

PLASMA TREATMENT

This invention relates to apparatus and method for plasma treatment, typically of materials and in one embodiment seeds.

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It is known that various seeds can be subject to infections from viruses, bacteria and fungi. An example of this is *Pastinaca sativa* (parsnip) seeds, which can be infected by, amongst other fungi, *Itersonilia pastinaceae*. It is desirable to be able to treat these infections. Typically, at present, such seeds are immersed in hot water, which is cumbersome, often ineffective and requires drying of the seeds afterwards, or are treated with high temperatures (e.g. steam-based process) or with harsh chemical treatments, all of which are undesirable.

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More generally, it is desirable to provide an apparatus by means of which various materials could be treated.

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According to a first aspect of the invention, we provide a plasma treatment apparatus, comprising:

- a housing defining a void;
- a source of ionised gas plasma in communication with the void; and
- agitation apparatus arranged to agitate contents of the void.

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Thus, the agitation apparatus can allow for the contents of the void to be agitated in reactive species produced from the ionised gas plasma produced by the source in order to treat those contents. This is useful, in particular, for the treatment of materials comprising many small components, such as seeds, granular material, plastic beads and the like. The material could otherwise comprise biomass, waste water, milk (for sterilisation thereof), or water or other material contaminated by pollutants.

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Reactive species produced from the ionised gas plasma can be used to treat those materials, with the reactive species produced from the ionised gas plasma reaching more of the material than if the material were not agitated, or if there were not a source in communication with the void.

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In the example of seeds, we have appreciated that the apparatus can be used for the disinfection of seeds, and in particular to kill bacteria, fungus or fungal spores on seeds. It can also be used to promote seed germination.

- 5 The source may be within the void; alternatively, it may be in communication with the void through a conduit for the ionised gas plasma and/or for reactive species generated from the ionised gas plasma.

10 The agitation apparatus may comprise part of the housing comprising at least one rotating wall. Each rotating wall may be arranged for rotation around the source.

The apparatus may comprise drive means arranged to rotate each rotating wall around the source. Thus, each rotating wall can be driven for rotation about the source, so as to cause the agitation described above. Typically, the drive means will comprise a
15 motor, such as an electric motor. The drive means may also comprise a transmission member, such as a drive belt or drive gear, arranged to transmit rotational movement of a rotor of the motor to each rotating wall.

Typically the walls will comprise at least one fixed wall which is fixed relative to the
20 source. The at least one rotating wall may form a tube having two ends, and there may be a fixed wall at each end. Typically, the at least one rotating wall forms a cylinder and there is a fixed wall of circular shape at each end. The apparatus may comprise a bearing at each end through which each rotating wall is mounted on the fixed wall at that end.

25 The apparatus may be provided with a power conduit for transmitting electric power to the source from outside of the void. Typically, the conduit may comprise an electrical connection passing through a fixed wall, typically the fixed wall at an end. Thus, the conduit can be fixed in position (which is convenient when dealing with
30 electrical connections) whilst the drum rotates.

The apparatus may comprise a power supply for the source, in electrical communication with the source, typically through the power conduit.

The agitation apparatus may comprise at least one baffle for agitating material within the drum. Typically, each baffle will form at least part of a helix about an axis about which each rotating wall rotates. Alternatively, each baffle may be straight, and there may be a plurality of baffles potentially parallel to one another.

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The apparatus may be provided with a gas conduit through which a gas can be introduced into the void. The apparatus may also be provided with a gas exhaust conduit through which the gas can be exhausted from the void. As such, a gas, such as atmospheric air, dry air or an argon/oxygen mixture can be passed over the material
10 in the void, which can add to the treatment of the material. The gas may comprise water vapour, which can increase the humidity of the air or gas within the void.

The apparatus may be provided with a source of visible or ultra-violet radiation, arranged so as to provide the visible or ultra-violet radiation within the void. Thus,
15 light or ultra-violet radiation can be additionally used to treat the material in the void.

The source may be arranged to generate the ionised gas plasma from atmospheric air. This is plentiful, and is a useful source of both oxygen and nitrogen gas as precursors to form reactive species. Other oxygen and nitrogen containing gas mixtures such as
20 helium/oxygen and argon/oxygen admixtures may also be used. In these cases, the apparatus may comprise delivery means for delivering the gas mixture to the ionised gas plasma source, typically from re-usable or single use gas canisters.

The apparatus may comprise a source of water in communication with the void.
25 Typically, the source of water would be arranged to deliver water to the void. The source of water may comprise a valve by means of which the flow of water can be controlled.

The source of water may comprise a source of plasma activated water. Alternatively,
30 the water introduced into the void may be converted to plasma activated water by the action of the reactive species generated from the ionised gas plasma.

The source may comprise at least two electrodes. Each electrode may be elongate, having a length. The electrodes may form pairs; with two electrodes there will be a
35 single pair. Each pair of electrodes may be positioned so as to be skew, so that the

lengths of the electrodes are non-parallel but the electrodes are spaced apart. Each pair of electrodes will define a crossing zone between and around the points along the length of each electrode where the other electrode of each pair comes closest. The source may further comprise a voltage source arranged to apply a voltage between the electrodes. When this voltage is applied, ionised gas plasma will be produced in the crossing zone. The minimum distance between the electrodes may be between 10 micrometres and 30 millimetres, typically between 0.5mm and 1.5mm.

Each electrode may comprise a metallic member surrounded by an encapsulating dielectric shield, such as a glass tube or ceramic coating. This limits the discharge current although the same could be achieved by quickly pulsing the applied voltage.

Typically, the voltage applied to generate the plasma from the power supply will be at least 0.1 or 0.5 kilovolts (kV), 1kV, 5kV, 10kV, 20kV or 40kV. The voltage may be an alternating current (AC) voltage, having a frequency. The frequency may be between 50Hz and 2.45GHz, and the voltage may be modulated so as to comprise alternating plasma-on periods where the voltage varies at the frequency and plasma-off periods where the voltage does not vary and will typically be zero. This may minimize heating of the material treated and reduce power consumption. Alternatively, the voltage can be applied as pulses with a pulse width duration between 0.1 nanosecond and 1000 milliseconds.

Typically, the power supply will be arranged to draw electrical power to generate the plasma from mains, a low-voltage DC supply (e.g. USB charger), generator, or batteries.

Typically, the apparatus will be operable to produce ionised gas plasma at room temperature and pressure; but it may be so operable with the temperature of the gas from which the ionised gas plasma is formed between 0 and 50 degrees Celsius, typically between 10 and 40 degrees Celsius, potentially between 15 and 30 degrees Celsius, and at 1 atmosphere $\pm$ 0.2 atm, 0.1 atm, 0.05atm or 0.01atm. The source may provide reactive species formed from ambient air surrounding the ionised gas plasma source, without first heating, cooling, pressuring and/or depressurising the ambient air.

The reactive species may comprise ozone. The reactive species may additionally or alternatively comprise at least one of Nitric Oxide (NO), Hydrogen Peroxide (H₂O₂), Hydroxyl radicals (OH), Hydron ions (H⁺), Nitrate ions (NO₃⁻), Nitrite ions (NO₂⁻) and Oxygen atoms (O).

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According to a second aspect of the invention, there is provided a method of treating a material, comprising placing the material within the void of an apparatus in accordance with the first aspect of the invention, and then causing the source of ionised gas plasma to produce ionised gas plasma in the void whilst also causing each
10 rotating wall to rotate about the source.

Thus, this aspect describes how the apparatus of the first aspect can be used to treat a material. Typically, the ionised gas plasma will generate reactive species which will accumulate in the void, through which the material will be tumbled by the action of
15 the rotating walls.

Reactive species produced from the ionised gas plasma can be used to treat the material, with the reactive species produced from the ionised gas plasma reaching more of the material than if the walls did not rotate to tumble the material, or if the
20 source was not within the void.

This is useful, in particular, where the material comprises many small components; as such the material may comprise seeds, granular material, plastic beads or the like. The material could otherwise comprise biomass, waste water, milk (for sterilisation thereof), or water or other material contaminated by pollutants.
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In the example of seeds, we have appreciated that the method can be used for the disinfection of seeds, and in particular to kill bacteria, fungus or fungal spores on seeds. It can also be used to promote seed germination.
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The method may comprise driving the rotating walls around the source using the drive means.

The method may comprise introducing a gas into the void through the gas conduit, and
35 optionally exhausting the gas through the gas exhaust conduit. The gas may comprise

atmospheric air, dry air or an argon/oxygen mixture. As such, a gas can be passed over the material in the void, which can add to the treatment of the material. The gas may comprise water vapour, which can increase the humidity of the air or gas within the void.

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The method may comprise irradiating the material with visible or ultra-violet radiation.

Typically, the ionised gas plasma will be produced from ambient air at room
10 temperature and pressure; that is with the temperature of the air from which the ionised gas plasma is formed between 0 and 50 degrees Celsius, and at 1 atmosphere $\pm$ 0.2 atm, 0.1 atm, 0.05atm or 0.01atm. The ionised gas plasma may be formed in ambient air surrounding the ionised gas plasma source, without first heating, cooling, pressuring and/or depressurising the ambient air.

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The reactive species may comprise ozone. The reactive species may additionally or alternatively comprise at least one of Nitric Oxide (NO), Hydrogen Peroxide (H₂O₂), Hydroxyl radicals (OH), Hydron ions (H⁺), Nitrate ions (NO₃⁻), Nitrite ions (NO₂⁻) and Oxygen atoms (O).

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There now follows, by way of example only, description of embodiments of the invention described with reference to the accompanying drawings, in which:

Figure 1 shows a perspective view of an apparatus in accordance with a first
25 embodiment of the invention;

Figure 2 shows a part-sectional perspective view of the apparatus of Figure 1;

Figure 3 shows an elevation of the apparatus of Figure 1;

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Figure 4 shows a plan view of the electrodes of the apparatus of Figure 1;

Figure 5 shows a side-view cross-section of the electrodes of Figure 4;

Figure 6 shows a graph demonstrating the fungus-killing properties of the apparatus of Figure 1;

5 **Figure 7** shows a graph demonstrating the effect that the apparatus of Figure 1 has on the germination of seeds;

Figures 8 to 12 show alternative embodiments of the electrodes of the apparatus of Figure 1; and

10 **Figure 13** shows schematically an apparatus in accordance with a seventh aspect of the invention.

Figures 1 to 5 of the accompanying drawings show an apparatus 1 of the form of a reactor in accordance with a first embodiment of the present invention. The apparatus
15 1 comprises a base 10 on which are mounted two fixed disc-shaped end walls 11 at opposing ends of the apparatus.

Separating the end walls 11 there is a rotatable cylindrical wall 12. This can rotate about the axis of the cylinder it forms relative to the fixed end walls 11. Whilst in
20 this embodiment a single cylindrical rotating wall 12 is provided, there need not be a single rotating wall, nor need it be cylindrical – for example, any prismoidal shape could be used, such as a hexagon made up of six walls, one for each face.

The fixed end walls 11 and the rotatable cylindrical wall 12 define a void 13. Within
25 this void is provided a source of ionised gas plasma 14. The source 14 is mounted on the fixed end walls 11 so that the rotatable wall 12 is free to rotate around it.

The source 14 comprises two sets of electrodes 15. One set of electrodes 15 is shown in Figures 4 and 5 of the accompanying drawings. Each set of electrodes 15
30 comprises a pair of electrodes 5 being connected to an output stage of a power supply 8 through electrical connections 16 through one fixed wall 11. Each electrode 5 comprises a central conducting wire 7, surrounded by a dielectric tube 6. The wire 7 is typically metallic, but could comprise graphite, stainless steel, copper, a conductive liquid or water, or any other suitable conductor; the dielectric is typically borosilicate
35 glass, but could comprise polytetrafluoroethylene (PTFE) or other plastics, ceramics,

alumina, Macor (RTM) or other machineable glass-ceramic mixtures, reinforced glass fibre or quartz, or any other suitable dielectric.

- The two electrodes 5 are provided so their lengths are parallel to a common plane.
- 5 However, the electrodes 5 are skew to each other, in that they are non-parallel but do not intersect, being spaced apart from each other vertically; in plan view (as shown in Figure 4 of the accompanying drawings) they form an X-shape, with only a small gap (1 mm) where they cross.
- 10 The power supply 8 is arranged to provide a voltage between the two electrodes 5. Typically, the voltage will be a sinusoidal excitation wave of around 20 kilovolts (kV) peak to peak at a frequency of around 30kHz. The signal can be modulated to comprise pulses having a 5% duty cycle (so each cycle would comprise 5% of the cycle with the voltage comprising a 20kV sinusoidal signal and the other 95%
- 15 essentially at zero voltage).

When this voltage is applied between the electrodes, an ionised gas plasma 9 is formed in the region where the electrodes 5 cross, from the ambient air at the local temperature and pressure. This ionised gas plasma 9 then generates reactive species

20 from air such as Nitric Oxide (NO), Ozone (O₃), Hydrogen Peroxide (H₂O₂), Hydroxyl radicals (OH), Hydron ions (H⁺), Nitrate ions (NO₃⁻), Nitrite ions (NO₂⁻) and Oxygen atoms (O). The ionised gas plasma can also generate ultraviolet (UV) radiation. These reactive species 9 diffuse throughout the void 13.

- 25 An electric motor 20 is provided which is arranged to rotate the rotatable wall 12 about its axis by means of drive belt 21. As such, the rotating walls provide an agitation apparatus for the contents of the void 13.

A gas inlet 22 is provided in one fixed wall 11 and a gas outlet 23 is provided in the

30 other fixed wall 11. As such, gas, such as humidified air, can be introduced at one end of the void 13, passed over material in the void, and exhausted at the other end.

As such, in use, the reactive species are generated by the plasma generated by the source 14. These diffuse throughout the void. Material – particular material made up

35 of many small parts, or liquid – will be tumbled through the reactive species in order

to react with those reactive species. This tumbling effect can be increased by the use of linear or helical baffles on the inner wall of the rotatable wall 12.

5 This is useful, in particular, for the treatment of materials comprising many small components, such as seeds, granular material, plastic beads and the like. The material could otherwise comprise biomass, waste water, milk (for sterilisation thereof), or water or other material contaminated by pollutants.

10 In the particular example of seeds, we have found that this can have an effect of killing fungal infections of seeds. Figure 6 of the accompanying drawings show the effect of the use of the apparatus 1 on parsnip seeds (*Pastinaca sativa*). The seeds had been contaminated with *Itersonilia*. The seeds were placed in the reactor, and the apparatus activated for between zero and ten hours as shown in the graph in Figure 6. One hundred of the seeds from each treatment time were then placed on agar with
15 chloramphenicol and monitored for fungal growth after three days.

Figure 6 shows the percentage of seeds that were growth free after that time. It can be seen that increasing use of the apparatus increases the percentage of seeds that were free of fungal infection, and so indicates that the apparatus can be useful for killing
20 this fungus on seeds. The error bars show the variability between the three times the experiment was run.

Figure 7 of the accompanying drawings shows the effect that the reactor has on germination rates. The same experiment as for Figure 6 was carried out and one
25 hundred seeds per treatment placed on damp filter paper in petri dishes. The dishes were wrapped in parafilm and incubated at constant 24°C incubator with constant light. Figure 7 shows the percentage of seeds that had germinated (rupture of the testa and emergence of radicle) after 21 days.

30 As can be seen in Figure 7, there was no substantial decrease in germination rate, and indeed an increase in germination rate for exposure times of over six hours.

Alternative embodiments of the electrodes are shown in Figures 8 to 15 of the accompanying drawings. These could generally be used in place of the electrodes 15

shown above. The dielectric and electrode material can be as suggested above with respect to the first embodiment.

5 In the second embodiment of the invention shown in Figure 8, a dielectric plate 26 is used mounted within the void 13. On the upper surface of the dielectric plate are mounted two encapsulated parallel electrodes 25; wires 34 lead to a power supply (not shown) for the application of the voltage. The electrodes 25 are backed by resin insulation 33.

10 In this embodiment, application of the voltage will cause ionised gas plasma to be formed on the bottom surface of the dielectric plate 26, above the well 23. Reactive species generated in the plasma will then diffuse outwards into the void 13.

15 In the third embodiment of the invention shown in Figure 9 of the accompanying drawings, the reference numerals have been raised by 20 with respect to the second embodiment. In this embodiment, there are two electrodes 45 each comprising a central metallic rod 47 (with wires 54 to connect to the unshown power supply) surrounded by dielectric 46. The ends of the electrodes 45 are adjacent; on application of a voltage between the electrodes 45, plasma 49 will form between the ends of the electrodes 45 and reactive species generated in the plasma diffuse outwards into the void 13.

25 In the fourth embodiment of the invention shown in Figure 10 of the accompanying drawings, the reference numerals have been raised by 40 with respect to the second embodiment. In this embodiment, there is a single electrode 63 (with wire 74 to connect to the unshown power supply) terminated by a dielectric plate 26. A further electrode is provided elsewhere in the void 13. On application of a voltage between the electrodes, plasma 69 will form underneath the dielectric plate 26 beneath the electrode 63 and reactive species generated in the plasma diffuse outwards into the void 13.

35 In the fifth embodiment of the invention shown in Figure 11 of the accompanying drawings, the reference numerals have been raised by 60 with respect to the second embodiment. In this embodiment, a well 82 contains an aqueous solvent 91 and as its bottom face has a porous membrane 96. Electrodes 85 are placed underneath, with

their ends uppermost. Each electrode 85 comprises a central metallic (etc) rod 87 surrounded by a dielectric crucible. Air is passed upwards around the electrodes through the porous membrane to form bubbles 97 in the aqueous solvent.

5 In order to form a plasma 89 adjacent to the ends of the electrodes 85 and the porous membrane 96, the aqueous solvent can be used as another electrode as in the fifth embodiment (so that a wire would be placed in the conductive aqueous solvent 91) or the porous membrane could be conductive and used an electrode. Applying a voltage between either the membrane 96 or the aqueous solvent 91 on the one hand and the
10 electrodes 85 on the other will cause a plasma to be formed adjacent to the underside of the porous membrane 96 and swept up with airflow 98 to form the bubbles 97. The content of the bubbles 97, including reactive species generated in the ionised gas plasma, will then dissolve in the aqueous solvent 91 to form plasma activated water, and/or will evolve out of the water into the void 13.

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In the sixth embodiment of the invention shown in Figure 12 of the accompanying drawings, the reference numerals have been raised by 80 with respect to the second embodiment. In this embodiment, a dielectric sheet 106 separates two sets of electrodes 105a, 105b; a single planar electrode 105a on the top side of the dielectric
20 sheet and a plurality of patch or elongate electrodes 105b on the bottom side. On application of a voltage between the electrodes 105a, 105b, plasma 109 will form around the electrodes 105b on the bottom side of the dielectric plate 106, and reactive species generated in the plasma diffuse outwards into the void.

25 In the seventh apparatus of the invention shown in Figure 13 of the accompanying drawings, a void 150 is depicted which has an agitator 152 such as a vibrator, shaker or the like associated with it. The void can contain a material such as seeds or other particulate material to be treated.

30 A plasma generator 154 is connected to the void 150 through a conduit 156 (such as a pipe). As such, the plasma generator 154 generates ionised gas plasma from the surrounding air and passes that plasma, or more likely reactive species formed from the action of the ionised gas plasma in the air, through conduit 156 into the void in order to treat the material.

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The apparatus further comprises a source 158 of plasma activated water (PAW). This can either be simple water, which is then passed into the void to be acted upon by reactive species there, or it can contain water that has already had such reactive species dissolved therein (for example, by the use of another source of ionised gas plasma).

An air sampling unit 160 is provided to determine the concentration of at least one reactive species within the void 150; the sampled air can be returned to the void 150 or vented elsewhere. The sampling unit 160 can then control a power supply unit (PSU) 112 for the plasma source 154 to control how much plasma and so how much of the reactive species is produced. This can form a system of closed-loop control.