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(54) Title: USE OF PYROLYTIC CARBON FOR CONTROLLING SOIL-BORNE PLANT PATHOGENIC FUNGI

(57) Abstract: The present invention relates to the use of pyrolytic carbon for controlling soil-borne phytopathogenic fungi. Further the invention relates to methods for controlling soil-borne phytopathogenic fungi, wherein the fungi, their habitat, their locus, or the plants, the soil, the potting mixes, the multiplication or growth substrate containers or plant propagation material are treated with an effective amount of pyrolytic carbon.

Use of pyrolytic carbon for controlling soil-borne plant pathogenic fungi

Description

- 5 The present invention relates to the use of pyrolytic carbon for controlling soil-borne phytopathogenic fungi. Further the invention relates to methods for controlling soil-borne phytopathogenic fungi, wherein the soil, the potting mixes, the growth substrate containers or the plant propagation material are treated with an effective amount of a pyrolytic carbon.
- 10 Typical problems arising in the control of soil-borne phytopathogenic fungi are that those pathogens are typically hidden in the soil or substrate provoking the need to bring the PCC in contact with the fungi. Soil is a complex composition of biotic and abiotic components often interacting with the material thought to lower disease incidence levels. On the other side, the material mixed into the soil or substrate may on itself influence other biotic or abiotic processes some of
- 15 them being perceived as positive others as negative.

State of current practice is the drenching of root zones as a spot, band or broadcast application of water with the treatment agent, which could be a chemical or micro-biological fungicide or a plant health promoting compound. Besides drenching the treatment agent can be incorporated

20 into soil or substrate before planting or treated seeds or other plant propagation material is covered by the treatment agent and as such carrying it into the root zone. The described types of application allow to bring the treatment agent close to the root zone to express its protective or curative activity. Disadvantage of such treatments is its timely limited activity against such soil-borne pathogens as the treatment agent is either limited strongly by amount, e.g. with seed

25 treatment, or the need of water volumes to ensure contact of treatment agent with roots as with drenching. In addition, the treatment agent often is interacting with soil components leading to its degradation and inactivation over time. Furthermore, the treatment agent may leach into the ground water, reduced the effectiveness and leading to unwanted contamination of the ground water. In addition, the treatment agent may interact with the soilborne minerals and/or fertilized

30 nutrients in the soil and influence negatively.

WO 2021/122503 and WO 2021/122500 disclose granular pyrolytic carbon and carbon black as soil conditioner to reduce erosion by wind and to minimize moisture losses. It also describes improved water infiltration. The application of both granular pyrolytic carbon and Carbon Black increases the formation of plant biomass. It shows that neither granular pyrolytic carbon nor carbon black caused any CO₂ evolution in contrast to bio-charcoal. An influence of pyrolytic carbon

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itself on soil-borne phytopathogenic fungi was neither studied nor predicted in these WO publications. It is assumed that such a pyrolytic carbon can support different organic or inorganic additives like agrochemical active substance from the group of fungicides, bactericides, herbicides and/or plant growth regulators although it is a dense material with low specific surface area.

Biochar is known to promote many parameters beneficial for plant growth or uptake efficiency of fertilizer components (*Schmidt et al. 2021, Pflanzenkohle in der Landwirtschaft, Agroscope Science, 2021, 112*). This influence on the soil physics is based on the hydrophilicity, the functionalization and the high porosity of the biochar. The large surface areas of biochar could lead to a long-term water storage, the functional groups could bind nutrient and work as an embodiment or matrix for different soil components being abiotic or biotic ones like e.g. nitrogen or fungi, respectively. In addition, the black color could improve soil warming. The relatively easy oxidation of the carbon of the biochar seems to have a significant influence on the microbiome and as such helps to suppress plant pathogenic fungi (*Zhongmin et.al, 2021 Association of biochar properties in changes in soil bacteria, fungal, and fauna communities and nutrient cycling processes. Biochar 2021, 3:239-254, and Zhongmin et al, 2018: Soil fungal taxonomic and functional community composition as affected by biochar properties. Soil Biology and Biochemistry, 2018, 126: 159-167*). However, the relatively quick oxidation of carbon of the biochar (as O:C molar ratios are > 0.2 of biochar, Spokas, 2010) allows only a temporary sequestration of carbon into soil, being beside the costs of biochar one of the main disadvantages.

Dai et al. ("Soil fungal taxonomic and functional community composition as affected by biochar properties", SOIL BIOLOGY AND BIOCHEMISTRY, PERGAMON, OXFORD, GB, vol. 126, 5 September 2018 (2018-09-05), pages 159-167, XP085483416, ISSN: 0038-0717, DOI: 10.1016/J.SOILBIO.2018.09.001) discloses that biochar greatly influences the soil bacterial community and nutrition transformation. The biochar property of easily mineralized C and inorganic nutrients favors saprotroph growth over soil-borne fungal pathogens.

WO 2019/118986 describes a functionalized biochar having high levels of soluble signaling compounds like cyanohydrins, butenolides and/or karrikins. Karrikins are known to stimulate seed germination. The treated biochars generally have a high cation exchange capacity and a high anion exchange capacity. In addition, it is disclosed that a high hydrophilicity is preferred, the more hydrophilic the more the biochar can accept the needed inoculants or infiltrates.

CN 105 432 381 B discloses biochar containing trichoderma viride which is known as a soil fungus and an antagonist (antibiotic-forming agent) against soil-borne pathogenic fungi to control pepper phytophthora blight. Biochar is described to be a solid product produced by pyrolysis of

biomass such as biological residues or organic wastes showing the typical structures of carboxyl, phenolic hydroxyl, aliphatic double bond, aromatization and the like enabling the biochar to have extremely strong adsorption capacity.

- 5 CN 107 668 086 A discloses a preparation method of biochar by carbonizing dried straws at the temperature of 450-550°C for preventing and controlling a soil-borne disease. The disclosed biochar has a highly aromatic structure, and the surface of the biochar contains carboxyl, phenolic hydroxyl, carbonyl, acid anhydride and other groups. The structural characteristics enable the biochar to have good adsorption characteristics and stability.

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The objective of the present invention is to find an inert, sequestrable, environmentally friendly, and oxidation-resistant elemental carbon material for controlling soil-borne phytopathogenic fungi which is active per se without adding any agrochemical active substances like fungicides, bactericides, herbicides and/or plant growth regulators. Such an inert carbon material with its O:C molar ratio close to 0 should not be oxidized or mineralized, such an inert carbon should have no effect on the soil biology and no interaction to it and would allow carbon sequestration. In addition, this oxidation-resistant elemental carbon material should increase plant health leading to higher biomass growth. In addition, this carbon material should protect soil macro-and mega-fauna. In addition, this carbon material should be an alternative to biochar being nutrient for microorganism.

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The present invention provides the use of hydrophobic pyrolytic carbon for controlling soil-borne phytopathogenic fungi, wherein the pyrolytic carbon has a density of 1 to 3 g/cc, a carbon content of 95 to 100 weight-%, an ash content of 0.001 to 5 weight-%, 85 weight-% of the carbon is not-functionalized with a O:C molar ratio below 0.1, and the cation exchange capacity of the pyrolytic carbon is 0.001 to 0.75 cmol/kg, wherein the pyrolytic carbon is produced from gaseous hydrocarbons.

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Surprisingly, a positive fungicidal effect of such pyrolytic carbon could be found, although this carbon is – in contrast to biochar – inert, insoluble and has almost no functional groups. Such pyrolytic carbon is not easily mineralized (shown in example 3), having a low cation exchange capacity and being hydrophobic. In contrast to biochar, this hydrophobic pyrolytic carbon is neither an organic nor an inorganic nutrition for microorganism.

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The invention provides a method for controlling soil-borne phytopathogenic fungi, wherein the fungi, their habitat, their locus, or the plants, the soil, potting mixes or plant propagation material

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are treated with an effective amount of pyrolytic carbon, wherein the pyrolytic carbon has a density of 1 to 3 g/cc, a carbon content of 95 to 100 weight-%, an ash content of 0.001 to 5 weight-%, 85 weight-% of the carbon is not-functionalized with a O:C molar ratio below 0.1, and the cation exchange capacity of the pyrolytic carbon is 0.001 to 0.75 cmol/kg, wherein the pyrolytic carbon is produced from gaseous hydrocarbons.

The term "pyrolytic carbon" covers a solid carbon produced from sole pyrolysis of hydrocarbons, preferably light hydrocarbons like gaseous hydrocarbons, especially methane, in absence of oxygen (see for example Muradov, Nazim. "Low to near-zero CO₂ production of hydrogen from fossil fuels: Status and perspectives." International Journal of Hydrogen Energy 42.20 (2017): 14058-14088). Typically, the decomposition of light hydrocarbons, especially methane, is done by a plasma process, by a liquid metal process, by a microwave process, by a catalytic or non-catalytic process, e.g., in an electric heated fixed or moving bed reactor. Thus, the term "pyrolytic carbon" covers all kinds of carbon made by pyrolysis of hydrocarbons, e.g. light nanoscale carbon black and dense granular pyrolytic carbon with a O:C molar ratio below 0.1. In addition, the term "pyrolytic carbon" covers the following solid carbon black Acetylen-Black, Thermal-Black, Channel-Black, Lamp-Black, Gas-Black and/or Furnace Black, obtained by partial oxidation and/or pyrolysis.

The term "fungicidally effective amount" denotes an amount of the pyrolytic carbon, which is sufficient for controlling harmful fungi on cultivated plants or plant parts thought for propagation and which does not result in a substantial damage to the treated plants or plant parts. Such an amount can vary in a broad range and is dependent on various factors, such as the fungal species to be controlled, the treated cultivated plant or plant part, the climatic conditions, desired fungicidal effect and duration, locus, mode of application, and the like.

The term "plant propagation material" is to be understood to denote all the generative parts of the plant, such as seeds; and vegetative plant materials, such as cuttings and tubers (e. g. potatoes), which can be used for the multiplication of the plant. This includes seeds, roots, fruits, tubers, bulbs, rhizomes, shoots, sprouts and other parts of plants including seedlings and young plants. These young plants may also be protected before transplantation by a total or partial treatment by immersion or pouring. In a particularly preferred embodiment, the term propagation material denotes seeds.

The term "soil" also commonly referred to as earth is a mixture of organic matter, minerals, gases, liquids, and organisms that together support life. It is the living part of the topmost earth crust on which plants are cultivated but includes all mixtures of natural soil compositions with

natural or artificial soil improvement substrates, like e.g. peat, sand, vermiculite and similar, or as absorbing materials. Such soil-substrate compositions may be used in open fields, in protective structures like green houses. As such they may be sold in different kinds of bag/packages sizes.

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Pyrolytic carbon:

Granular pyrolytic carbon:

The pyrolytic carbon can be produced by decomposition of gaseous hydrocarbon compounds, preferably the decomposition of methane, and carbon deposition on suitable underlying substrates (carbon materials, metals, ceramics and a mixture thereof), preferably at temperatures ranging from 1000 to 2500 K and at pressures ranging from 0.5 – 10000 kPa (abs). The substrate can either be porous or non-porous and can be either be a support substrate in the reactor (a pre-installed part) or a granular and powderish material. In case of using a support containing catalytic active metals, such metals are preferred that have positive or no interaction to the seed germination and plant growth and can remain in the soil e.g. like a nutrient e.g. iron. The preferred substrate is a carbon-containing carrier, for example pyrolytic carbon, which means carbon derived from oxygen-free thermal decomposition of hydrocarbons in presence of a carboneous deposition carrier at temperatures > 1000 °C. The particle size of a preferred support carrier is in the range of 0.3 to 15 mm, preferably 0.5 to 10 mm, more preferably 1 to 8 mm, more preferably 3 to 8 mm. The decomposition can either be realized as fixed bed, moving bed, fluidized bed or entrained flow. The production of pyrolytic carbon is not limited to a specific energy supply, fossil-fired, solar-thermal, electrically heated, micro-wave-driven, plasma-driven, or liquid metal production reactors are possible.

A wide range of microstructures, e. g. isotropic, lamellar, substrate-nucleated and a varied content of remaining hydrogen, can occur in pyrolytic carbons, depending on the deposition conditions (pressure, temperature, type, concentration and flow rate of the source gas, surface area of the underlying substrate, etc.).

Typically, the cation exchange capacity (CEC) of granular pyrolytic carbon is about 0.01 to 1.5 cmol/kg, preferably of about 0.02 to 1 cmol/kg, preferably 0.025 to 0.75 cmol/kg, preferably 0.05 to 0.5 cmol/kg.

The degree of mineralization of granular pyrolytic carbon, if any, is negligible, below 0.01 weight-% (C as CO₂/solid C material) per year. By means of incubation experiments over more than half a year no CO₂ evolution is measurable. Thus, granular pyrolytic carbon can be considered to be an inert material.

Typically, the density of the granular pyrolytic carbon is in the range of 1.5 to 2.5 g/cc, 1.6 to 2.3 g/cc, preferably 1.8 to 2.2 g/cc, more preferably 1.9 to 2.15 g/cc (real density in xylene, ISO 8004). Typically, the bulk density of the granular pyrolytic carbon is in the range of 0.5 to 1.5 g/cc, preferably 0.6 to 1.3 g/cc, more preferably 0.7 to 1.1 g/cc.

Typically, the ash content of the granular pyrolytic carbon is in the range of 0.001 to 1 weight-%, preferably 0.005 to 0.5 weight-%, even more preferably 0.01 to 0.3 weight-%, even more preferably 0.01 to 0.2 weight-%.

Typically, the carbon content of the granular pyrolytic carbon is in the range of 95 to 100 weight-%, preferably 98 to 100 weight-%, more preferably 99 to 100 weight-%, even more preferably 99.5 to 100 weight-%, even more 99.75 to 100 weight-%, even more 99.9 to 100 weight-%. Typically, the impurities of the granular pyrolytic carbon are: S in the range of 0 to 1 weight-%, preferably 0 to 0.5 weight-%, more preferably 0 to 0.1 weight-%. Fe in the range of 0 to 1000 ppm, preferably 0 to 500 ppm, Ni in the range of 0 to 250 ppm, preferably 0 to 100 ppm, V in the range of 0 to 450 ppm, preferably 0 to 250 ppm, more preferably 0 to 100 ppm. Na in the range of 0 to 200 ppm, preferably 0 to 100 ppm. Oxygen is in the range of 0 to 100 ppm, preferably below the detection limit.

Typically, 85 weight-% of the carbon of the granular pyrolytic carbon is not-functionalized, preferably 90 weight-% of the carbon is not-functionalized, preferably 95 weight-% of the carbon is not-functionalized, preferably 98 weight-% of the carbon is not-functionalized, preferably 99 weight-% of the carbon is not-functionalized, preferably 99.5 weight-% of the carbon is not-functionalized, wherein carbon functionalization refers to a reaction in which a carbon-carbon bond is broken and replaced by a carbon-X bond (where X is usually hydrogen, oxygen, sulfur, phosphorus, nitrogen, halogens, and/or metals).

The oxygen to carbon, O:C, molar ratio is preferably below 0.05, even more preferably below 0.01. The O:C molar ratio is preferably in the range of 0 to 0.05, even more preferably in the range of 0 to 0.01.

Typically, the carbon content of the granular pyrolytic carbon that is not-functionalized is in the range of 85 to 100 weight-%, preferably of 90 to 100 weight-%, preferably 95 to 100 weight-%, more preferably 98 to 100 weight-%, even more preferably 99 to 100 weight-%, even more 99.75 to 100 weight-%.

Typically, the particle size of the granular pyrolytic carbon directly resulting of the decomposition of gaseous hydrocarbon compounds is in the range of 0.3 mm (d10) to 8 mm (d90), preferably 0.5 mm (d10) to 5 mm (d90), more preferably 1 mm (d10) to 4 mm (d90).

- 5 This particle size is of the same size as fine gravel (typically 2 to 6 mm) or coarse sand (typically 0.5 to 2 mm).

Optionally, the granular pyrolytic carbon directly resulting of the decomposition of gaseous hydrocarbon compounds can be classified to a desired particle size or a desired particle size distribution if needed for specific agricultural applications. Multi-surface classifiers are commonly used for such kind of separation/classifying processes.

10 Typically, the crystal size (XRD) of the granular pyrolytic carbon is in the range of 20 to 60 Å, preferably 30 to 50 Å, (XRD, ISO 20203).

15 Typically, the porosity of the granular pyrolytic carbon granule is between 0% to 15%, preferably 0.2% to 10%, most preferably 0.2% to 5% (Hg porosimetry, DIN66133).

Porosity can be divided into two categories: open porosity and closed porosity. Open porosity includes channels and cavities that are accessible to other particles depending on their size. This includes pores in a solid surface ("external porosity") as well as inside a solid ("internal porosity"). If, on the other hand, the inner pores are not accessible even to small gas molecules, they can be assigned to closed porosity.

25 Typically, the open porosity of the granular pyrolytic carbon is between 0% to 7.5%, preferably 0.1% to 5%, most preferably 0.1% to 2.5%. Typically, the closed porosity of the granular pyrolytic carbon is between 0% to 7.5%, preferably 0.1% to 5%, most preferably 0.1% to 2.5%.

30 Typically, the granular pyrolytic carbon is a macro-structured solid material. The wording "macro-structured" includes material with median pore diameters (i. e. pore diameter at 50% of total pore volume as measured by Hg porosimetry) ranging from 1 to 100 µm, preferably 5 to 100 µm and, more preferably 10 to 80 µm, in particular 15 to 60 µm.

35 Typically, the specific surface area of the granular pyrolytic carbon measured by Hg porosimetry (DIN66133) is in the range of 0.001 to 10 m²/g, preferably 0.001 to 5 m²/g, more preferably 0.01 to 2 m²/g, even more preferably 0.05 to 2 m²/g.

The granular pyrolytic carbon is a hydrophobic material with a preferred contact angle of water droplets of greater than 90° , more preferably than 100° , even more preferably greater than 105° as determined with the sessile droplet method (Bachmann, J. et al. (2000), Modified sessile drop method for assessing initial soil-water contact angle of sandy soil. Soil Science Society of America Journal 64, 564–567). The granular pyrolytic carbon is a hydrophobic material with a preferred contact angle of water droplets in the range of $\geq 90^\circ$ to $\leq 180^\circ$, preferably in the range of 100° to 170° , preferably in the range of 105° to 160° .

Typically, the granular pyrolytic carbon produced by decomposition of gaseous hydrocarbon compounds and carbon deposition on suitable underlying substrates does not tend to form dust.

Preferably, the granular pyrolytic carbon produced by decomposition of gaseous hydrocarbon compounds and carbon deposition on suitable underlying substrates can directly be used as a protective agent for soil macro-fauna. Preferably, there is no need for any pelleting step. Preferably, there is no need to add any binder, filler etc.

Carbon Black:

Carbon black is well known in the state of the art and e. g. described in Ullmann, Encyclopedia of Industrial Chemistry or in Kirk-Othmer Encyclopedia of Chemical Technology. The carbon black is typically characterized in ASTM classifications.

Carbon black is a commercial form of aggregates of carbon particles. Carbon black typically contains more than 95 % pure carbon with minimal quantities of oxygen, hydrogen and nitrogen. In the manufacturing process, carbon black particles are formed that range from 10 nm to approximately 500 nm in size. These fuse into chain-like aggregates, which define the structure of individual carbon black grades.

The carbon content of the carbon black is preferably 80 to 99.8 weight-%, more preferred 85 to 99.5 weight-%, even more preferred 90 to 99.5 weight-%, even more preferred 95 to 99.5 weight-%. Typically, the impurities of the carbon black are: S in the range of 0 to 2 weight-%, preferably 0 to 1 weight-%, more preferably 0 to 0.5 weight-%. H₂ in the range of 0 to 10 weight-%, preferably 0 to 5 weight-%, more preferably 0 to 2 weight-%, more preferably 0 to 1 weight-%. Oxygen in the range of 0 to 3 weight-%, preferably 0 to 2 weight-%, preferably 0 to 1.5 weight-%, more preferably 0 to 1 weight-%, more preferably 0 to 0.5 weight-%. N in the range of 0 to 5 weight-%, preferably 0 to 3 weight-%, more preferably 0 to 2 weight-%, more preferably 0 to 1 weight-%.

Typically, 85 weight-% of the carbon of the carbon black is not-functionalized, preferably 90 weight-% of the carbon of the carbon black is not-functionalized, preferably 95 weight-% of the carbon is not-functionalized, preferably 96 weight-% of the carbon is not-functionalized, preferably 97 weight-% of the carbon is not-functionalized, preferably 98 weight-% of the carbon is not-functionalized, wherein carbon functionalization refers to a reaction in which a carbon-carbon bond is broken and replaced by a carbon-X bond (where X is usually hydrogen, oxygen, sulfur, phosphorus, nitrogen, halogens, and/or metals).

The oxygen to carbon, O:C, molar ratio is preferably below 0.05, even more preferably below 0.01. The O:C molar ratio is preferably in the range of 0 to 0.05, even more preferably in the range of 0 to 0.01.

Typically, the carbon content of the carbon black that is not-functionalized is in the range of 85 to 100 weight-%, preferably 90 to 100 weight-%, preferably 95 to 100 weight-%, more preferably 96 to 100 weight-%, even more preferably 97 to 100 weight-%, even more 98 to 100 weight-%.

Typically, the cation exchange capacity (CEC) of carbon black is about 0.001 to 1 cmol/kg, preferably of about 0.005 to 0.75 cmol/kg, preferably 0.01 to 0.5 cmol/kg, preferably 0.01 to 0.25 cmol/kg, preferably 0.01 to 0.1 cmol/kg.

The degree of mineralization of carbon black, if any, is negligible, below 0.01 weight-% (C as CO₂/solid C material) per year. By means of incubation experiments over more than half a year no CO₂ evolution is measurable. Thus, carbon black can be considered to be an inert material.

Typically, the density of the carbon black is in the range of 1 to 3 g/cc, preferably 1 to 2.5 g/cc, preferably 1.5 to 2 g/cc (particle density). Typically, the bulk density of the carbon black is in the range of 0.01 to 0.75 g/cc, preferably 0.05 to 0.5 g/cc, more preferably 0.1 to 0.25 g/cc.

Typically, the ash content of the carbon black is in the range of 0.001 to 5 weight-%, preferably 0.005 to 3 weight-%, even more preferably 0.01 to 2 weight-%, even more preferably 0.01 to 1 weight-%.

Typically, the specific surface area of the carbon black measured by Hg porosimetry (DIN66133) is in the range of 5 to 1500 m²/g, preferably 10 to 1000 m²/g, preferably 10 to 500 m²/g, preferably 10 to 250 m²/g, more preferably 10 to 200 m²/g, even more preferably 20 to 150 m²/g.

Typically, the iodine number of the carbon black is between 1 and 200 mg/g, preferably 25 to 175 mg/g, measured in accordance with ASTM D1510.

The carbon black is a hydrophobic material with a preferred contact angle of water droplets of greater than 90° , preferably greater than 100° , more preferably greater than 110° , more preferably greater than 120° , more preferably greater than 130° , more preferably greater than 140° as determined with the sessile droplet method (Bachmann, J. et al. (2000), Modified sessile drop method for assessing initial soil-water contact angle of sandy soil. Soil Science Society of America Journal 64, 564–567). The carbon black is a hydrophobic material with a preferred contact angle of water droplets in the range of $\geq 90^\circ$ to $\leq 180^\circ$, preferably in the range of 100° to $\leq 180^\circ$, preferably in the range of 110° to 170° , more preferably in the range of 120° to 170° , even more preferably in the range of 130° to 170° , in particular in the range of 140° to 170° .

For example, plasma and/or micro-wave carbon black, liquid metal carbon black and/or catalytic carbon black as known in the art can be used as carbon black in this invention.

Method:

The method for controlling soil-borne phytopathogenic fungi, wherein the fungi, their habitat, their locus, or the plants, the soil, potting mixes or plant propagation material are treated with an effective amount of pyrolytic carbon, wherein the treatment is carried out before the infection of the plants, or plant propagation materials, such as seeds, by incorporating the pyrolytic carbon into the soil or substrate for propagation.

Preferably, the pyrolytic carbon is used as such without any treatment or addition of any chemical substances like known agrochemical active substances, for example fungicides, bactericides, herbicides, nutrients, heavy metals and/or plant growth regulators.

Optionally the pyrolytic carbon is mechanically processed, like sieving to the preferred particle size, before using for controlling soil-borne plant pathogenic fungi.

Treatment of soil, potting mixes or the substrate:

The invention provides a method for controlling soil-borne phytopathogenic fungi under field conditions or in pots and containers, wherein the soil, potting mixes and/or the substrate is treated with pyrolytic carbon in quantity ranging from 0.5 to 500 tons of pyrolytic carbon per ha, preferably 1 to 400 tons of pyrolytic carbon per ha, preferably 2 to 200 tons of pyrolytic carbon per ha, more preferably 1 to 60 tons of pyrolytic carbon per ha. A one-time application as well as repetitive applications at the beginning of each cropping cycle is foreseen.

Preferably, the pyrolytic carbon is worked into the soil, potting mixes and/or the substrate in the root area/zone. The root area/zone is typically 5 to 50 cm, preferably between 5 and 30 cm.

Preferably, the pyrolytic carbon is incorporated into a soil, potting mixes and/or substrate depth related to the root zone of the cultivated plant. Alternative to the incorporation into the root zone, a superficial application is considered with in some case only a shallow (1-5 cm) deep incorporation. With the latter method, an incorporation of the pyrolytic carbon is happening over time with typical conventionally used soil preparations (e.g. ploughing).

If granular pyrolytic carbon is used, the pyrolytic carbon can be easily applied and worked into the soil, potting mixes and/or substrate. The pyrolytic carbon can be deposited in a well-known spreader, e. g. fertilizer spreader, and pushed/pulled by hand or drawn by a tractor. Optionally the pyrolytic carbon is worked into the topsoil layer with soil tillage equipment.

If carbon black is used, in one embodiment, carbon black can be used directly, as produced e.g., via the plasma process, with a primary particle size of preferably 1 nm to 1 μ m, more preferred 5 to 500 nm more preferred 10 to 300 nm. In another embodiment, carbon black can be used as pellets with a particle size of preferably in the range of 0.3 to 15 mm, preferably 0.5 to 10 mm, more preferable 1 to 8 mm. Pelleting of carbon black is well known in the state of the art, typically, water can be used as binder.

Preferably, the pyrolytic carbon is worked in the topsoil homogeneously. The techniques to work pyrolytic carbon into the topsoil are known in the art, e. g. with soil tillage equipment.

The incorporation of pyrolytic carbon at effective rates can be done as a one-time or as a repetitive treatment, e.g. before each soil preparation for the next cropping cycle, being with horticultural crops preferably multiple ones per year like e.g. with salad or other short-cycle horticultural crops and being with perennial crops preferably once at planting.

Alternatively, the pyrolytic carbon is worked in the topsoil in rows, preferably in analogy to the crop/plant rows. Cultivation of plants in rows that have an even spacing of about 7-70 cm is well known, for example cereals, corn, sugar beets, sugarcane, cotton, rapeseed, potatoes, asparagus or all horticultural crops that are lately planted in the field such as e.g., lettuce are grown in rows solely. This holds also true for permanent crops as fruit trees, tree plantations, and alike, which may be spaced from 50 cm up to 5 m in rows.

Treatment of plant propagation material:

Plant propagation materials may be treated with pyrolytic carbon of the present invention prophylactically either at or before planting or transplanting by bringing into contact with the

plant propagation material or specific parts like e.g. stem basis. Wetting agents and other materials to enhance the adherence of the material may be added to the pyrolytic carbon .

Additionally, the invention also relates to a use of pyrolytic carbon for protection of plant propagation material, preferably seeds, from soil-borne phytopathogenic fungi and the invention relates to a method for protection of plant propagation material, preferably seeds, from soil-borne phytopathogenic fungi, comprising contacting the plant propagation materials with pyrolytic carbon.

Additionally, substrate containers, being pots of different sizes and shape made from substrate, e.g. peat, paper, compost, typically used for propagation can be treated or amended with effective rates of pyrolytic carbon instead of treated propagation material directly.

Treatment of horticultural substrates:

Horticultural substrates, being e.g. sand-soil-peat mixtures, or pots or containers made from such substrates are often but not exclusively used for propagating plants or for growing plants under more controlled conditions, e.g. in plastic or green houses. The addition of pyrolytic carbon could be in a range of 0,5 to 950 g pyrolytic carbon per kg substrate, preferably 1 to 900 g pyrolytic carbon per kg substrate, more preferably 2 to 500 g pyrolytic carbon per kg substrate, even more preferably 10 to 100 g pyrolytic carbon per kg substrate.

The present invention therefore includes substrate containers or pots containing pyrolytic carbon.

As an auxiliary, commonly used agents like oils, wetters, adjuvants, fertilizers, superabsorbent or micronutrients can be used.

As further active components, pesticides like fungicides, growth regulators, herbicides, insecticides, safeners can be used or mixed with the pyrolytic carbon before spreading onto soil or amending substrate used for propagation.

Optionally, the particle size of the pyrolytic carbon can be adapted to the co-conditioning substrate, e. g. via milling and classifying.

The present pyrolytic carbon can be mixed with at least one auxiliary and/or further active component or the present pyrolytic carbon can support at least one auxiliary and/or further active component.

Fungi and Plants:

The pyrolytic carbon as described in the present invention are suitable to act against a broad spectrum of soil-borne phytopathogenic fungi, in particular against species of Rhizoctonia, Fusarium, Pythium, Phytophthora, Plasmodiophora, Verticillium, Typhulla, Gaeumanomyces, Spongospora.

The pyrolytic carbon of the present invention are preferably useful in the control of soil-borne phytopathogenic fungi on various cultivated plants, such as cereals, e. g. wheat, rye, barley, triticale, oats, or rice; beet, cotton, leguminous plants such as soybean, oil plants, cucurbits, fiber plants, vegetables, lauraceous plants, energy and raw material plants, corn; tobacco; nuts; coffee; tea; apple; pear; cherry; different kinds of citrus trees, bananas; vines (table grapes and grape juice grape vines); natural rubber plants; or ornamental and forestry plants; on the plant propagation material, such as seeds; and on the crop material of these plants.

More preferably, pyrolytic carbon of the present invention are used for controlling soil-borne phytopathogenic fungi on field crops, such as potatoes, sugar beets, tobacco, wheat, rye, barley, oats, rice, corn (including field corn, sweet corn, or other corns), cotton, soybeans, oilseed rape (both summer and winter oilseed rape), legumes, sunflowers, or sugar cane, on perennial crops such as fruits, vines, citrus, topical fruits like coffee, rubber, mango, pome fruits like apples or pears, plums, nectarines, citrus or on vegetables, such as cucumbers, tomatoes, beans, peas, melons or squashes, or on annual or perennial ornamentals such as tulips, or roses.

According to the invention all of the above cultivated plants are understood to comprise all species, subspecies, variants, varieties and/or hybrids which belong to the respective cultivated plants, including but not limited to winter and spring varieties, in particular in cereals such as wheat and barley, as well as oilseed rape, e.g. winter wheat, spring wheat, winter barley etc.

Corn is also known as Indian corn or maize (*Zea mays*) which comprises all kinds of corn such as field corn and sweet corn. According to the invention all soybean cultivars or varieties are comprised, in particular indeterminate and determinate cultivars or varieties.

The term "cultivated plants" is to be understood as including plants which have been modified by mutagenesis or genetic engineering to provide a new trait to a plant or to modify an already present trait.

Advantages:

Current measures to combat soil-borne phytopathogenic fungi are using fungicides, biological agents or bio-stimulants, applied on seed as seed treatment or propagation material or via drench into the soil. Other methods are general ways of soil improvements and changes in the crop rotation to lower the number of susceptible crops in the crop rotation.

- 5 Particularly fungicides may lead to side effects and are costly. Soil improvements and crop rotation are often not feasible, or not economical viable.

Soil improvements could be achieved by soil amendments using sand, peat, any kind of compost or charcoal.

- 10 Using pyrolytic carbon have the advantage that they are easily added to soil or propagation or horticultural substrates before transplanting. Based on the inert structure of the pyrolytic carbon, no impact on fauna like e.g. earthworms, nor on ground water is expected. The repetitive incorporation of the pyrolytic carbon can easily be done using standard working procedures not requiring substantial addition efforts or machinery.

Experimental Part:

1 Characteristics

In the experiments, two types of pyrolytic carbon are tested, dense granular Pyrolytic Carbon and light nanoscale Carbon Black were tested:

Table 1a: Characteristic of the granular Pyrolytic Carbon (BASF Pyro C) and Carbon Black (Thermax N990 Ultra Pure)

	BASF Pyro C	Thermax N990
Carbon content	98 weight-%	>95 weight-%
O:C molar ratio	< 0.1	< 0.1
Particle size	1.5 - 2.0 mm	280 nm
BET	< 0.05 m ² /g	10.3 m ² /g
Langmuir surface	0.13 m ² /g	15 m ² /g
Density	1.98 g/ cc	1.7-1.9 g/ cc
Hydrophobicity: Contact angle of water droplets	109° ±8°	150° ±3°

The BASF Pyro C was produced by decomposition of natural gas and deposition on calcined petroleum coke carrier material (having a particle size of 0.5-2.5 mm, a sulfur content of 1.1 weight-% and a real density in xylene of 2.09 g/cm³) in a fluidized bed at temperatures from 1100-1300 °C and at pressures from 1-2 bar(abs).

BET: measured as described in DIN ISO 9277

Density: The specific weight (density) was determined by the Archimedes principle in pure water (see Wikipedia). Part of the experiments were done in water amended with a wetting agent to lower the surface tension of the water so that also hydrophobic particles may sink into the water if the specific weight is ≥ 1 g/cc.

Bulk Density: ASTM C559 "Standard test method for bulk density by physical measurement of manufactured carbon and graphite articles"

Hydrophobicity: Bachmann, J. et al. (2000) Modified sessile drop method for assessing initial soil-water contact angle of sandy soil. Soil Science Society of America Journal 64, 564–567

Table 1b: Characteristic of Biochar

	Carbuna CPK 1-2 mm (Biochar)
Biochar	Made from wood
Carbon content	89.5 wt.-%
Particle size	1-2 mm
Specific surface	417 m ² /g
Bulk density	339 kg/m ³

Table 1c: Effective cation exchange capacity

	pH value	Effective cation exchange capacity (cmol/kg), DIN EN ISO 11260:2018
Carbon Clack (Cancarb Thermax N990 ultra pure)	5,69	0,02
granular Pyrolytic Carbon (BASF Pyro C)	6,87	0,10
Carbuna CPK 1-2 mm (Biochar)	8,45	1,9
Soil < 2 mm	7,05	6,2

- 5 In the present study, a CEC of approximately 2 cmol/kg was determined for the biochar Carbuna CPK. The CEC of the pyrolytic carbon is in the range of 0.02 to 0.1 cmol/kg and more than a factor of 10 lower than the CEC of the biochar.

2. Fungicidal action against selected soil- borne, pathogenic fungi

2.1 Activity against *Rhizoctonia solani* on corn

2.1.1 Test method

- 5 The plant pathogenic fungus *Rhizoctonia solani* (=RHIZSO) was cultivated on millet in glass containers suitable for such propagation. A portion of 20g of the millet materials on which *Rhizoctonia solani* was actively growing was mixed with 10g of oat flakes, milled (= fungus inoculation mixture) and incorporated into 1 kg of mineral soil ("Limburgerhof" soil). As reference treatments, the Limburgerhof soil was used without the fungus-inoculation mixture.

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Into the mineral soil, the test concentration (16g/1kg) of either the Thermax N990 Ultra Pure or the BASF test material "BASF Pyro C" was evenly incorporated. As reference treatments, the soil was used without adding the respective pyrolytic carbon mixture. The ready mixture was filled into 8cm plastic pots using 9 replicates per treatment. Per pot 5 corn seeds (ZEAMX; Variety: Ronaldino) were placed evenly into the soil or substrate, covered with an additional layer of 1 cm and grown in a greenhouse chamber at 20 C.

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2.1.2 Measurements:

14 days after seeding the number of plants per pot (=germination rate), the plant height from stem basis to leaf tip and the root mass were assessed. In addition, roots and stem basis were inspected for typical disease symptoms, being typically discolorations and in rare cases lesions of roots, stem base or leaves.

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2.2.2 Activity in mineral soil ("Limburgerhof" soil)

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As a reference for a typical agriculturally used soil, "Limburgerhof" soil was selected. Emergence of plants was even and neither significantly affected by the fungus nor the addition of one of the two pyrolytic carbon. In addition, no impact of the addition of one of the two pyrolytic carbon was observed when analyzing root mass or plant height (Treatment 1,3,5). Typical disease symptoms were well expressed in soil, leading to depression of plant growth expressed as reduced plant height or root mass (see Table 2).

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Statistical difference for the infection rate could be found comparing not inoculated variants (treatment 2,4,6). The disease was most expressed with treatment 2 without any addition of a pyrolytic carbon. The addition of Thermax (treatment 4) and BASF Pyro C (treatment 6) reduced the percentage of visible infection significantly, whereas the highest reduction was reached with Thermax.

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For plant height and root mass neither significant impact was detected in the absence of infection nor with the addition of one the two pyrolytic carbon (treatments 1,3,5). In presence of the phytopathogenic fungus, a very clear and statistically significant reduction of plant height and root mass was observed when comparing to non-infected (treatment 2, 4 and 6). The reduction of plant growth was significantly less in the presence of one of the two pyrolytic carbon (treatment 2 versus treatment 4 and 6). Obviously, the addition of a pyrolytic carbon did partly compensate the impact of the fungus.

Table 2: Activity of the addition of 16 g/kg Thermax N990 or BASF Pyro C in controlling the soil-borne phytopathogenic fungi "Rhizoctonia solani" in mineral Limburgerhof soil (9 repetitions, standard deviation shown)

Treatment		germination %	infection % shoot	plant height in cm / (relative %)	root mass %
1	Limburgerhof soil w/o Rhizoctonia solani	100,0 ± 0	0,0 ± 0	17.9 ± 2.0 (100)	100,0 ± 0
2	Limburgerhof soil with Rhizoctonia solani	91,1 ± 14.5	60,0 ± 26.5	6.1 ± 2.9 (33,9)	20,6 ± 12.1
3	Limburgerhof soil w/o Rhizoctonia solani + Thermax N990 Ultra Pure (16 g/kg)	100,0± 0	0,0 ± 0	17.3 ± 2.0 (96,4)	100,0 ± 11.5
4	Limburgerhof soil with Rhizoctonia solani + Thermax N990 Ultra Pure (16 g/kg)	100,0± 0	24,4 ± 24.0	9.2 ± 1.8 (51,2)	30,0 ± 5.0
5	Limburgerhof soil w/o Rhizoctonia solani + BASF Pyro C (16 g/kg)	100,0± 0	0,0 ± 0	18.1 ± 1.3 (101,0)	101,1 ± 6.0
6	Limburgerhof soil with Rhizoctonia solani + BASF Pyro C (16 g/kg)	95,6± 13.3	48,9 ± 17.6	8.3 ± 1.4 (46,3)	32,2 ± 5.1

3. CO2 Release

The CO₂ release from an incubation medium (mg Carbon/kg) without and with addition of different external carbon sources was measured over a period of 161 days. In Tab. 3 mean values (n=4) and standard deviations are shown. The incubation was performed at a constant temperature of 22°C and a water content in the incubation medium of 60% of the maximum water holding capacity.

It can be seen from Tab 3. that straw causes a strong CO₂ emission. While the emission of the incubation medium with pyrolytic carbon caused similar emissions than the reference without any carbon addition, the CO₂ emission of the incubation medium with biochar is increased.

Tab. 3: CO₂ emission of incubation medium (mg Carbon/kg) without and with addition of different external carbon sources.

[illegible]

- compost from green waste (degree of rotting: 5; 1000 mg C kg ⁻¹)	53	78	103	120	149	175	209	249		±11
- straw (winter wheat; 902 mg C kg ⁻¹)	99	204	327	388	454	502	553	604		±11

List of figures

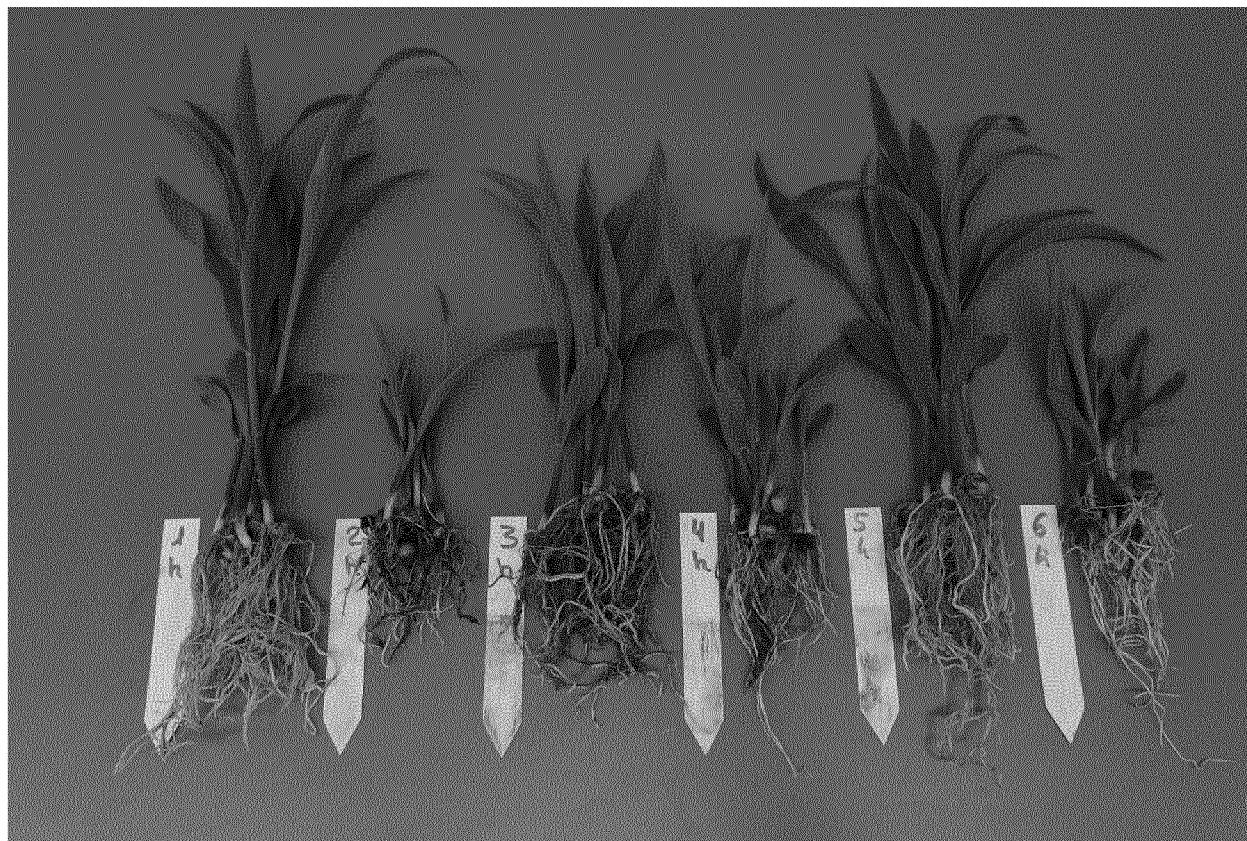
- 5 Figure 1: Picture of plant development 14 days after inoculation with *Rhizoctonia solani*

Claims

1. Use of hydrophobic pyrolytic carbon for controlling soil-borne phytopathogenic fungi, wherein the pyrolytic carbon has a density of 1 to 3 g/cc, a carbon content of 95 to 100 weight-%, an ash content of 0.001 to 5 weight-%, 85 weight-% of the carbon is not-functionalized with a O:C molar ratio below 0.1 and the cation exchange capacity of the pyrolytic carbon is 0.001 to 0.75 cmol/kg, wherein the pyrolytic carbon is produced from gaseous hydrocarbons.
2. Use according to claim 1, wherein the carbon content is of 98 to 100 weight-%.
3. Use according to claim 1 or 2, wherein the pyrolytic carbon is a hydrophobic material with a contact angle of water droplets of greater than 100°.
4. Use according to at least one of claims 1 to 3, wherein the degree of mineralization of granular pyrolytic carbon is below.
5. Use according to at least one of claims 1 to 4, wherein the pyrolytic carbon is used as such without any treatment or addition of any chemical substances.
6. Use according to at least one of claims 1 to 5, wherein 90 weight-% of the carbon is not-functionalized.
7. Use according to at least one of claims 1 to 6, wherein the density is of 1 to 2.5 g/cc.
8. Use according to at least one of claims 1 to 7, wherein the ash content is of 0.001 to 2 weight-%.
9. Use according to at least one of claims 1 to 8, wherein the soil-borne phytopathogenic fungi is from genera Pythium, Fusarium, Rhizoctonia, Phytophthora, Verticillium, Plasmodiophora, Spongospora, Typhulla and/or Gaeumanomyces.
10. Use according to at least one of claims 1 to 9, wherein the soil-borne phytopathogenic fungi is combated in field crops, leguminous crops, vegetables, perennial crops and/or ornamental crops.

11. Use according to claim 10, wherein the soil-borne phytopathogenic fungi is combated in wheat, rye, barley, triticales, oats, rice, beet, soybean, corn, tobacco, oil plants, fruting vegetables, leavy vegetables, brassica species, fiber plants, citrus fruits, pome fruits, laura-
ceous plants, energy and raw material plants, nuts, coffee, tea, mango, bananas, vines,
5 natural rubber plants, ornamental and forestry plants.
12. A method for controlling soil-borne phytopathogenic fungi, wherein soil, multiplication sub-
strate, growth substrate containers, plant propagation material and/or potting mixes is
treated with an effective amount of hydrophobic pyrolytic carbon, wherein the pyrolytic car-
10 bon has a density of 1 to 3 g/cc, a carbon content of 95 to 100 weight-%, an ash content of 0.001 to 5 weight-%, 85 weight-% of the carbon is not-functionalized with a O:C molar ratio below 0.1 and the cation exchange capacity of the pyrolytic carbon is 0.001 to 0.75 cmol/kg, wherein the pyrolytic carbon is produced from gaseous hydrocarbons.
13. The method according to claim 12, wherein the soil-borne phytopathogenic fungi is from
15 genera Pythium, Fusarium, Rhizoctonia, Phytophthora, Verticillium, Plasmodiophora, Spongospora, Typhulla or Gaeumanomyces.
14. The method according to the claim 12 or 13, wherein the plants are selected from field
20 crops, leguminous crops, vegetables, perennial crops and/or ornamental crops.

Figure 1:



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2023/069994

A. CLASSIFICATION OF SUBJECT MATTER

INV. A01N61/00 A01P3/00

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2021/122503 A1 (BASF SE [DE]) 24 June 2021 (2021-06-24) cited in the application	1-14
Y	the claims, the examples and page 6, in particular the last paragraph -----	1-14
X	DAI ZHONGMIN ET AL: "Soil fungal taxonomic and functional community composition as affected by biochar properties", SOIL BIOLOGY AND BIOCHEMISTRY, PERGAMON, OXFORD, GB, vol. 126, 5 September 2018 (2018-09-05), pages 159-167, XP085483416, ISSN: 0038-0717, DOI: 10.1016/J.SOILBIO.2018.09.001 cited in the application	1-14
Y	the whole document ----- -/--	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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PCT/EP2023/069994

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2019/118986 A1 (COOL PLANET ENERGY SYSTEMS INC [US]) 20 June 2019 (2019-06-20)	1-14
Y	the claims and paragraphs 288-289, 329-361 and 438 -----	1-14
X	CN 105 432 381 B (JIANGSU ACAD AGRICULTURAL SCI) 20 April 2018 (2018-04-20)	1-14
Y	the whole document -----	1-14
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Y	the claims, the examples and paragraphs 4-20 -----	1-14
Y	WO 2021/122500 A1 (BASF SE [DE]) 24 June 2021 (2021-06-24) cited in the application the whole document -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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