

APPARATUS FOR PRODUCTION OF CARBON NANOTUBES AND HYDROGEN FROM PYROLYSIS GASES

Field of Invention

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The current invention relates to an apparatus, use of apparatus and a method of producing carbon nanotubes (CNTs) and hydrogen gas (H₂) from a pyrolysis gas.

Background

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15 Pyrolysis is a thermal process for decomposition of carbonaceous feedstock in the absence of air or in oxygen deprived atmosphere. Typical pyrolysis products are carbonized solid residues with ashes (black carbon, coke, char, biochar and charcoal), liquid products (bio-oil, oil, naphtha) and a mixture of non-condensable gases, containing hydrocarbon compounds, hydrogen, carbon monoxide (CO), carbon dioxide (CO₂) and traces of other compounds.

20 Depending on the origin, carbonized solid residues could be utilized as a soil amendment, high-calorific fuel or a material for upgrading, for instance, into activated carbon and carbon dots. Liquid products from some plastics, especially, derived from polyolefins (referred to as naphtha) are considered a substitute of petroleum oil for petrochemical industry. There are also ongoing studies to valorize liquid products from other types of carbonaceous feedstock.

25 Pyrolysis gas is a type of gas produced during the thermal decomposition of organic material at high temperatures in the absence of oxygen via a process called pyrolysis. Pyrolysis gas typically consists of hydrocarbon compounds, hydrogen, carbon monoxide, carbon dioxide, and may also contain other compounds such tar, oxygenated organic compounds, nitrogen, oxygen, water vapor, hydrogen sulfide, carbonyl sulfide, ammonia, hydrogen cyanide,

30 hydrogen chloride. Pyrolysis gas is typically combusted to recover energy and avoid undesirable emissions of greenhouse gases (i.e. hydrocarbon compounds), CO and hydrogen into atmosphere.

In the past decades, significant progress was made to convert pyrolysis gases into value-added products, such as carbon nanotubes (CNTs). Carbon nanotubes (CNTs) are high-performance additives in manufacturing of polymer composites, inks, coatings, sensors, energy storage devices, electronics, automobile and aerospace manufacturing. Chemical

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vapor deposition (CVD) method is one of the methods that can be employed for the synthesis of CNTs due to relatively low cost, easy scale up and possibility to control morphology of CNT products in a wide range. CVD is typically carried out using transition metal catalysts (e.g., Fe, Ni, Co, Mo and their mixtures) and carbon precursors such as non-condensable hydrocarbon gases (e.g., methane (CH₄), acetylene) or carbon monoxide. During the catalytic reactions, carbon monoxide decomposes into C and CO₂ via disproportionation, while hydrocarbon gases decompose into C and H₂ molecules. The former reaction pathway provides an opportunity for generation of hydrogen-rich gas during the production of CNTs. Hydrogen is considered an important source of energy for decarbonized economy. However, production of CNTs consumes substantial amounts of fossil-derived feedstock. Purified methane (Oh, E. et al., *ACS Appl. Mater. Interface* **2020**, *12*, 13107), ethylene (Gommes, C. et al., *Carbon* **2004**, *42*, 1473) and propylene (Jiang, J.-J. et al., *Diam. Relat. Mater.* **2020**, *110*, 108109) that are used as precursors for the growth of CNTs at industrial scale are obtained from processing of natural gas and crude oil. Hydrogen is being co-fed into a synthesis reactor together with carbon precursors. Similarly with hydrocarbon compounds, its manufacturing is far from being renewable. Almost entirely hydrogen is produced by steam reforming of natural gas or gasification of coal (Hermesmann, M. & Müller, M., *Prog. Energ. Combust. Sci.* **2022**, *90*, 100996). One of the key drivers for sustainability is to obtain products with low environmental footprint, which would account for lesser usage of fossil resources throughout the life cycle.

As an alternative to usage of conventional precursors, substantial progress has been achieved in the synthesis of CNTs and hydrogen using pyrolysis gases obtained from plastics and mixtures of plastics with biomass. Table 1 summarizes the system configurations that were used for CNT synthesis from plastic-derived pyrolysis gas. A transition to the utilization of only renewable biomass as a feedstock could be the next step towards achieving responsible production of these valuable chemicals.

Table 1. Conversion of plastics and plastics-biomass mixtures into multi-walled CNTs and obtained product yields. (HDPE: high-density polyethylene; LDPE: low-density polyethylene; PP: polypropylene; PS: polystyrene; PET: polyethylene terephthalate)

Feedstock	Process, catalyst, conditions	CNT yield per catalyst ass, g/g _{cat}	Ref.
LDPE, PP	Catalytic or non-catalytic pyrolysis – oil condensation - conversion of gases into CNTs, Co-Mo supported on MgO, 700 °C	0.90-38.30	[1], [2]
LDPE and PP (+10% PS, +10% PET)	Pyrolysis – oil condensation – conversion of gases into CNTs, Ni supported on CaCO ₃ , 500 and 800 °C	0.21-0.31	[3]

Feedstock	Process, catalyst, conditions	CNT yield per catalyst ass, g/g _{cat}	Ref.
PET, PS	Pyrolysis – oil condensation – conversion of gases into CNTs, Ni supported on CaCO ₃ , 800 °C	<0.01, not suitable	[3]
LDPE and PP	Pyrolysis – oil condensation – conversion of gases into CNTs, Ni supported on La, Mg and Sr oxides, 700 °C	0.35-0.86	[4]
LDPE, PP, HDPE, PS and PET	Pyrolysis – oil condensation – conversion of gases into CNTs, Ni-Mo/Al ₂ O ₃ , 650 °C	5.80 (LDPE), 5.00 (PP), 3.86 (HDPE), 0.52 (PET), 0.2 (PS)	[5]
PU, EVA, PE	Pyrolysis – oil condensation – conversion of gases into CNTs, Fe supported on Mg oxide, 1000 °C	0.020 (PU), 0.064 (EVA), 0.078 (PE)	[6]
Flexible laminate plastics	Pyrolysis – catalytic cracking – oil condensation – CNT synthesis on Ni supported on CaCO ₃ , 500 and 800 °C	Not reported	[7]
LDPE, HDPE, PP mixture	Pyrolysis – thermal cracking – oil condensation – 2 CVD reactors for CNT synthesis on Co-Mo supported on MgO, 700 °C and 1000 °C, respectively	14±4 (multi-walled) and 0.18 ± 0.09 (few-walled)	[8]
Oiltea camellia shells (50 wt.%) and PP (50 wt.%)	Pyrolysis – oil condensation – conversion of gases into CNTs over X-Mo@MgO (X = Ni, Fe, Co, where metal content X was 10 wt.% and Mo content was either 0 or 5 wt.%)	0.04-1.44	[9]
Herb residue (50 wt.%) and PP (50 wt.%)	Catalytic pyrolysis over Ni-X/biochar and Ni-X/ZSM-5 catalysts (X = Fe, Co, Cu, where metal content X and Ni contents were 5 wt.%) – oil condensation – conversion of gases into CNTs over NiMo/SiO ₂ (Ni and Mo contents were 5 wt.%)	0.2-1.9	[10]
Cellulose, lignin, wheat straw and sawdust	Pyrolysis – oil condensation – gas purification with alkali solution – conversion of gases into graphene film over a Ni foam at 950 °C	Not applicable	[11]

[1] Aboul-Enein, A.A. et al., *Mater. Chem. Phys.*, **2019**, 238, 121879; [2] Aboul-Enein, A.A. & Awadallah, A.E., *Fuller. Nanotub. Carbon Nanostructures*, **2018**, 26, 591; [3] Veksha, A. J. *Analytical Appl. Pyrolysis*, **2017**, 124, 16; [4] Jia, J. et al., *J. Clean. Production*, **2020**, 258, 120633; [5] Aboul-Enein, A.A. et al., *Fuller Nanotub. Carbon Nanostructures*, **2018**, 26, 443; [6] Chen, W.Q. et al., *J. Clean. Production*, **2022**, 356, 131868; [7] Veksha, A. et al., *J. Hazard. Mater.*, **2020**, 387, 121256; [8] Veksha, A. et al., *J. Hazard. Mater.*, **2022**, 421, 126717; [9] Dong, H. et al., *Sci. Tot. Environ.*, **2022**, 831, 154751; [10] Luo, W. et al., *Bioresource Technol.*, **2022**, 349, 126845; [11] Zhang, S. et al., *Nat. Sustain.*, **2020**, 3, 753.

- 10 Pyrolysis was carried out with the aid of a catalyst that facilitates the decomposition of plastics into hydrocarbon precursors (Aboul-Enein, A.A. et al., *Mater. Chem. Phys.*, **2019**, 238,

121879). Alternatively, adding the catalyst into pyrolysis reactor can be omitted (Aboul-Enein, A.A. & Awadallah, A.E., *Fuller. Nanotub. Carbon Nanostructures*, **2018**, 26, 591; Veksha, A. *J. Analytical Appl. Pyrolysis*, **2017**, 124, 16; Jia, J. et al., *J. Clean. Production*, **2020**, 258, 120633; Aboul-Enein, A.A. et al., *Fuller Nanotub. Carbon Nanostructures*, **2018**, 26, 443; Chen, W.Q. et al., *J. Clean. Production*, **2022**, 356, 131868). The produced pyrolysis products comprise mixtures of hydrocarbons that condense after cooling into liquid products and mixtures of pyrolysis gases. The condensed oil can be returned to a pyrolysis reactor for thermal decomposition into pyrolysis gases (Aboul-Enein, A.A. & Awadallah, A.E., *Fuller. Nanotub. Carbon Nanostructures*, **2018**, 26, 591). Depending on the plastic composition, the quality of produced oil can be upgraded through the catalytic reforming process installed after pyrolysis reactor and before oil condenser (Veksha, A. et al., *J. Hazard. Mater.*, **2020**, 387, 121256). The reforming process demonstrated the decomposition of oxygenated hydrocarbons released during pyrolysis of oxygen-containing polymers (e.g., polyethylene terephthalate). In other study, after pyrolysis, the products were transferred into a thermal cracker for non-catalytic decomposition prior to oil condensation and CVD synthesis (Veksha, A. et al., *J. Hazard. Mater.*, **2022**, 421, 126717). The proposed system configurations were used for conversion of pyrolysis gases from PE, PP, PS, PET, PU, EVA, and plastic mixtures containing these polymers (Aboul-Enein, A.A. et al., *Mater. Chem. Phys.*, **2019**, 238, 121879; Aboul-Enein, A.A. & Awadallah, A.E., *Fuller. Nanotub. Carbon Nanostructures*, **2018**, 26, 591; Veksha, A. *J. Analytical Appl. Pyrolysis*, **2017**, 124, 16; Jia, J. et al., *J. Clean. Production*, **2020**, 258, 120633; Aboul-Enein, A.A. et al., *Fuller Nanotub. Carbon Nanostructures*, **2018**, 26, 443; Chen, W.Q. et al., *J. Clean. Production*, **2022**, 356, 131868; Veksha, A. et al., *J. Hazard. Mater.*, **2020**, 387, 121256; Veksha, A. et al., *J. Hazard. Mater.*, **2022**, 421, 126717).

Mixtures of biomass (50 wt.%) and PP (50 wt.%) have been utilized to produce pyrolysis gas for the growth of CNTs (Dong, H. et al., *Sci. Tot. Environ.*, **2022**, 831, 154751; Luo, W. et al., *Bioresource Technol.*, **2022**, 349, 126845). The setups consisted of a pyrolysis reactor, condenser for liquids and CVD reactor for catalytic synthesis of CNTs. Dong et al. (2022) used a mixture of oiltea camellia shells (50 wt.%) and PP (50 wt.%) (Dong, H. et al., *Sci. Tot. Environ.*, **2022**, 831, 154751). The growth of CNTs was conducted over six X-Mo@MgO catalysts (X = Ni, Fe, Co, where metal content X was 10 wt.% and Mo content was either 0 or 5 wt.%). The feedstock was pyrolyzed followed by condensation of liquid products. The remaining gaseous products were utilized for the growth of CNTs. The yield of CNTs over Ni@MgO, Fe@MgO, Co@MgO catalysts was 0.08, 0.04 and 0.21 g/g- catalyst, respectively, and over Ni-Mo@MgO, Fe-Mo/MgO and Co-Mo/MgO catalysts was 1.43, 1.44 and 1.23 g/g- catalyst, respectively. In another study, a mixture of herb residue (50 wt.%) and PP (50 wt.%) were first catalytically decomposed by Ni-X/biochar and Ni-X/ZSM- 5 catalysts (X = Fe, Co,

Cu, where metal content X and Ni contents were 5 wt.%). The produced oil was condensed while pyrolysis gas was catalytically treated over NiMo/SiO₂ (Ni and Mo contents were 5 wt.%) (Luo, W. et al., *Bioresource Technol.*, **2022**, 349, 126845). According to the temperature programmed oxidation, the content of carbon deposits in the spent NiMo/SiO₂ catalyst varied between around 15 and 65 wt.%, depending on the type of Ni-X/biochar and Ni-X/ZSM-5 catalyst. From these values it can be derived that the yield of carbon per NiMo/SiO₂ mass was between around 0.2 and 1.9 g/g-catalyst. The higher amounts of deposited carbon were attributed to the higher production yields of gaseous carbon precursors over Ni-X/biochar and Ni-X/ZSM-5 catalysts. According to Luo et al., CH₄ and CO were the probable precursors for carbon deposition.

Notably, as will be shown in the examples below, pyrolysis gases from some plastic mixtures (for instance, plastics from cosmetics packaging, containing PET, PETG (polyethylene terephthalate glycol) and plastics with a label code “Others”, and contaminated by leftovers of personal care products) yield negligible or low quantities of CNTs, even when they contain hydrocarbon precursors and CO.

In addition, when pyrolysis gases derived from biomass are used at similar conditions to those reported for plastics in studies (Aboul-Enein, A.A. et al., *Mater. Chem. Phys.*, **2019**, 238, 121879; Aboul-Enein, A.A. & Awadallah, A.E., *Fuller. Nanotub. Carbon Nanostructures*, **2018**, 26, 591; Veksha, A. *J. Analytical Appl. Pyrolysis*, **2017**, 124, 16; Jia, J. et al., *J. Clean. Production*, **2020**, 258, 120633; Aboul-Enein, A.A. et al., *Fuller Nanotub. Carbon Nanostructures*, **2018**, 26, 443; Chen, W.Q. et al., *J. Clean. Production*, **2022**, 356, 131868; Veksha, A. et al., *J. Hazard. Mater.*, **2020**, 387, 121256; Veksha, A. et al., *J. Hazard. Mater.*, **2022**, 421, 126717; Dong, H. et al., *Sci. Tot. Environ.*, **2022**, 831, 154751; Luo, W. et al., *Bioresource Technol.*, **2022**, 349, 126845), the growth of CNT structures is also inhibited. This is despite the presence of hydrocarbon gases and CO in pyrolysis gas from biomass. The majority of real-world plastic waste is contaminated by biomass residues (e.g., food and agricultural residues), personal care products and consists of a mixture of various polymers, including PET, PETG and plastics labelled as “Others”. Biomass-derived feedstock is generated in agriculture, forestry, food processing. Municipal solid waste can contain the mixtures of various plastics and biomass in different ratios. Due to feedstock diversity, it is advantageous to find the solution for the utilization of pyrolysis gases from different types of feedstock to grow CNTs and produce hydrogen in a more efficient way. One study observed the inhibition of carbon growth using biomass when producing graphene films (Zhang, S. et al., *Nat. Sustain.*, **2020**, 3, 753). The authors of the above papers proposed to use gas purification with alkaline solution after oil condensation. Such process was shown to increase

graphene film yield but generated considerable amount of liquid waste contaminated by organic chemicals from pyrolysis gas, having negative environmental impact and increased cost. No data for hydrogen generation was reported. Considering that hydrogen is an important by-product from CNT synthesis, it is advantageous to co-generate increased quantities of hydrogen and decrease liquid waste generation.

As such, there remains a need for new methods to generate CNTs.

Summary of Invention

It is the objective of this invention to provide an apparatus, use of apparatus and a method of producing carbon nanotubes (CNTs) and hydrogen gas from a pyrolysis gas.

Disclosed herein is an apparatus for production of CNTs comprising a first reactor (sorber reactor), which is connected to a second reactor (chemical vapor deposition reactor) in series; wherein the sorber reactor is configured to hold a heated sorber bed, wherein the sorber bed generates an intermediate gas and captures a part of pyrolysis gas when the sorber bed is in contact with pyrolysis gas received from an inlet of apparatus; and the chemical vapor deposition reactor is configured to hold a catalyst bed comprising a second catalyst, wherein the second catalyst bed generates the CNTs and releases hydrogen when the catalyst bed is in contact with the intermediate gas received from the first reactor (FIG. 1). A condenser and a moisture trap are installed between the two reactors for the removal of liquid products and water vapor.

The current invention also discloses a method of producing CNTs from a pyrolysis gas obtained by decomposition of a carbonaceous feedstock, comprising the steps of: (a) flowing the pyrolysis gas into a first reaction zone containing a sorber, wherein a portion of the pyrolysis gas is partially removed by the sorber to produce an intermediate gas; and (b) flowing the intermediate gas into a second reaction zone containing a catalyst, wherein a portion of the intermediate gas is converted into CNTs and hydrogen.

Aspects and embodiments of the invention are provided in the following numbered clauses.

1. An apparatus for the production of carbon nanotubes and hydrogen from a pyrolysis gas, the apparatus comprising:
a sorber reactor portion comprising:

a first reaction vessel having an inlet configured to accept a pyrolysis gas from a pyrolysis gas source and an outlet;

a solid sorbent and/or a solid sorbent precursor, where the solid sorbent is suitable to adsorb CO₂ from a pyrolysis gas situated within the reaction vessel, such that a pyrolysis gas passes

over the sorbent in its passage from the inlet to the outlet; and

a heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the first reaction vessel;

a liquid trapping means or apparatus attached to the outlet of the sorbent reactor portion;

a chemical vapour deposition reactor portion comprising:

a second reaction vessel having an inlet configured to accept a pyrolysis gas that has passed through the liquid trapping means or apparatus and an outlet;

a catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas situated within the reaction vessel, such that a pyrolysis gas passes over the

catalyst in its passage from the inlet to the outlet; and

a heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the second reaction vessel.

2. The apparatus according to Clause 1, wherein the apparatus further comprises a pyrolysis gas source.

3. The apparatus according to Clause 2, wherein the pyrolysis gas source is selected from one or more of the group selected from a pyrolyser, a pyrolyser in fluid communication with an upgrader, and a storage device comprising a pyrolysed gas.

4. The apparatus according to any one of the preceding clauses, wherein:

(ai) the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas is selected from one or more of the group consisting of CaO, MgO, Ca(OH)₂, Mg(OH)₂, a serpentinite mineral, magnesium silicate hydroxide, (Mg,Fe)₂SiO₄ (olivine), a molecular sieve suitable to adsorb CO₂, a metal organic framework suitable to adsorb CO₂, and activated carbon; and/or

(aii) the solid sorbent precursor is selected from one or more of the group consisting of CaCO₃, and MgCO₃, and CaMg(CO₃)₂ (dolomite); and/or

(aiii) the solid sorbent suitable to adsorb CO₂ and the solid sorbent precursor are present in the sorbent reactor portion.

5. The apparatus according to Clause 4, wherein the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas is in one or more of a particulate form, a pelletized form and a granulated form.

6. The apparatus according to Clause 4 or Clause 5, wherein the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas comprises CaO, optionally wherein:

(bi) the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas further comprises Ca(OH)₂; and/or

(bii) the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas further comprises CaCO₃;

and/or

(biii) the solid sorbent is in particulate form and has a particle size of from 1 to 5 mm.

7. The apparatus according to any one of the preceding clauses, wherein the liquid trapping means or apparatus comprises a condenser and moisture trap.

8. The apparatus according to any one of the preceding clauses, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas comprises one or more elements selected from the group consisting of Fe, Ni, Co, Mo, W, Al, Si, C and Mg.

9. The apparatus according to Clause 8, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas is selected from one or more of the groups consisting of:

Fe₂O₃ and Al₂O₃ (e.g. 20 wt.% Fe₂O₃ and 80 wt.% Al₂O₃); and

Co, Mo and MgO (e.g. 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO), optionally wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas is selected from one or more of the groups consisting of 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO, more optionally wherein the catalyst is 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO.

10. The apparatus according to any one of the preceding clauses, wherein the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the first reaction vessel and the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the second reaction vessel is an electric heater.

11. The apparatus according to any one of the preceding clauses, wherein the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the first reaction vessel and the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the second reaction vessel generate a temperature from 150 to 1,000 °C, such as from 400 to 700 °C, such as about 600 °C.

12. The apparatus according to any one of the preceding clauses, wherein the pyrolysis gas is a gas obtained from a carbonaceous feedstock, optionally wherein the pyrolysis gas is obtained from one or more of the group consisting of municipal sewage sludge and, more particularly, plastics, biomass, and refuse derived fuel obtained from combustible components of municipal waste.

13. Use of an apparatus according to any one of Clauses 1 to 12 in the production of carbon nanotubes and hydrogen from a pyrolysis gas.

14. A method of producing carbon nanotubes and hydrogen gas from a pyrolysis gas, comprising the steps of:

- (a) passing a pyrolysis gas through a first reactor zone having a temperature of greater than 100 °C that houses a solid sorbent suitable for adsorbing CO₂, where a portion of the pyrolysis gas is adsorbed by the sorbent to produce an intermediate gas; and
- (b) passing the intermediate gas through a second reactor zone having a temperature of greater than 100 °C that houses a catalyst, where the catalyst converts at least a portion of the intermediate gas into carbon nanotubes and hydrogen gas.

15. The method according to Clause 14, wherein the pyrolysis gas is obtained from a carbonaceous feedstock supplied by one or more of the group selected from a pyrolyser, a pyrolyser in fluid communication with an upgrader, and a storage device comprising a pyrolysed gas.

16. The method according to Clause 15, wherein the carbonaceous feedstock is a plastic and/or biomass, optionally wherein the carbonaceous feedstock is plastic and biomass.

17. The method according to any one of Clauses 14 to 16, wherein: the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas is selected from one or more of the group consisting of CaO, MgO, Ca(OH)₂, Mg(OH)₂, a serpentinite mineral, magnesium silicate hydroxide, (Mg,Fe)₂SiO₄ (olivine), a molecular sieve suitable to adsorb CO₂, a metal organic framework suitable to adsorb CO₂, and activated carbon.

18. The method according to any one of Clauses 14 to 17, wherein the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas is generated from a solid sorbent precursor that is selected from one or more of the group consisting of CaCO₃, and MgCO₃ and CaMg(CO₃)₂ (dolomite) prior to step (a) of Clause 14 by calcination of the solid sorbent precursor.

19. The method according to Clause 17 or Clause 18, wherein the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas is in one or more of a particulate form, a pelletized form and a granulated form.

20. The method according to any one of Clauses 17 to 19, wherein the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas comprises CaO, optionally wherein:

(ci) the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas further comprises Ca(OH)₂; and/or

(cii) the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas further comprises CaCO₃; and/or

(ciii) the solid sorbent is in particulate form and has a particle size of from 1 to 5 mm.

21. The method according to any one of Clauses 14 to 20, wherein the method further comprises a step (di) of trapping any liquid generated in step (a) before conducting step (b) of the method according to Clause 14.

22. The method according to Clause 21, wherein step (di) of Clause 21 is accomplished using a liquid trapping means or apparatus, optionally wherein the liquid trapping means or apparatus comprises a condenser and moisture trap.

23. The method according to any one of Clauses 14 to 22, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas is selected from one or more of the group consisting of:

Fe₂O₃ and Al₂O₃ (e.g. 20 wt.% Fe₂O₃ and 80 wt.% Al₂O₃); and

Co, Mo and MgO (e.g. 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO).

24. The method according to Clause 23, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas comprises one or more elements selected from the group consisting of Fe, Ni, Co, Mo, W, Al, Si, C and Mg.

25. The method according to Clause 24, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas is selected from one or more of the groups consisting of:

Fe_2O_3 and Al_2O_3 (e.g. 20 wt.% Fe_2O_3 and 80 wt.% Al_2O_3); and

5 Co, Mo and MgO (e.g. 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO).

26. The method according to any one of Clauses 14 to 25, wherein the temperature in the first reactor zone and/or the temperature in the second reactor zone is from 150 to 1,000 °C, such as from 400 to 700 °C, such as about 600 °C.

Drawings

FIG. 1 depicts the feedstock examples: (a) pine sawdust, (b) coconut coir pith, (c) refuse derived fuel pellets (RDF) and (d) cosmetics packaging prior to shredding.

FIG. 2 depicts the system for synthesis of CNTs and H_2 integrated with CO_2 capture from pyrolysis gas: (1) pyrolyzer equipped with an electric heater, (2) double valve feeding unit, (3) pressure gauge, (4) nitrogen (N_2) supply line, (5) CO_2 sorbent reactor equipped with an electric heater, (6) liquid condenser, (7) moisture trap, (8) CVD reactor equipped with an electric heater, (9) gas bag.

FIG. 3 depicts an apparatus for CNT synthesis.

FIG. 4 depicts the yield of CNTs produced without and with the use of sorbent (feeding rate: 10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 700 °C). The results are reported as averages and error bars represent standard deviations.

FIG. 5 depicts the morphology of spent catalyst after the synthesis using gas (A, B) without the use of sorbent and (C, D) with the use of sorbent (feedstock: pine sawdust pellets, feeding rate: 10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 700 °C).

FIG. 6 depicts the TEM images of CNTs after the synthesis using gas after the use of sorbent: (A) coconut coir pith, (B) RDF, (C) cosmetics packaging and (D) sewage sludge (feeding rate:

10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 700 °C).

FIG. 7 depicts the distribution of outer diameters of multi-walled CNTs after the synthesis from gas after the use of sorbent (feeding rate: 10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 700 °C).

FIG. 8 depicts the composition of pyrolysis gas (feedstock: pine sawdust pellets, feeding rate: 10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis temperature: 600 °C).

The results are reported as averages $\pm$ standard deviations based on triplicated experiments

FIG. 9 depicts the contents of main gaseous components at the inlet of the CVD reactor: (A, B) without the use of sorbent and (C, D) with the use of sorbent (feeding rate: 10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 700 °C). The results are reported as averages and error bars represent standard deviations.

FIG. 10 depicts the contents of main gaseous components at the outlet of CVD reactor. The synthesis was conducted with the use of sorbent (feeding rate: 10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 700 °C). The results are reported as averages and error bars represent standard deviations.

FIG. 11 depicts the process flow diagram for synthesis of CNTs and H₂ integrated with CO₂ capture from pyrolysis gas.

FIG. 12 depicts the X-ray diffraction patterns of natural calcite, fresh Ca-based sorbent (calcination temperature: 850 °C) and spent Ca-based sorbent after 40 min of CO₂ removal (CO₂ removal temperature: 600 °C). Quantitative analysis: natural calcite (wt. %): CaCO₃ – 93.4, CaMg(CO₃)₂ – 6.6; Fresh Ca-based sorbent: CaCO₃ – 86.5, CaO – 8.7, Ca(OH)₂ – 4.9, spent Ca-based sorbent: CaCO₃ – 100.

FIG. 13 depicts the transmission electron microscopy (TEM) image of CNTs synthesized after CO₂ capture from pyrolysis gas derived from coconut coir pith (feeding rate: 10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis, carbon removal and CVD reactor temperatures: 600, 600 and 700 °C).

FIG. 14 depicts the influence of CVD synthesis time on CNT yield. The experiments were conducted using the pyrolysis gas after CO₂ removal by the sorbent (feedstock: pine sawdust pellets, feeding rate: 10 g/10 min, catalyst: 40Co-10Mo, pyrolysis, CO₂ removal and CVD reactor temperatures: 600, 600 and 700 °C). The results are reported as averages and error bars represent standard deviations.

FIG. 15 depicts the influence of gas treatment on the evolution of main components at the outlet of CVD reactor (feedstock: pelletized pine sawdust, feeding rate: 10 g/10 min, synthesis time: 40 min, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 700 °C). A: hydrocarbon compounds and B: inorganic compounds. Error bars represent standard deviations of three runs.

FIG. 16 depicts the layout of setup with alkaline scrubber (top) and NaOH solution contaminated by organic compounds after the completion of a synthesis run (bottom) (feedstock: pine sawdust, feeding rate: 10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis reactor and CVD reactor temperatures: 600 and 700 °C).

FIG. 17 depicts the influence of synthesis time on the gas composition (A) CH₄, C₂H₄, C₂H₆, C₃H₆; and (B) CO₂, CO, H₂ at the outlet of CVD reactor (feedstock: pine sawdust pellets, feeding rate: 10 g/10 min, catalyst: 40Co-10Mo, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 700 °C). The results are reported as averages and error bars represent standard deviations.

FIG. 18 depicts the Influence of feeding rate on (A) carbon yield and (B) gas evolution from the outlet of CVD reactor. The experiments were conducted using the gas with the treatment by sorbent (feedstock: pine sawdust pellets, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 700 °C). The results are reported as averages and error bars represent standard deviations.

FIG. 19 depicts the CNTs synthesized over 2Co-3Mo catalyst in the improved system integrated with the semi-continuous pyrolyzer (feedstock: pine sawdust pellets, synthesis time: 20 min, pyrolysis reactor, sorbent reactor and CVD reactor temperatures: 600, 600 and 1000 °C). The experiments were conducted using the gas treated with sorbent.

Description

In a first aspect of the invention, there is provided an apparatus for the production of carbon nanotubes and hydrogen from a pyrolysis gas, the apparatus comprising:

5 a sorbent reactor portion comprising:

a first reaction vessel having an inlet configured to accept a pyrolysis gas from a pyrolysis gas source and an outlet;

a solid sorbent and/or a solid sorbent precursor, where the solid sorbent is suitable to adsorb CO₂ from a pyrolysis gas situated within the first reaction vessel, such that a pyrolysis gas
10 passes over the sorbent in its passage from the inlet to the outlet; and

a heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the first reaction vessel;

a liquid trapping means or apparatus attached to the outlet of the sorbent reactor portion;

15 a chemical vapour deposition reactor portion comprising:

a second reaction vessel having an inlet configured to accept a pyrolysis gas that has passed through the liquid trapping means or apparatus and an outlet;

a catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas situated within the second reaction vessel, such that a pyrolysis gas passes
20 over the catalyst in its passage from the inlet to the outlet;

and

a heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the second reaction vessel.

25 In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations
30 can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to
35 a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure,

such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

As used herein, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a composition” includes mixtures of two or more such compositions, reference to “an oxygen carrier” includes mixtures of two or more such oxygen carriers, reference to “the catalyst” includes mixtures of two or more such catalysts, and the like.

In certain embodiments of the invention that may be mentioned herein, the apparatus may further comprise a pyrolysis gas source. Any suitable pyrolysis gas source may be used. Examples of suitable pyrolysis gas sources include, but are not limited to a pyrolyser, a pyrolyser in fluid communication with an upgrader, a storage device comprising a pyrolysed gas, and combinations thereof.

As noted herein, the first reaction vessel houses one or both of a solid sorbent and a solid sorbent precursor. As will be appreciated, when the apparatus is used, the solid sorbent precursor material may be converted into the solid sorbent material. As such, in certain embodiments of the invention, the solid sorbent suitable to adsorb CO₂ and the solid sorbent precursor may be present in the sorbent reactor portion.

Any suitable solid material that may absorb CO₂ may be used in the apparatus. Examples of such solid sorbents suitable to adsorb CO₂ from a pyrolysis gas include, but are not limited to, CaO, MgO, Ca(OH)₂, Mg(OH)₂, a serpentinite mineral, magnesium silicate hydroxide, (Mg,Fe)₂SiO₄ (olivine), a molecular sieve suitable to adsorb CO₂, a metal organic framework suitable to adsorb CO₂, activated carbon, and combinations thereof.

Any suitable material that can form a solid sorbent suitable to adsorb CO₂ from a pyrolysis gas may be used herein. For example, the solid sorbent precursor may be selected from one or more of the group consisting of CaCO₃, and MgCO₃, and CaMg(CO₃)₂ (dolomite).

The solid sorbent suitable to adsorb CO₂ from a pyrolysis gas may be provided in any suitable form. For example, the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas may be provided in one or more of a particulate form, a pelletized form and a granulated form.

In certain embodiments that may be mentioned herein, the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas may comprise CaO. As will be appreciated, the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas may only be CaO or it may contain further suitable sorbents

(or it may include precursor materials that may form CaO or said other suitable sorbents). In particular embodiments of the invention, when the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas comprises CaO, then it may also further comprise:

- (bi) Ca(OH)₂; and/or
- 5 (bii) CaCO₃ as well.

That is, the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas may comprise: CaO and Ca(OH)₂, CaO and CaCO₃, or CaO, Ca(OH)₂ and CaCO₃.

- 10 In embodiments of the invention, the solid sorbent may be in particulate form. When the solid sorbent is in particulate form, it may have any suitable particle size. For example, the solid sorbent may have a particle size of 1 to 5 mm. As will be appreciated, when the term particle size is used herein it may mean that the particles that make up the particulate material generally fall within the particle size range provided. This may be achieved by sieving the
- 15 material (e.g. once with a sieve to remove smaller particles and one with a sieve to remove larger particles) to ensure that the desired particle size range is obtained.

- As noted above, the apparatus also incorporates a liquid trapping means or apparatus attached to the outlet of the sorbent reactor portion. That is, to the outlet of the first reaction
- 20 vessel. Any suitable liquid trapping means or apparatus may be used herein. For example, the liquid trapping means or apparatus may comprises a condenser and a moisture trap.

- As noted hereinabove, the liquid trapping means or apparatus is connected to a chemical vapour deposition reactor portion. This portion includes a second reaction vessel having an
- 25 inlet configured to accept a pyrolysis gas that has passed through the liquid trapping means or apparatus and an outlet. The second reaction vessel incorporates a catalyst that is suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas. Any suitable catalyst for this purpose may be used. For example, the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas may comprise
- 30 one or more elements selected from the group consisting of Fe, Ni, Co, Mo, W, Al, Si, C and Mg.

- In more particular embodiments of the invention that may be mentioned herein, the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen
- 35 gas may be selected from one or more of the groups consisting of:

Fe₂O₃ and Al₂O₃ (e.g. 20 wt.% Fe₂O₃ and 80 wt.% Al₂O₃); and

Co, Mo and MgO (e.g. 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO).

In certain embodiments that may be mentioned herein, the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas may be selected from one or more of the groups consisting of 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO. For example, the catalyst may be 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO.

The heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the first reaction vessel and the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the second reaction vessel may be any suitable device. For example, an electric heater.

As will be appreciated the heating means or apparatus discussed above must be capable of generating and maintaining a temperature of greater than 100 °C. This may a temperature that may be used to allow the generation of the desired materials. For example, the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the first reaction vessel and the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the second reaction vessel may be able to generate (and maintain) a temperature from 150 to 1,000 °C, such as from 400 to 700 °C, such as about 600 °C.

As will be appreciated, the pyrolysis gas may be obtained from the pyrolysis gas source. Said gas may be a gas obtained from a carbonaceous feedstock. For example, the pyrolysis gas may be obtained from one or more of the group consisting of municipal sewage sludge, and (more particularly) plastics, biomass, and refuse derived fuel obtained from combustible components of municipal waste.

In a second aspect of the invention there is provided a use of an apparatus as described herein in the production of carbon nanotubes and hydrogen from a pyrolysis gas.

In a third aspect of the invention, there is provided a method of producing carbon nanotubes and hydrogen gas from a pyrolysis gas, comprising the steps of:

(a) passing a pyrolysis gas through a first reactor zone having a temperature of greater than 100 °C that houses a solid sorbent suitable for adsorbing CO₂, where a portion of the pyrolysis gas is adsorbed by the sorbent to produce an intermediate gas; and

(b) passing the intermediate gas through a second reactor zone having a temperature of greater than 100 °C that houses a catalyst, where the catalyst converts at least a portion of the intermediate gas into carbon nanotubes and hydrogen gas.

- 5 As the method makes use of the apparatus described hereinbefore, details of the apparatus will not be defined further here in order to minimise repetition.

As will be appreciated, the pyrolysis gas may be obtained from a carbonaceous feedstock supplied by one or more of the group selected from a pyrolyser, a pyrolyser in fluid
10 communication with an upgrader, and a storage device comprising a pyrolysed gas. The carbonaceous feedstock may be obtained from one or more of the group consisting of municipal sewage sludge, and (more particularly) plastics, biomass, and refuse derived fuel obtained from combustible components of municipal waste. In particular embodiments, the carbonaceous feedstock may be a plastic and/or biomass, optionally wherein the
15 carbonaceous feedstock is plastic and biomass.

As will be appreciated, the temperature in the first reactor zone and/or the temperature in the second reactor zone may be greater than 100 °C. For example, the temperature in the first reactor zone and/or the temperature in the second reactor zone may be from 150 to 1,000 °C,
20 such as from 400 to 700 °C, such as about 600 °C.

The system for synthesis of CNTs and hydrogen with increased efficiency includes, but is not limited to, the following advantages.

- (1) Increased outputs of CNTs and hydrogen.
25 (2) Less liquid waste generation.
(3) Suitable for various types of feedstock, including biomass, plastics and RDF.

Commercial applications of the invention includes manufacturing and/or upgrading equipment for synthesis of CNTs and H₂-rich gas from feedstock that generates undesired impurities upon pyrolysis, such as for instance, chlorine, sulfur, nitrogen, oxygen compounds and CO₂.
30 Examples of feedstock include but not limited to biomass, municipal solid waste, municipal sewage sludge, RDF, plastic waste contaminated with biomass, plastic waste (e.g., waste with high PET, PETG content), any carbonaceous feedstock with unknown composition or composition that fluctuates and is challenging to control.

35 Further aspects and embodiments of the invention will now be discussed by reference to the following non-limiting examples.

Examples

Materials – Catalysts

Two catalysts were used, consisting of 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO (denoted as 40Co-10Mo and prepared using a modified method from Aboul-Enein, A.A. et al. (Aboul-Enein, A.A. & Awadallah, A.E., *Fuller. Nanotub. Carbon Nanostructures*, **2018**, 26, 591) and Co 3 wt.%, Mo 2 wt.% and MgO 95 wt.% (denoted as 3Co-2Mo and synthesized using a modified method from Tang, S. et al. (Tang, S. et al., *Chem. Phys. Lett.*, **2001**, 350, 19). Both catalysts were used for chemical vapor deposition without pre-reduction.

Materials – Carbonaceous Feedstock

Five types of materials were used. FIG. 1 shows (1) pine sawdust pellets (pine sawdust), (2) coconut coir pith powder (coconut coir pith), (3) refuse derived fuel pellets (RDF) and (4) shredded cosmetics packaging waste (cosmetics packaging). Additionally, the experiments were conducted using dried municipal sewage sludge from a water treatment plant (sewage sludge). Pelletized pine sawdust contained 46.9 wt.% C, 6.5 wt.% H, 0.1 wt.% N, <0.1 wt.% S and 1.2 wt.% ash. Coconut coir pith contained 42.6 wt.% C, 5.4 wt.% H, 0.6 wt.% N, <0.1 wt.% S and 3.5 wt.% ash. The RDF consisted of a pelletized mixture of 35 wt.% plastics, 23 wt.% paper, 7.7 wt.% textile, 6.9 wt.% wood, 16 wt.% food residues and 11.4 wt.% horticultural waste by mass on a dry basis. The waste fractions were used without cleaning. The details are provided elsewhere (Chan, W.P. et al., *J. Environ. Manage.*, **2019**, 234, 65). Cosmetics packaging waste consisted of various disposed containers from personal care cosmetic products and was shredded prior to the use. The waste was used without cleaning.

Example 1. Synthesis of CNTs and H₂ Integrated with CO₂ Capture from Pyrolysis Gas and Characterisation of the CNTs

Preliminary experiments were conducted using a system built based on references (Veksha, A. et al., *Chemosphere*, **2022**, 297, 134148; Veksha, A. et al., *J. Hazard. Mater.*, **2022**, 435, 128949). Previously, the system in these two references (Veksha, A. et al., *Chemosphere*, **2022**, 297, 134148; Veksha, A. et al., *J. Hazard. Mater.*, **2022**, 435, 128949) was found suitable for the conversion of polyolefinic plastics (LDPE, HDPE and PP mixture) into multi-walled CNTs and was considered for the utilization of biomass. The reported outputs were as follows: multi-walled CNTs yield of 4.28 g/g-catalyst in case of a catalyst consisting of 20 wt.% Fe₂O₃ and 80 wt.% Al₂O₃ prepared by hydrothermal synthesis (Veksha, A. et al., *Chemosphere*, **2022**, 297, 134148) and 14 g/g-catalyst in case of a catalyst consisting of 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO (Veksha, A. et al., *Chemosphere*, **2022**, 297, 134148).

To generate volatile pyrolysis products according to system in (Veksha, A. et al., *Chemosphere*, **2022**, 297, 134148; Veksha, A. et al., *J. Hazard. Mater.*, **2022**, 435, 128949), feedstock was fed into the pyrolysis reactor pre-heated to 600 °C (10 g every 10 min). N₂ was used as a sweep gas (50 mL/min). The produced volatile pyrolysis products were directed into a thermal cracking reactor, comprising a hollow tube heated to 600 °C. The purpose of the cracking reactor was to increase the residence time of volatile pyrolysis products at high temperature to facilitate decomposition into pyrolysis gas (Mastral, F.J. et al., *J. Anal. Appl. Pyrolysis*, **2002**, 63, 1). Liquid pyrolysis products were collected in a condenser maintained at ambient temperature (23 °C). The pyrolysis gas was directed into a CVD reactor, typically, containing 0.25 g of the 40Mo-10Co catalyst. The catalyst was pre-heated to 700 °C. The CVD synthesis was started 10 min after the beginning of pyrolysis and continued for 40 min. When biomass was used as a feedstock, carbon deposition was negligible and filamentous carbon resembled the structure of nanofibers. For clarity, the experiments conducted as described above are denoted as experiments “without sorbent”.

Synthesis of CNTs and H₂ Integrated with CO₂ Capture from Pyrolysis Gas

Herein discloses an improved system design for synthesis of CNTs and H₂ integrated with CO₂ capture from pyrolysis gas, as shown in FIG. 2. The improved system is designed to hold a bed of a sorbent. Therefore, the experiments conducted as described below are denoted as experiments “with sorbent”. To generate volatile pyrolysis products, feedstock was fed into the pyrolysis reactor pre-heated to 600 °C (10 g every 10 min). N₂ was used as a sweep gas (50 mL/min). The produced volatile pyrolysis products were directed into a sorbent reactor configured to hold a packed bed of a sorbent heated to 600 °C. For the purpose of demonstration of invention, natural calcite with particle sizes 1-5 mm and calcined in air for 2 h at 850 °C was utilized as a Ca-based sorbent (therefore, “Ca-based sorbent” and “sorbent” are used interchangeably in the description).

After CO₂ removal, liquid pyrolysis products exiting the sorbent reactor were collected in a condenser maintained at ambient temperature. The pyrolysis gas was directed into a silica gel trap to remove moisture followed by a CVD reactor, containing 0.25 g of a catalyst. The catalyst was pre-heated to 700 °C in case of 40Mo-10Co and 1000 °C in case of 2Co-3Mo. The CVD synthesis was started 10 min after the beginning of pyrolysis and continued for 20-80 min.

Yield of Solid Carbon Extracted from the CVD Reactor

The yield of solid carbon extracted from the CVD reactor was calculated as Eq. (1):

$$Y \text{ (g g}^{-1}\text{-catalyst)} = (m - m_{\text{cat}}) / m_{\text{cat}} \quad \text{Eq. (1)}$$

where m is the mass of recovered carbon deposits, containing the catalyst, and m_{cat} is the mass of catalyst loaded into the CVD reactor.

Transmission Electron Microscopy (TEM) and Field Emission Scanning Electron Microscopy (FESEM)

The morphology of CNTs was characterized by transmission electron microscopy (TEM, JEOL JEM-1400Plus) and field emission scanning electron microscopy (FESEM, JEOL JSM-7600F).

Gas Composition

Gas composition in mol.% was obtained using a calibrated gas chromatograph equipped with one flame ionization and two thermal conductivity detectors. To calculate the production rates of gases (mL/min), in all experiments, an inert N_2 gas was co-fed into the pyrolyzer at a constant flow rate of 50 mL/min. Knowing N_2 flow rate, concentration of N_2 and concentrations of gas components of interest, the flow rates of the gas components of interest were derived.

X-Ray Diffraction (XRD) Measurements

The crystal structure of the sorbent material was characterized using X-ray diffraction (XRD) spectrometry with Cu K α radiation (XRD, D8 Advance, AERIS-1004X).

Results and Discussions

The synthesis of CNTs from biomass without modification of known processes is challenging. We attempted the growth of CNTs using pyrolysis gas from five types of materials: (1) pine sawdust pellets (pine sawdust), (2) coconut coir pith powder (coconut coir pith), (3) refuse derived fuel pellets (RDF), (4) shredded cosmetics packaging waste (cosmetics packaging), and (5) dried municipal sewage sludge from a water treatment plant (sewage sludge). The synthesis setup had a proven design adapted from Dong, H. et al. and Veksha et al. (Dong, H. et al., *Sci. Tot. Environ.*, **2022**, 831, 154751; Veksha, A. et al., *Chemosphere*, **2022**, 297, 134148) and a highly active Co-Mo/MgO catalyst from Veksha group (Veksha, A. et al., *J. Hazard. Mater.*, **2022**, 435, 128949) (FIG. 3). A distinctive difference of the current invention is that instead of having a thermal cracker, it is equipped with a heated reactor designed to hold a bed of a CO_2 sorbent.

The yields of CNTs produced without and with sorbent use are shown in FIG. 4. Without the use of sorbent, the outputs of CNTs from 4 types of feedstock (pine sawdust, coconut coir pith, RDF and cosmetics packaging) were negligible. Specifically, the highest carbon yield was obtained using RDF (0.5 ± 0.7 g/g-catalyst). With the use of sorbent, the yields increased for all feedstock types. The increase was more pronounced for the feedstock, containing plastics compared to the feedstock consisting of biomass only. Specifically, the yields of CNTs obtained from pyrolysis gas of pine sawdust, coconut coir pith, RDF and cosmetics packaging waste were 2.4 ± 0.8 , 0.6 ± 0.1 , 8.2 ± 2.6 , 13.1 ± 2.7 g/g-catalyst, respectively. The experiments with sewage sludge were duplicated, resulting in CNT yields of 3.93 and 3.43 g/g-catalyst.

FIG. 5 demonstrates the morphology of carbon nanomaterials recovered from the CVD reactor after the use of pyrolysis gas obtained from pine sawdust. Without the use of sorbent, most of catalyst particles were represented by dark spots in TEM images in FIG. 5A and FIG. 5B, and encapsulation of catalyst particles with non-filamentous coke was observed. Carbon yield was negligible. Minor quantities of carbon filaments can be seen in the images as well. Notably, the filaments were lacking hollow channels specific to nanotubes and resembled the morphology of nanofibers. This suggests that the differences in pyrolysis gas composition could deteriorate the carbon deposition. On the contrary, the use of sorbent enabled the growth of CNTs as evidenced by the presence of hollow channels inside the filaments (FIG. 5C and FIG. 5D). In some channels, bamboo-like knots can be observed. According to FIG. 6, CNTs were also grown from the other 4 types of feedstock using pyrolysis gases after the use of sorbent.

To investigate the influence of feedstock on the sizes of CNTs, outer diameters of approx. 150-160 individual CNTs from each feedstock were characterized using TEM images. FIG. 7 shows the distribution of outer diameters of CNTs from the four types of feedstock. Regardless of the feedstock type, the majority of CNTs had diameters between 10 and 20 nm. The results above demonstrate advantages of the proposed method for producing CNTs from pyrolysis gases, characterized by the improved product yield and selective formation of nanotubes. Based on outer diameter distribution, the proposed method also can allow for the synthesis of CNTs with comparable dimensions from different types of feedstocks.

Gas composition was characterized to investigate the reasons for the improved synthesis of CNTs using the method described in this Example. Chromatographic analysis of the pyrolysis gas showed the presence of C_1 - C_4 hydrocarbon compounds, including methane, ethylene and propylene, CO , CO_2 , H_2 and N_2 (carrier gas) (FIG. 8). Compared to the previous reports for

CNT synthesis from feedstock containing plastics (Table 1), the striking difference was the high concentration of CO₂ (~24 vol.%).

FIG. 9A and FIG. 9B show the content of main gaseous components in gas from the four types of feedstocks after pyrolysis without the use of sorbent. The main gaseous components were methane, ethylene, ethane, propylene, CO₂, CO and H₂. FIG. 9C and FIG. 9D show the content of the same components after pyrolysis and the subsequent treatment of gas with the sorbent. There were little if any changes in the contents of hydrocarbon compounds and CO, suggesting that dry reforming reactions were not catalyzed by the sorbent at the experimental conditions. The quantities of CO₂ declined drastically, while the quantities of H₂ increased. The removal of CO₂ was attributed to the capture by the sorbent, containing CaO formed by calcite heating at 850 °C. It is known that at temperatures of around 600-700 °C, CaO reacts with CO₂ Eq. (2) (Erans, M. et al., *Applied Energy*, **2016**, 180, 722):



The formation of H₂ could be ascribed to the participation of hydrocarbon compounds in the side cracking reactions, producing H₂ and coke. The coke formation was observed visually by the change of color of the sorbent from white before use to black after use. Based on the little changes in the contents of methane, ethane, ethylene and propylene in FIG. 9A and FIG. 9C, the hydrocarbon compounds with more than 3 carbon atoms were susceptible to the cracking reaction.

FIG. 10 shows the composition of CVD gas at the outlet of CVD reactor from the four types of feedstock. Due to different composition of feedstock, biomass derived gases had higher concentrations of methane and almost no C₂H₄, C₂H₆ and C₃H₆ compared to gases derived from RDF and cosmetics packaging. Nearly complete decomposition of C₂₊ gases in biomass derived feedstock also suggests that the low yields of CNTs from biomass could be attributed to insufficient quantities of precursor hydrocarbons. That is, increasing the content of hydrocarbons contacting a catalyst, for instance, by increasing the growth time could further increase the CNT yield. The similar transformation was observed previously in studies using pyrolysis gas from plastics and was attributable to simultaneous catalytic and non-catalytic decomposition of hydrocarbon compounds over the catalyst and CNTs (Yao, D. et al., *Chemosphere* **2022**, 297, 134148).

Regardless of the feedstock, the main gaseous component in the effluent gas from the CVD reactor was hydrogen. The main gaseous product from the CVD process was H₂. In this

respect, the growth of CNTs from biomass pyrolysis gas after CO₂ capture resembles that from plastics pyrolysis gas. According to FIG. 10B, the production of H₂ increased significantly after the CVD process. Compared to pyrolysis gases from pelletized pine sawdust and coconut coir pith, containing 0.43 and 0.14 wt.% molecular H₂ per feedstock mass, the corresponding CVD gases contained 1.36 and 1.48 wt.% molecular H₂ per feedstock mass. The release of H₂ from the CVD reactor using coconut coir pith was comparable to pelletized pine sawdust, despite the lower contents of ethylene and propylene. This indicates other hydrocarbon compounds that are present in pyrolysis gases, including volatile tar species (Han, J. & Kim, H.J., *Renew. Sustain. Energy Rev.* **2008**, *12*, 397), could be also involved in the H₂ and carbon formation. Based on these results, the proposed integrated process provides a potential strategy for enhanced H₂ recovery from biomass, while capturing CO₂ and generating CNTs.

Example 2. Effect of CO₂ on Product Outputs

Model gas mixtures containing CO₂ were previously utilized as precursors for the growth of CNTs and the results were contradictory. On the one hand, high yield growth of carbon nanofilaments could be achieved at 650-750 °C when a gas mixture containing ethylene and CO₂ at molar ratio of 1:3 was used for dry reforming over a Ni-based catalyst (Azara, A. et al., *Catalysts* **2019**, *9*, 1069). On the contrary, another study used various model gas mixtures containing ethylene and CO₂ in N₂ and showed that the presence of CO₂ at 1-20 vol.% lowered CNT yields and inhibited ethylene conversion (711-850 °C) (Zhuo, C. et al., *J. Energy Resour. Technol.*, **2018**, *140*, 085001). Yet another study investigated the effect of CO₂ on the growth of single-walled CNTs from methane and found that at small quantities at 900 °C, CO₂ in the precursor gas had beneficial effect on the CNT growth (CO₂:CH₄ volumetric ratio of approx. 1:20), while the excessive content of CO₂ had detrimental effect on the CNT yield (Li, Z. et al., *Chem. Commun.* **2008**, *28*, 3260). In this Example, the following effect of CO₂ were investigated: (1) the extent of CO₂ in pyrolysis gas from biomass could impact the CNT growth, (2) if CO₂ was the main cause for the lack of catalytic activity, and (3) if CO₂ can be effectively managed to improve the yield.

Gas composition and TEM characterizations were performed by following the protocol disclosed in Example 1.

Raman Spectroscopy

Raman spectroscopy was conducted at a laser wavelength of 532 nm (XploRA PLUS, Horiba Scientific).

N₂ Adsorption Measurements

N₂ adsorption at -196 °C was conducted to characterize specific surface areas of CNTs using a Brunauer–Emmett–Teller (BET) model and calculate total pore volume at relative pressure of 0.95-0.96 (Quantachrome Autosorb-1 Analyzer).

5

Results and Discussions

To investigate the impact of CO₂, an improved system for the synthesis of CNTs was designed with an embedded high temperature CO₂ removal reactor after pyrolysis gas generation (FIG. 11). Natural calcite with particle sizes 1-5 mm was calcined in air for 2 h at 850 °C to prepare
10 a calcium-based sorbent, containing CaO and Ca(OH)₂. It was prepared from a low-cost and abundant calcite mineral (FIG. 12). FIG. 12 shows the crystalline phase composition of the natural calcite, fresh Ca-based sorbent and spent Ca-based sorbent.

After the removal of CO₂ from pyrolysis gas, condensable oil was retained in a trap, while non-
15 condensable gases were utilized in a CVD reactor. FIG. 5C and FIG. 5D demonstrate how the application of CO₂ removal step facilitated the growth of CNTs. Clearly defined hollow channels inside the tubular filaments can be observed. The length of nanotubes was several nm. Usage of pyrolysis gas from coconut pith coir resulted in the growth of similar nanostructures (FIG. 13), suggesting that CO₂ removal from the gas can enable utilization of
20 various types of renewable feedstocks for CNTs synthesis and reduce reliance on fossil fuels. The yields of CNTs calculated as wt.% per feedstock mass and g/g-catalyst were influenced by the type of biomass, being lower for coconut coir pith (Table 2). This could be attributed to the lower content of hydrocarbon compounds in pyrolysis gas (see FIG. 9A). The catalyst utilization is an important characteristic of process efficiency. Using pelletized pine sawdust it
25 was demonstrated that the growth of CNTs on the catalyst can be increased from 2.4 g/g-catalyst to 4.5 g/g-catalyst when the duration of CVD synthesis increased from 40 to 80 min (FIG. 14), thus conveniently reducing the catalyst consumption. The changes in CNT properties when switching the biomass feedstock are shown in Table 2. The CNTs were synthesized under the similar conditions as disclosed in Example 1 and purified with
30 hydrochloric acid prior to the characterization. The CNTs from pelletized pine sawdust and coconut coir pith had similar outer diameters of around 5-30 nm characterized by TEM and similar graphitization degrees based on the areas of D and G Raman peaks. According to N₂ adsorption data, BET specific surface area of CNTs from coconut coir pith was around 21% lower, while the total micropore volume was 9% lower than the corresponding characteristics
35 of CNTs from pelletized pine sawdust.

Table 2. Characteristics of CNTs from biomass pyrolysis gas.^[a]

	Pelletized pine sawdust	Coconut coir pith
Yield (wt.% per feedstock mass) ^[b]	1.52±0.48	0.37±0.01
Yield (g/g-catalyst) ^[b]	2.4±0.8	0.6±0.1
Outer diameters (nm) ^[c]	5-30 (N=164)	5-30 (N=155)
BET specific surface area (m ² /g)	201	159
Total pore volume (mL/g)	0.43	0.39
I _D /I _G (-) ^[d]	1.0±0.1	1.1±0.1

^[a] Feeding rate: 10 g/10 min, synthesis time: 40 min, catalyst: 40Co-10Mo, pyrolysis, CO₂ removal and CVD reactor temperatures: 600, 600 and 700 °C; ^[b] reported as averages and standard deviations of three runs; ^[c] a range of outer diameters of at least 90% CNTs, N - represents the total number of characterized CNTs; ^[d] reported as averages and standard deviations of five measurements.

To clarify the effect of CO₂ on the growth of CNTs, the gas stream produced from pine sawdust was first treated with the CO₂ sorbent and then mixed with 65 mL/min CO₂ supplied by a mass flow controller from a gas tank. The quantity of introduced CO₂ was comparable to the content of CO₂ found in the gas without the CO₂ capture with the sorbent (FIG. 9B). The CO₂ stream was injected into a gas port installed between the condenser and the moisture trap for the duration of the CVD synthesis (synthesis time: 40 min, catalyst: 40Co-10Mo, temperature: 700 °C). The quantity of introduced CO₂ was comparable to the content of CO₂ found in the gas without the use of sorbent (FIG. 9B). The CO₂ stream was injected into a gas port installed after the bio-oil condenser and before the CVD reactor. After the addition of CO₂, the yield of carbon decreased to a negligible level (0.2±0.2 g/g-catalyst), confirming that the removal of CO₂ by the sorbent was the main prerequisite for achieving the successful synthesis of multi-walled CNTs.

FIG. 15 sheds the light on the effect of CO₂ addition on the gas composition at the outlet of CVD reactor ("CO₂ sorbent + CO₂" compared to "CO₂ sorbent"). The addition of CO₂ to the gas stream inhibited catalytic and non-catalytic decomposition of hydrocarbon compounds containing in the gas as suggested by decreased methane production and higher outputs of unreacted ethylene, propylene and ethane. The product gas also contained a fraction of unreacted CO₂ and elevated quantities of CO. The increase in CO evolution from the reactor could be attributed to the reaction of CO₂ with carbon deposits. According to FIG. 5A and FIG. 5B, the presence of CO₂ favoured the formation of non-filamentous coke on the surface of catalyst nanoparticles. An earlier study of gasification of carbon deposits grown on alumina supported Co catalyst showed that such non-filamentous carbon can be gasified by CO₂ at

temperatures as low as approx. 450 °C.[13] Another reason for increasing CO content is the intensification of reverse water gas shift reaction (Eq. (3)).



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Example 3. Comparison with an Alkaline Liquid Scrubber

As an alternative method to CO₂ capture by a calcium-based sorbent, liquid scrubbing at ambient conditions using alkaline solution can be utilized (Zhang, S. et al., *Nat. Sustain.* **2020**, 3, 753–760).

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Alkaline Liquid Scrubber Setup

Two traps, each containing 20 g NaOH in 100 mL deionized water, were used to remove CO₂ from the pyrolysis gas of pelletized pine sawdust (FIG. 16). The traps were installed in series between oil condensation unit and moisture trap as shown in FIG. 16.

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Results and Discussions

Initially transparent and colourless solution of NaOH changed colour after synthesis runs to light brown due to absorption of organic compounds. The synthesis experiments were triplicated, and the obtained CNT yield was 3.4±0.5 g/g-cat. Based on the two-tailed t-test for two independent means and significance level of 0.95, this value was not significantly different from the CNT yield obtained with sorbent under the similar experimental conditions (2.4±0.8 g/g-cat), suggesting that both methods could enable the growth of CNTs.

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However, there were at least two benefits of using CO₂ capture with the solid sorbent using the apparatus described above. Initially transparent and colorless solution of NaOH changed color after synthesis to light brown due to absorption of organic compounds (FIG. 16), creating a stream of organic liquid waste. On the contrary, spent Ca-based sorbents are regenerable via calcination and can be reused multiple times, providing the mechanical properties are intact and sintering is avoided. Hydrogen from the system utilizing the Ca-based sorbent was nearly 2 times larger due to cracking of organic compounds over the sorbent and in CVD reactor instead of absorption by the liquid scrubber (FIG. 15, “CO₂ sorbent” compared to “NaOH scrubber”). These results suggest that the proposed apparatus allows for more efficient hydrogen recovery from feedstock compared to the liquid CO₂ scrubbing.

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Example 4. Effect of Feeding Rate and Time on the CNT and Gas Production

The experimental conditions can be further varied to modulate the CNT and/or gas production using the method and apparatus of this invention.

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Study on Feeding Rate and Time on the CNT and Gas Production

The pyrolysis gas was treated using the sorbent. For demonstration purposes, the impacts of synthesis time and feedstock feeding rate are provided in FIG. 17.

10 Results and Discussions

FIG. 14 shows an increase in carbon yield from 1.4 ± 0.2 to 4.1 ± 2.2 g/g-catalyst when reaction time was increased from 20 to 80 min. FIG. 17A demonstrates the evolution of hydrocarbon compounds from the outlet of CVD reactor during the CNT growth. The contents of all hydrocarbon compounds increased with the longer reaction time due to the decreasing activity
 15 of the catalyst towards the decomposition of hydrocarbon compounds into solid carbon and H_2 . These changes in gas composition were accompanied by the decreasing content of H_2 (FIG. 17B). The concentration of CO_2 remained low. However, the concentration of CO increased gradually, suggesting that CO_2 could evolve from the sorbent reactor due to the limited capacity of CaO-containing sorbent. This could be addressed by using a larger capacity
 20 of the sorbent reactor. Upon entrance to the CVD reactor, CO_2 was likely converted into CO either via carbon gasification, dry reforming or reverse water gas shift reactions.

FIG. 18 shows the effect of feeding rate on the carbon growth and gas production. At three feeding rates (5, 10 and 15 g/10 min), the CNT production did not change significantly,
 25 suggesting that at the increased feeding rate, side reactions are intensified (e.g., methane and CO production as shown in FIG. 18B and FIG. 18C). However, one benefit from using the higher feeding rate was the increased generation of H_2 . In this respect, the data in this section demonstrate that by varying experimental conditions, such as feeding rate and reaction time, the output of desired products (i.e. CNTs and H_2) can be conveniently optimized.

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Example 5. Effect of Catalyst on CNT Diameter from Pine Sawdust

To demonstrate if the proposed method and apparatus are suitable for the growth of CNTs using various catalysts and at various conditions, CNTs were synthesized from pine sawdust
 35 derived pyrolysis gas after the use of sorbent using the 2Co-3Mo catalyst and temperature of 1000 °C. TEM images were taken by following the protocol disclosed in Example 1.

Results and Discussions

FIG. 19 demonstrates that the proposed method and apparatus are suitable for the growth of CNTs using various catalysts and at various conditions. The TEM image shows that the produced CNTs had diameters of 3.9-7.2 nm.

Claims

1. An apparatus for the production of carbon nanotubes and hydrogen from a pyrolysis gas, the apparatus comprising:

a sorbent reactor portion comprising:

a first reaction vessel having an inlet configured to accept a pyrolysis gas from a pyrolysis gas source and an outlet;

a solid sorbent and/or a solid sorbent precursor, where the solid sorbent is suitable to adsorb CO₂ from a pyrolysis gas situated within the first reaction vessel, such that a pyrolysis gas passes over the sorbent in its passage from the inlet to the outlet; and

a heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the first reaction vessel;

a liquid trapping means or apparatus attached to the outlet of the sorbent reactor portion;

a chemical vapour deposition reactor portion comprising:

a second reaction vessel having an inlet configured to accept a pyrolysis gas that has passed through the liquid trapping means or apparatus and an outlet;

a catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas situated within the reaction vessel, such that a pyrolysis gas passes over the catalyst in its passage from the inlet to the outlet; and

a heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the second reaction vessel.

2. The apparatus according to Claim 1, wherein the apparatus further comprises a pyrolysis gas source.

3. The apparatus according to Claim 2, wherein the pyrolysis gas source is selected from one or more of the group selected from a pyrolyser, a pyrolyser in fluid communication with an upgrader, and a storage device comprising a pyrolysed gas.

4. The apparatus according to any one of the preceding claims, wherein:

(ai) the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas is selected from one or more of the group consisting of CaO, MgO, Ca(OH)₂, Mg(OH)₂, a serpentinite mineral, magnesium silicate hydroxide, (Mg,Fe)₂SiO₄ (olivine), a molecular sieve suitable to adsorb CO₂, a metal organic framework suitable to adsorb CO₂, and activated carbon; and/or

- (aii) the solid sorbent precursor is selected from one or more of the group consisting of CaCO_3 , and MgCO_3 , and $\text{CaMg}(\text{CO}_3)_2$ (dolomite); and/or
- (aiii) the solid sorbent suitable to adsorb CO_2 and the solid sorbent precursor are present in the sorbent reactor portion.

5. The apparatus according to Claim 4, wherein the solid sorbent suitable to adsorb CO_2 from a pyrolysis gas is in one or more of a particulate form, a pelletized form and a granulated form.

6. The apparatus according to Claim 4 or Claim 5, wherein the solid sorbent suitable to adsorb CO_2 from a pyrolysis gas comprises CaO , optionally wherein:

- (bi) the solid sorbent suitable to adsorb CO_2 from a pyrolysis gas further comprises $\text{Ca}(\text{OH})_2$; and/or
- (bii) the solid sorbent suitable to adsorb CO_2 from a pyrolysis gas further comprises CaCO_3 ; and/or
- (biii) the solid sorbent is in particulate form and has a particle size of from 1 to 5 mm.

7. The apparatus according to any one of the preceding claims, wherein the liquid trapping means or apparatus comprises a condenser and moisture trap.

8. The apparatus according to any one of the preceding claims, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas comprises one or more elements selected from the group consisting of Fe, Ni, Co, Mo, W, Al, Si, C and Mg.

9. The apparatus according to Claim 8, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas is selected from one or more of the groups consisting of:

Fe_2O_3 and Al_2O_3 (e.g. 20 wt.% Fe_2O_3 and 80 wt.% Al_2O_3); and

Co, Mo and MgO (e.g. 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO), optionally wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas is selected from one or more of the groups consisting of 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO, more optionally wherein the catalyst is 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO.

10. The apparatus according to any one of the preceding claims, wherein the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the first reaction vessel and the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the second reaction vessel is an electric heater.
11. The apparatus according to any one of the preceding claims, wherein the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the first reaction vessel and the heating means or apparatus suitable to provide and maintain a temperature of greater than 100 °C within the second reaction vessel generate a temperature from 150 to 1,000 °C, such as from 400 to 700 °C, such as about 600 °C.
12. The apparatus according to any one of the preceding claims, wherein the pyrolysis gas is a gas obtained from a carbonaceous feedstock, optionally wherein the pyrolysis gas is obtained from one or more of the group consisting of municipal sewage sludge, plastics, biomass, and refuse derived fuel obtained from combustible components of municipal waste.
13. Use of an apparatus according to any one of Claims 1 to 12 in the production of carbon nanotubes and hydrogen from a pyrolysis gas.
14. A method of producing carbon nanotubes and hydrogen gas from a pyrolysis gas, comprising the steps of:
 - (a) passing a pyrolysis gas through a first reactor zone having a temperature of greater than 100 °C that houses a solid sorbent suitable for adsorbing CO₂, where a portion of the pyrolysis gas is adsorbed by the sorbent to produce an intermediate gas; and
 - (b) passing the intermediate gas through a second reactor zone having a temperature of greater than 100 °C that houses a catalyst, where the catalyst converts at least a portion of the intermediate gas into carbon nanotubes and hydrogen gas.
15. The method according to Claim 14, wherein the pyrolysis gas is obtained from a carbonaceous feedstock supplied by one or more of the group selected from a pyrolyser, a pyrolyser in fluid communication with an upgrader, and a storage device comprising a pyrolysed gas.
16. The method according to Claim 15, wherein the carbonaceous feedstock is a plastic and/or biomass, optionally wherein the carbonaceous feedstock is obtained from one or more

of the group consisting of municipal sewage sludge and, more particularly, plastics, biomass, and refuse derived fuel obtained from combustible components of municipal waste.

17. The method according to any one of Claims 14 to 16, wherein: the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas is selected from one or more of the group consisting of CaO, MgO, Ca(OH)₂, Mg(OH)₂, a serpentinite mineral, magnesium silicate hydroxide, (Mg,Fe)₂SiO₄ (olivine), a molecular sieve suitable to adsorb CO₂, a metal organic framework suitable to adsorb CO₂, and activated carbon.

18. The method according to any one of Claims 14 to 17, wherein the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas is generated from a solid sorbent precursor that is selected from one or more of the group consisting of CaCO₃, and MgCO₃ and CaMg(CO₃)₂ (dolomite) prior to step (a) of Claim 14 by calcination of the solid sorbent precursor.

19. The method according to Claim 17 or Claim 18, wherein the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas is in one or more of a particulate form, a pelletized form and a granulated form.

20. The method according to any one of Claims 17 to 19, wherein the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas comprises CaO, optionally wherein:

(ci) the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas further comprises Ca(OH)₂; and/or

(cii) the solid sorbent suitable to adsorb CO₂ from a pyrolysis gas further comprises CaCO₃; and/or

(ciii) the solid sorbent is in particulate form and has a particle size of from 1 to 5 mm.

21. The method according to any one of Claims 14 to 20, wherein the method further comprises a step (di) of trapping any liquid generated in step (a) before conducting step (b) of the method according to Claim 14.

22. The method according to Claim 21, wherein step (di) of Claim 21 is accomplished using a liquid trapping means or apparatus, optionally wherein the liquid trapping means or apparatus comprises a condenser and moisture trap.

23. The method according to any one of Claims 14 to 22, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas is selected from one or more of the group consisting of:

Fe_2O_3 and Al_2O_3 (e.g. 20 wt.% Fe_2O_3 and 80 wt.% Al_2O_3); and
Co, Mo and MgO (e.g. 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO).

24. The method according to Claim 23, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas comprises one or more elements selected from the group consisting of Fe, Ni, Co, Mo, W, Al, Si, C and Mg.

25. The method according to Claim 24, wherein the catalyst suitable to convert at least a portion of the pyrolysis gas into carbon nanotubes and hydrogen gas is selected from one or more of the groups consisting of:

Fe_2O_3 and Al_2O_3 (e.g. 20 wt.% Fe_2O_3 and 80 wt.% Al_2O_3); and
Co, Mo and MgO (e.g. 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO or 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO).

26. The method according to any one of Claims 14 to 25, wherein the temperature in the first reactor zone and/or the temperature in the second reactor zone is from 150 to 1,000 °C, such as from 400 to 700 °C, such as about 600 °C.