 500 °C for 6 h in Ar gas at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (clear LDPE in enclosed bomb), **Fig. 12**.

[084] (ix) Step annealing at 120 °C for 3 h, and 500 °C for 6 h in Ar gas at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (opaqueLDPE in enclosed bomb), **Fig. 13**.

[085] (x) Step annealing at 500 °C for 3 h in Ar gas at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (clear LDPE in enclosed bomb), **Fig. 14**.

[086] (xi) Step annealing at 600 °C for 3 h in Ar gas at ramp rate of 5 °C/min with Ar flow of 10 cc/min. (clear PET in enclosed bomb), **Fig. 15**.

[087] Upscaling Description

[088] The upscaling process is done in several steps. The first step is to pass flowing inert gases such as N₂ or Ar into the pyrolysis chamber (filled with waste plastics) which is heated with reference to the heating profiles shown in **Fig. 2**. After which different octane gases are released from the pyrolysis chamber and passed through the distillation column (i.e. low octane gas C₁-C₅, high octane gas ≥C₆). Inside the distillation column, gases are sorted as feedstock in synthesizing carbon nanotubes (CNT) or made into fuel while the by-products are collected at the end of the pyrolysis process and purified. Inside the chemical vapour deposition (CVD) reactor, the gaseous feedstock is heated in inert condition depending on the final CNT requirements needed, and the catalysts may be introduced. The CNTs are then collected and purified. The final reinforced products are made using CNT and mineral fibers from waste plastics in different proportions.

[089] The parameters involved include: -

[090] Gas Flow rate : 250 sccm to 50 m³/hr

[091] Temperature of reaction: 200 °C to 1,600 °C

[092] Additives: H₂S, H₂O, helium bubbled through benzene to enhance productivity of the carbonaceous nanostructured materials

[093] CVD reactor (Assuming cylindrical) Diameter: 5 cm to 5 m

[094] CVD reactor (Assuming cylindrical) Length: 50 cm to 10 m

[095] CVD reactor shape: Trapezoid (like funnel), cylindrical, rectangular or combination of different shapes including cylinders within a cylinder or cuboids within cylinders

- [096] CVD reactor Orientation: Horizontal, vertical or tilted within an inclination
- [097] Pyrolysis reactor Shape: Cylindrical, cubical, spherical, conical, Trapezoid etc.
- [098] Pyrolysis reactor Volume: 100 cm^3 to $1,000 \text{ m}^3$
- [099] The CVD reactor and pyrolysis reactor may be designed in trapezoidal shape to act as a cyclone separator, for example.

Claims

1. A method of forming carbonaceous and mineral nanostructured materials from plastics, comprising:

annealing the plastics in an inert or vacuum environment comprised in an enclosed reactor to form mineral nanostructured materials and carbonaceous gaseous products; and

feeding the carbonaceous gaseous products to a chemical vapour deposition reactor and heating the carbonaceous gaseous products therein to form carbonaceous nanostructured materials,

wherein the annealing comprises a first annealing stage and a second annealing stage,

wherein the first annealing stage comprises constant heating at a temperature range of between 100 °C and 200 °C for a period of 1 h to 4 h; and

wherein the second annealing stage comprises constant heating at a temperature range of between 400 °C and 1,500 °C for a period of 3 h to 11 h.

2. The method of claim 1, wherein the first annealing stage comprises constant heating at a temperature range of between 100 °C and 120 °C for a period of 1 h to 4 h.

3. The method of claim 2, wherein the first annealing stage comprises constant heating at 100 °C or 120 °C for 3 h.

4. The method of any one of claims 1-3, wherein the second annealing stage comprises constant heating at a temperature range of between 400 °C and 1,200 °C for a period of 3 h to 11 h.

5. The method of claim 4, wherein the second annealing stage comprises constant heating at a temperature range of between 500 °C and 800 °C for a period of 3 h.

6. The method of any one of claims 1-5, wherein prior to feeding the carbonaceous gaseous products to the chemical vapour deposition reactor, the carbonaceous gaseous products are fed to a distillation column.

7. The method of any one of claims 1-6, wherein heating the carbonaceous gaseous products comprises heating at a temperature range of between 200 °C and 1,600 °C.
8. The method of any one of claims 1-7, wherein heating the carbonaceous gaseous products comprises heating the carbonaceous gaseous products in the presence of a catalyst.
9. The method of claim 8, wherein the catalyst is selected from the group consisting of an organo-metallic material, a metal, a metal oxide, a transition metal, and a derivative thereof.
10. The method of claim 9, wherein the catalyst is selected from the group consisting of ferrocene, iron oxide, cobaltocene, nickelocene, copper oxide, tungsten, titanium, platinum, nickel, vanadium, chromium, manganese, cobalt, zinc, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, and a mixture thereof.
11. The method of claim 6, wherein a portion of the carbonaceous gaseous products after passing through the distillation column is condensed to form a fuel.
12. A method of forming mineral nanostructured materials from plastics, comprising:
 - annealing the plastics in an inert or vacuum environment comprised in an enclosed reactor to form mineral nanostructured materials,
 - wherein the annealing comprises a first annealing stage and a second annealing stage,
 - wherein the first annealing stage comprises constant heating at a temperature range of between 100 °C and 200 °C for a period of 1 h to 4 h; and
 - wherein the second annealing stage comprises constant heating at a temperature range of between 400 °C and 1,500 °C for a period of 3 h to 11 h.