

APPARATUS AND METHOD USING ULTRASOUNDS FOR GAS CONVERSION

INCORPORATION BY REFERENCE

- 5 The content of WO2013/093527 is hereby incorporated by reference. The content of Wang et al, J. Phys. Chem. Lett. 2010, 1, 48-53, is hereby incorporated herein by reference.

TECHNICAL FIELD

- 10 The present invention relates to the handling and treatment of greenhouse gases. In particular but not exclusively the invention relates to handling and treatment of greenhouse gases such as combustion gases emitted from an industrial source such as a coal, oil or gas-fired power station or from one or more other sources such as internal combustion engines. In certain aspects the invention also relates to treatment of liquids in storage
15 vessels.

BACKGROUND

- 20 It is understood that emissions of combustion gases from industrial plants such as coal, oil or gas-fired power stations and other sources including internal combustion engines are harmful to the environment. Emissions of carbon dioxide are of particular concern and there is substantial interest in reducing the amount of carbon dioxide emitted into the atmosphere.

- 25 One method of reducing emissions is to capture the carbon dioxide and store it until an economical treatment method is available for converting carbon dioxide to a less harmful or even beneficial form, such as to carbon and oxygen (O₂). However, storage of carbon dioxide is costly and merely postpones the problem of conversion of the gas.

- 30 It is an aim of the present invention to address disadvantages associated with the prior art.

SUMMARY OF THE INVENTION

Embodiments of the invention may be understood with reference to the appended claims.

- 35 Aspects of the present invention provide an apparatus and a method.

In an aspect of the invention for which protection is sought there is provided gas conversion apparatus for converting one or more reactant chemical species comprised in a first gas to one or more product chemical species, comprising:

means for introducing first gas into a liquid medium; and

5 an ultrasonic energy generator arranged to generate ultrasonic energy,

the apparatus being configured to launch ultrasonic energy generated by the ultrasonic energy generator into the liquid medium such that first gas is exposed to ultrasonic energy so as to convert one or more of the reactant chemical species to one or more product chemical species,

10 the apparatus being arranged to allow collection of one or more of the product chemical species,

wherein the apparatus further comprises a gas lift column through which liquid medium may be pumped by gas lift; and

15 wherein the means for introducing first gas into the liquid medium comprises means for introducing first gas into the column,

the apparatus being configured to launch ultrasonic energy generated by the ultrasonic energy generator into liquid medium in the column such that first gas passing through the column by gas lift is exposed to ultrasonic energy generated by the generator.

20 Embodiments of the present invention have the feature that first gas may be subject to ultrasonic energy resulting in the conversion of the first gas or one or more chemical species thereof to one or more other chemical species such as one or more other gases. The first gas may also be referred to herein as a process gas.

25 By launching the ultrasonic energy into a liquid medium into which first gas has been introduced, the first gas may be subjected to cavitation in collapsing bubbles, resulting in the conversion of the first gas from one chemical species, such as carbon dioxide, to one or more other chemical species, such as one or more hydrocarbons and/or optionally one or more further species. For example, in some embodiments the first gas may be or may
30 comprise carbon dioxide as reactant chemical species, carbon dioxide being converted to product chemical species methane and oxygen. Other conversion reactions may also be useful. For example in some embodiments carbon dioxide may be converted to a different hydrocarbon in addition or instead, such as ethane, propane, or any other suitable hydrocarbon or hydrocarbons. In some embodiments carbon dioxide may be converted to a
35 non-hydrocarbon material. In some embodiments, one or more compounds other than carbon dioxide may be converted to one or more other forms, whether elemental form,

compound form or any other form.

Furthermore, some embodiments of the present invention offer the opportunity to employ alternative energy sources such as renewable energy sources in the production of chemical compounds for use in industry, for example compounds for use as feedstock materials or as sources of chemical energy when reacted, for example when oxidised, optionally by burning in an oxygen-bearing atmosphere. Thus some embodiments of the present invention may be useful in providing means for storing energy generated by renewable energy sources such as solar, wind, wave and/or tidal energy. This renewable energy may be used for example to power a compressor for driving the ultrasonic energy generator, and/or to power a separator for separating chemical species following exposure of first gas to ultrasonic energy.

In some embodiments the first gas may comprise carbon dioxide that is converted to one or more hydrocarbons by exposure to the ultrasonic energy. The hydrocarbon(s) may subsequently be used as a feedstock material, or burned as a fuel when required. In some embodiments the one or more hydrocarbons may be converted to one or more further compounds such as one or more higher alkanes, one or more alkenes, alcohols, or any other suitable compound.

20

In some embodiments one or more catalyst materials may be used to promote conversion of one or more reactant chemical species to one or more product chemical species, such as copper, zinc oxide, aluminium oxide (alumina, Al_2O_3). In some embodiments one or more of these catalysts may be employed to promote synthesis of methanol. In some embodiments, carbon dioxide first gas may be converted to short chain olefins such as ethylene and propylene, either directly or via one or more intermediate compounds such as methanol.

It is to be understood that alkane hydrocarbons of short (1 - 4) C-chain lengths (methane, ethane, propane, butane) are gaseous at room temperature and pressure, and alkanes only become liquid at such temperatures and pressures at or above to C-5 (pentane). At or above C-16 they are typically solid under these conditions. Some embodiments of the present invention may generate C-n alkanes where n is greater than 1, optionally by use of a suitable catalyst. If one or more hydrocarbons in the form of liquids or solids are produced, a suitable means for separation of the hydrocarbon from the liquid medium or other gaseous or solid medium may be employed.

Advantageously, the ultrasonic generator may be configured to generate ultrasonic energy in response to a flow of a drive gas therethrough.

5 This has the advantage that first gas may be subject to ultrasonic energy in a highly efficient manner. It is to be understood that relatively high intensity ultrasonic energy may be generated by means of flow of drive gas through a suitable generator, which may for example comprise a whistle device. The amount of energy required to be input to the generator in order to generate the relatively high intensity ultrasonic energy may be less than that which would be required if other ultrasonic energy generation technologies were
10 employed such as electrical generation technologies such as ultrasonic generation technologies based on piezoelectric device technologies.

The apparatus may be configured to cause a flow of first gas in carrier liquid medium through a conduit, and to expose the first gas to ultrasonic energy in the conduit. The
15 conduit may be of any required orientation in some embodiments, such as substantially horizontal. The apparatus may be configured wherein the first gas is exposed to ultrasonic radiation as it travels in a substantially horizontal direction through the conduit. In the case of a conduit mounted in a substantially vertical direction, the first gas may be caused to travel upwardly or downwardly as required. In some embodiments a conduit having an
20 orientation that is neither horizontal nor vertical may be employed. Other arrangements may be useful in some embodiments.

Advantageously, the ultrasonic energy generator may comprise a whistle device, the whistle device being arranged to generate the ultrasonic energy when drive gas is driven through
25 the device.

The apparatus may be arranged to feed the drive gas into the liquid medium after driving the gas through the ultrasonic energy generator.

30 The apparatus may be arranged wherein the first gas provides or constitutes the drive gas.

That is, the first gas may be caused to pass through the ultrasonic energy generator to generate ultrasonic energy, thereby providing or constituting the drive gas, subsequently passing into the liquid medium where the gas is subjected to ultrasonic energy generated by
35 the ultrasonic energy generator.

In some alternative embodiments, the drive gas and first gas may be different or may be from different sources. For example, in some embodiments the drive gas may be supplied in a closed loop arrangement whereby drive gas that has been forced through the whistle device may be recompressed and forced through the whistle device again, in a substantially continuous loop.

The drive gas may be any suitable gas such as air, nitrogen, carbon dioxide, argon or any other suitable gas or mixture of gases.

The apparatus may comprise a microbubble generator, the apparatus being configured to cause microbubbles of first gas to be generated in the liquid medium and to be subject to irradiation by ultrasonic energy generated by the ultrasonic energy generator.

This feature has the advantage that cavitation of microbubbles of the first gas may be caused. It has been found that if the first gas is in the form of microbubbles containing carbon dioxide, the carbon dioxide may be converted to a hydrocarbon and oxygen as a consequence of irradiation by ultrasonic energy in a highly effective manner.

The apparatus may be operable to pass gas that has been exposed to ultrasonic energy through a separator such as a gas separator to separate gas molecules according to chemical species. The separator may be any suitable separator such as a hollow fibre membrane separator.

It is to be understood that first gas that has been exposed to ultrasonic energy in the manner described above may no longer be of the same chemical species or composition as the first gas prior to exposure to ultrasonic energy. However it is to be understood that gas introduced as first gas and one or more product chemical species may subsequently be passed through a gas separator to separate gas molecules according to chemical species. In some embodiments, gas that has been exposed to ultrasonic energy generated by the ultrasonic energy generator is introduced to a separator for separation of product chemical species therefrom. In some embodiments, gas and liquid that has been exposed to ultrasonic energy is introduced to a separator. The separator may be configured to separate liquid chemical species such as one or more hydrocarbon species from other liquid, optionally in addition to separate gas from liquid. Thus, if in some embodiments the product chemical species include a gas such as molecular oxygen and a liquid, such as a liquid hydrocarbon, for example ethanol or any other liquid hydrocarbon, the separator may

separate the molecular oxygen and the product liquid from the liquid medium of the apparatus, which may for example comprise water.

5 The apparatus may be configured to separate hydrocarbon gases from one or more other gases.

10 The apparatus may be operable to separate product chemical species such as hydrocarbon chemical species such as hydrocarbon gases from chemical species of the first gas. Thus the apparatus may separate product chemical species such as hydrocarbon gases from one or more chemical species comprised by the first gas prior to irradiation with ultrasonic energy, such as one or more reactant chemical species, which have not reacted to form product chemical species.

15 The apparatus may be operable to return separated chemical species found in the first gas to the liquid medium for further exposure to ultrasonic energy. Thus, one or more chemical species comprised by the first gas prior to irradiation with ultrasonic energy, such as carbon dioxide, may be subject again to irradiation with ultrasonic energy.

20 In some embodiments in which the ultrasonic energy generator is powered by a drive gas. The generator may comprise one or more whistle devices in some embodiments. The drive gas may be of substantially the same chemical composition as the first gas. The drive gas may provide the first gas for the apparatus. Thus in some embodiments at least a portion of the process gas that drives the ultrasonic energy generator may be introduced into the column. This may provide at least in part the means for causing pumping of liquid medium in the column by gas lift. Optionally, introduction of process gas into the column may provide substantially all of the gas lift that provides pumping of liquid through the column. In some embodiments process gas may be introduced into the column for exposure to ultrasonic energy

30 The column may be immersed in the liquid medium, optionally in a tank in which the liquid medium is contained. Alternatively the column may be provided externally of the tank.

35 The present applicant has found that the column of a gas lift pump device provides a beneficial environment in which to subject process gas to ultrasonic energy. This is at least in part because at least some of the process gas introduced into the liquid medium in the column may be confined to the column during exposure to ultrasonic energy. The process

gas may thereby be exposed to ultrasonic energy in a more controlled manner than if the gas is introduced into a tank unconstrained. It is to be understood that an intensity of ultrasonic energy to which process gas is subject may depend at least in part on a distance between the source of ultrasonic energy provided by the generator and the process gas as it
5 passes through or past the generator, for example the distance between the source of ultrasonic energy provided by the generator and a bubble of process gas in the liquid medium. The greater the distance, the lower the intensity of the ultrasonic energy in some embodiments. Accordingly it is in general advantageous to expose the process gas to ultrasonic energy as close to the source of ultrasonic energy as possible. The presence of a
10 conduit through which process gas passes and in which the process gas is exposed to ultrasonic energy assists in promoting exposure of process gas to ultrasonic energy close to the source.

The apparatus may be configured to feed drive gas into liquid medium in the column of the
15 gas lift device such that the drive gas is exposed to ultrasonic energy in the column.

In addition or instead, the apparatus may be configured to cause microbubbles generated by the microbubble generator to be subject to irradiation by ultrasonic energy generated by the ultrasonic energy generator.
20

The apparatus may be arranged wherein the process gas comprises carbon dioxide.

The apparatus may be arranged wherein the process gas comprises at least about 50% carbon dioxide by volume.
25

The apparatus may be arranged wherein the process gas consists essentially of carbon dioxide.

The apparatus may be configured to separate hydrocarbon gas from gas that has passed
30 through the column. In some embodiments the apparatus may be configured to separate methane from gas that has passed through the column.

In another aspect of the invention for which protection is sought there is provided apparatus according to the previous aspect of the present invention or any embodiment thereof
35 installed in a liquid tank, optionally a liquid holding tank.

Optionally, the tank contains liquid.

Optionally, the liquid is provided with particles of a catalyst material suspended, dissolved or otherwise dispersed therein.

5

The catalyst particles may comprise iron, optionally iron oxide, optionally a hematite-bearing compound, optionally wherein the catalyst particles consist substantially of hematite.

10 In an aspect of the invention for which protection is sought there is provided apparatus according to any preceding aspect coupled to a power generating station or a power generating station in combination with apparatus according to any preceding claim, arranged wherein combustion gases generated by the station provide at least a portion of, optionally the whole of, the first gas of the apparatus.

15 In an aspect of the invention for which protection is sought there is provided a fuel burning engine in combination with apparatus according to any preceding aspect arranged wherein combustion gases generated by the engine provide at least a portion of, optionally the whole of, the first gas of the apparatus.

20 In one aspect of the invention for which protection is sought there is provided apparatus according to a previous aspect of the invention or any embodiment thereof installed in-line in a processing facility, optionally a liquid processing facility, optionally a waste liquid processing facility. The apparatus may be configured to treat liquid such as waste liquid with a process gas and ultrasonic energy, optionally to treat wastewater, optionally sewage. The
25 apparatus may be configured to destroy one or more biological species such as organisms such as bacteria or virus organisms or other biological species in order to kill the one or more biological species. In some embodiments the apparatus may be configured to convert one or more chemical species in the liquid to one or more other chemical species.

30 In a further aspect of the invention for which protection is sought there is provided a method of converting one or more reactant chemical species comprised in a first gas to one or more product chemical species comprising:

introducing first gas into a liquid medium; and

generating ultrasonic energy by means of an ultrasonic energy generator,

35 the method comprising launching ultrasonic energy generated by the ultrasonic energy generator into the liquid medium such that first gas is exposed to ultrasonic energy

so as to convert one or more of the reactant chemical species to one or more product chemical species,

whereby introducing first gas into a liquid medium comprises introducing first gas into a column of a gas lift pump apparatus and causing pumping of liquid medium through the column by gas lift, and whereby launching ultrasonic energy generated by the generator into the liquid medium comprises launching ultrasonic energy into liquid medium in the column whereby first gas passing through the column is exposed to ultrasonic energy, the method further comprising collecting one or more product chemical species.

10 The ultrasonic energy may be generated in response to a flow of a drive gas through the generator.

This feature has the advantage that ultrasonic energy may be generated in a relatively energy efficient manner compared with means of generating ultrasonic energy electrically, such as by means of a piezo-electric generator.

The method may further comprise collecting process gas that has been exposed to ultrasonic energy.

20 The method may comprise generating ultrasonic energy by means of a whistle device of the generator by driving drive gas through the device.

The method may comprise feeding drive gas into the liquid medium after passing the gas through the whistle device.

25

Optionally, the process gas provides or constitutes the drive gas.

The method may comprise causing microbubbles to be generated in the liquid medium and to be subjected to irradiation by ultrasonic energy generated by the ultrasonic energy generator.

30

This feature has the advantage that cavitation of microbubbles of the process gas may be caused. It has been found that if the process gas comprises carbon dioxide, the carbon dioxide may be converted to a hydrocarbon and oxygen in the process of irradiation by ultrasonic energy.

35

The method may comprise causing gas that has been subjected to ultrasonic energy to be separated according to chemical species by means of a gas separator.

5 Optionally, causing gas to be separated comprises separating hydrocarbon gases from one or more other gases.

10 Optionally, causing gas to be separated comprises separating hydrocarbon gases from one or more gases comprised by process gas. For example, causing gas to be separated may comprise separating hydrocarbon gases from gases that are not hydrocarbon gases. The non-hydrocarbon gases may include one or more further reaction products from the conversion of at least some process gas such as one or more chemical compounds or species comprised by the process gas, to hydrocarbon. In addition or instead the non-hydrocarbon gases may comprise one or more chemical compounds or species that were originally comprised by the process gas and which are substantially unchanged.

15 The method may comprise returning separated one or more chemical species originally comprised by the process gas to the liquid medium and subjecting the separated chemical species to ultrasonic energy in the liquid medium. Alternatively or in addition the method may comprise returning any gases and/or liquids that are not required to be extracted from the apparatus to the liquid medium, so that they can be exposed to ultrasonic energy in the liquid medium.

The process gas may comprise carbon dioxide.

25 The process gas may comprise at least about 10% carbon dioxide by volume.

Optionally the process gas may comprise at least about 14% carbon dioxide by volume, further optionally at least about 20%, still further optionally at least about 40%, still further optionally at least about 50% carbon dioxide by volume.

30 The process gas may consist essentially of carbon dioxide.

The method may comprise separating hydrocarbon gas from other gas that has passed through the column. Optionally, the method comprises separating methane gas from other gas that has passed through the column.

35

The method may comprise separating one or more other chemical species such as oxygen gas from other gas and liquid that has passed through the column.

5 The method may comprise drawing liquid medium into the column from a liquid storage tank.

The liquid may be provided with particles of a catalyst material suspended, dissolved or otherwise dispersed therein.

10 Optionally the method comprises providing particles of catalyst material suspended, dissolved or otherwise dispersed in the liquid, wherein the catalyst particles comprise iron, optionally iron oxide, optionally a hematite-bearing compound, optionally wherein the catalyst particles consist substantially of hematite.

15 In some embodiments, the catalyst material may comprise CdSe. The apparatus may comprise means for exposing the catalyst material to visible light, optionally light with a wavelength in excess of about 420nm, to promote conversion of carbon dioxide to one or more hydrocarbon compounds. The CdSe may act as a photocatalyst to promote conversion of CO₂. The CdSe may act in combination with cavitation in collapsing bubbles to
20 promote conversion of carbon dioxide to one or more hydrocarbons. The catalyst material may in some embodiments be in the form of a CdSe/Pt/TiO₂ heterostructure catalyst, such as that described in Wang et al, J. Phys. Chem. Lett. 2010, 1, 48-53, the content of which is hereby incorporated herein by reference. Other catalyst materials may also be useful in addition or instead.

25

The apparatus may comprise a whistle device operable to generate the ultrasonic energy by passage of gas therethrough. The apparatus may be arranged to pass carbon dioxide through the whistle device to generate the ultrasonic energy.

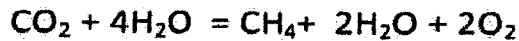
30 The gas may be released into the liquid medium following passage through the whistle device. Alternatively the gas may be recirculated through the whistle device. Still further alternatively the gas may be vented to the atmosphere. Optionally the gas may be stored in storage means such as a storage vessel.

35 The apparatus may be arranged to generate microbubbles of carbon dioxide in the liquid medium by means of a microbubble generator, and to expose the microbubbles to ultrasonic

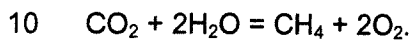
energy. Exposure of the microbubbles to ultrasonic energy may be arranged to result in the conversion of carbon dioxide to at least methane and oxygen.

The reaction may be represented by the following equation:

5



or, alternatively,



Experiments demonstrate that exposure of the microbubbles containing carbon dioxide to ultrasonic energy under suitable conditions may result in the conversion of carbon dioxide to methane and oxygen.

15

The microbubbles may advantageously be formed to have a diameter in the range of about 50 microns or less. The microbubbles may be formed to have a diameter in the range of about 1 micrometer to about 50 micrometers.

20

The gas may be contained in an ullage space of a liquid tank in some embodiments, at least initially following passage through the column. Alternatively or in addition the gas may be fed directly from the column to a separate storage or processing volume, optionally through a separator. In some embodiments the column may be coupled to or extend to form a conduit through which gas passing along the conduit is conveyed to a storage or processing volume.

25

Certain constructions of bubble generator *per se* for use in embodiments of gas conversion apparatus of any of the above-defined aspects of the invention, as well as in other treatment apparatuses such as various gas lift pump apparatuses, e.g. for circulation of liquid in a liquid storage or ballast tank of a vessel, will now be described.

30

A bubble generator for generating bubbles, preferably microbubbles, of a gas in a liquid medium in a treatment apparatus, may comprise:

35

a bubble forming portion for location in the liquid medium and configured for forming bubbles of the gas therein;

an input portion for delivering an input flow of the gas to the bubble forming portion;
and

an output portion for emitting an output flow of the formed gas bubbles from the bubble forming portion;

5 wherein the bubble forming portion comprises one or more vortex-inducing elements configured for inducing a vortex in a flow of gas therethrough.

A bubble generator for generating bubbles, preferably microbubbles, of a gas in a liquid medium in a treatment apparatus, may comprise:

10 a vortex-inducing portion;

an input portion for delivering an input flow of the gas to the vortex-inducing portion;
and

an output portion for emitting an output flow of gas bubbles;

15 wherein the vortex-inducing portion comprises one or more vortex-inducing elements configured for inducing a vortex in a flow of gas therethrough.

Optionally, the one or more vortex-inducing elements may comprise one or more, preferably a plurality of, vortex-inducing blade elements located within a gas flowpath between the input portion and the outlet portion. The or each blade element preferably includes an
20 impingement face and the impingement face of the or each blade element may preferably be oriented so as to be non-parallel to a direction of input gas flow in the input portion. In this manner the input flow of gas impinging on the impingement face(s) of the blade element(s) is forced to change direction as it flows onto and past the blade element(s), thereby creating a swirling or vortex effect in the gas flowpath as it flows from the input
25 portion to the output portion.

In some embodiments of the above-defined bubble generator a plurality of blade elements may be provided and they may preferably be equi-spaced relative to each other, especially in a circular arrangement, around a longitudinal axis normal to a direction of input gas flow
30 in the input portion.

Optionally, in the above-defined bubble generator the vortex-inducing portion may comprises a dome member for channelling gas flowing into the vortex-inducing portion towards the vortex-inducing element(s). In a preferred form the dome member may have a
35 radiused internal shape configured for reducing the generation of eddy currents as gas flows in the gas flowpath therewithin.

Optionally, there may be further provided therein an accelerator portion downstream of the one or more vortex-inducing elements for accelerating the output flow of the gas, especially in a direction towards an outlet of the output portion where the flow of gas enters the liquid medium in the apparatus. The accelerator portion may for example define a portion of the gas flowpath which comprises a conical passageway having an internal shape which tapers radially inwardly towards its outlet. In this manner the vortex or swirling flow of the gas may be enhanced, thereby improving the degree of cavitation of the bubbles of the gas in the liquid medium, especially - in preferred practical embodiments - upon their exposure to ultrasonic energy provided by the one or more ultrasonic energy generator(s) which may also be present.

In some practical examples of the above-defined bubble generator the input portion for delivering an input flow of the gas to the vortex-inducing portion may comprise a conduit mounted in the apparatus via a proximal end thereof, e.g. in the manner of a cantilevered-type fixing, and carrying the vortex-inducing portion at a distal end thereof. The conduit may support the vortex-inducing portion in a liquid medium away from a sidewall of the apparatus such as a sidewall of a storage tank, pipeline, or column of a gas lift pump apparatus, optionally within the column of the gas lift pump apparatus. To assist the supporting of the conduit, especially given that flow of liquid medium in or through the apparatus may exert relatively high forces on the exterior of the conduit, the mounting of the conduit in the apparatus may be enhanced by one or more support members or webs, e.g. one or more strengthening webs, brackets, buttresses or like elements or members provided between the conduit and its anchoring location on or in the apparatus. In some embodiments a direction of gas flow in the conduit and a direction of flow of liquid past the input portion may be oriented substantially perpendicular to one another.

In preferred embodiments of the above-defined bubble generator *per se* it is preferably a generator of microbubbles, which preferably means it is constructed and arranged to generate gas bubbles of a diameter in the range of about 50 microns or less. The bubble generator may be configured to generate bubbles of a diameter in the range from about 1 micron to about 50 microns, optionally in the range from about 10 microns to around 50 microns, further optionally in the range from about 20 microns to about 50 microns.

Further advantageous features of examples of a bubble generator will be described further below in connection with certain specifically described embodiments of the invention.

Examples of the above-defined bubble generator *per se* may be put to various uses in a variety of treatment apparatuses. In some preferred applications the treatment apparatus may be a gas conversion apparatus and the gas is a process gas for conversion to one or more other gases by the apparatus. Such gas conversion apparatus may be a gas conversion apparatus according to various embodiments of the present invention in its various aspects as defined hereinabove.

However in other applications the treatment apparatus may be a gas lift pump apparatus, for example a gas lift pump apparatus for use in, or when used in, a liquid storage or ballast tank of a vessel such as a ship or other sea-going or waterborne craft, e.g. for circulation of water or other liquid therein in a process for the killing of bacterial or non-bacterial aquatic nuisance species (ANS).

The bubble generator may be arranged to cause bubbles to be formed in liquid medium as it passes through the column. Alternatively the bubble generator may be arranged to cause bubbles to be formed in a liquid medium which is then supplied to the column.

The gas lift pump apparatus may be comprised by, or constitute at least a portion of, a ballast water treatment apparatus. The apparatus may be provided onboard a vessel. The apparatus may be configured to treat ballast water of one or more ballast tanks. The apparatus may be configured to generate microbubbles in the ballast water and, optionally, expose the microbubbles in the ballast water to ultrasonic energy. The microbubbles may comprise ships flue gas, optionally a combustion gas, and comprise carbon dioxide. The gas employed by the microbubble generator to generate microbubbles may have an oxygen concentration of less than 2%, optionally less than 1.5%, further optionally less than 1%. The oxygen concentration may be greater than 0.1%. the oxygen concentration may be around 0.5% or around 0.6% in some embodiments.

In preferred embodiments of the above-defined gas lift pump apparatus the bubble forming portion of the bubble generator may advantageously be positioned substantially coaxially within the column.

Embodiments of the above defined gas lift apparatus may take a wide variety of forms. Some particular useful forms are those as disclosed and illustrated in our co-pending International Patent Application WO2013/093527, the entire contents of the specification

and drawings of which published application are hereby implicitly incorporated herein by reference thereto.

Within the scope of this application it is expressly envisaged that the various aspects, 5
embodiments, examples and alternatives set out in the preceding paragraphs, in the claims and/or in the following description and drawings, and in particular the individual features thereof, may be taken independently or in any combination. Features described in connection with one embodiment are applicable to all embodiments, unless expressly stated otherwise or such features are incompatible.

10

BRIEF DESCRIPTION OF THE DRAWINGS

Various embodiments of the invention in its various aspects will now be described, by way of example only, with reference to the accompanying drawings, in which:

15

FIGURE 1 is a schematic illustration of an apparatus according to an embodiment of the present invention;

FIGURE 2 is a schematic illustration of a microbubble generator according to an 20
embodiment of the present invention in (a) cross-sectional view along a substantially horizontal axis and (b) as viewed down a column of the apparatus;

FIGURE 3 is a schematic illustration of an array of ultrasonic generators employed in the apparatus of FIG. 1 in (a) side view and (b) as viewed along a direction of flow of fluid along 25
a column of the apparatus;

FIGURE 4 shows (a) a side view of a whistle device suitable for use in apparatus according to an embodiment of the invention and (b) a cross-sectional view along the same viewing direction as in (a);

30

FIGURE 5 shows a converter portion according to a further embodiment of the invention, in (a) sectional view and (b) plan view;

FIGURE 6 shows a microbubble generator of the embodiment of FIG. 5;

35

FIGURE 7 shows an ultrasonic generator of the embodiment of FIG. 5;

FIGURE 8 is an enlarged view of a nozzle member of the embodiment of FIG. 7 in (a) side view, (b) a view along direction V1 of (a), and (c) a section view along line B-B of (b);

- 5 FIGURE 9 is a schematic illustration of a boiler exhaust gas processing system according to an embodiment of the present invention arranged to process power station boiler exhaust gases; and

10 FIGURE 10 is a schematic illustration of a further embodiment of a gas lift pump apparatus in which is provided a microbubble generator of the embodiment of Figure 6.

DETAILED DESCRIPTION OF EMBODIMENTS

15 FIG. 1 is a schematic illustration of a gas conversion apparatus 100 according to an embodiment of the present invention. The apparatus 100 of FIG. 1 is configured to convert a carbon dioxide process (or 'first') gas into methane gas and oxygen gas.

20 The apparatus 100 has a compressor 105 for compressing carbon dioxide process gas supplied to the apparatus 100 from an external source. Process gas that has been compressed by the compressor 105 is supplied to a converter portion 115 of the apparatus 100 that is located within a liquid holding tank 110. The tank 110 contains a sufficient amount of water to substantially immerse the converter portion 115. Liquids other than water may also be useful. The liquid may contain one or more additives in order to promote gas conversion, inhibit corrosion and/or inhibit bacterial growth.

25 The converter portion 115 has a microbubble generator portion 120 connected to an upright conduit or column 125. The microbubble generator portion 120 is configured to receive carbon dioxide process gas at a gas inlet 130G and liquid from the tank 110 at a liquid inlet 120L. As described in more detail below, the microbubble generator portion 120 generates
30 microbubbles and allows them to rise upwardly into the column 125.

35 The column portion 125 is provided with an ultrasonic generator portion 140 in a lower part thereof. The ultrasonic generator portion 140 has an array of whistle devices 150 that generate ultrasonic energy when pressurised gas is forced through them. The ultrasonic energy causes cavitation of microbubbles rising through the column portion 125, resulting in conversion of at least some carbon dioxide to methane and oxygen.

Gas in the column rising through the ultrasonic generator portion 140 is exhausted from the column 140 at a free end 140E thereof, and rises to a headspace 110H of the tank 110 above a level of liquid 110LL in the tank 110. A mixture of methane, oxygen and
5 unconverted carbon dioxide therefore collects in the headspace 110H. In some embodiments, one or more other hydrocarbons may collect in the headspace 110H in addition or instead.

The tank 110 has first and second gas outlet ports 110G1, 110G2 that connect to the tank
10 110 through an upper wall 110U of the tank 110 at a level above a maximum expected level of liquid in the tank 110 in use.

First gas outlet port 110G1 is coupled to a gas separator portion 190 whilst second gas outlet port 110G2 is coupled to an inlet of compressor 105. Gas passing out from the tank
15 110 via the second gas outlet port 110G2 is therefore recirculated through the converter portion 115. This feature enables a concentration of carbon dioxide in the headspace 110H to be reduced, thereby reducing the amount of gas from the headspace 110H that must be processed by the separator 190 in order to obtain a given amount of methane. The relative amounts of gas that flow from the headspace 110H to the compressor 105 and separator
20 190 may be controlled in order to control the concentration of carbon dioxide and one or more other gases in the headspace 110H.

Microbubble generator

25 The microbubble generator portion 120 of the apparatus 100 of FIG. 1 is a cyclone (or 'cyclonic') microbubble generator 120. It is arranged to induce swirl in liquid passing into a bubble shear portion 130 of the generator 120. Swirl is induced in order to promote formation of microbubbles in liquid passing through the bubble shear portion 130.

30 The microbubble generator portion 120 is shown in further detail in FIG. 2. FIG. 2(a) is a cross-sectional view of the generator portion 120 as viewed normal to a cylinder axis A of the microbubble generator portion 120. FIG. 2(b) is a view along the cylinder axis A as viewed along the direction of arrow B.

35 The generator portion 120 is provided with a liquid inlet 120L for allowing liquid in the tank 110 to flow into the converter portion 115. As can be seen from FIG. 2(a), liquid entering the

generator portion 120 through inlet 120L does so in a direction substantially tangential to an inner wall of the generator portion 120. This feature promotes swirl flow of liquid through the generator portion 120.

- 5 Liquid flowing through the microbubble generator portion 120 is forced to flow through a choke or Venturi portion 121. The Venturi portion 121 has a converging portion C being a portion over which a cross-sectional area of the generator portion 140 decreases with distance from the liquid inlet 120L, a throat portion T of substantially constant cross-sectional area immediately downstream of the converging portion C, and a diverging portion
10 D of increasing cross-sectional area immediately downstream of the converging portion C.

Gas inlets 123 are provided in the throat portion T of the Venturi portion 121 and are arranged to allow process gas to be injected into liquid passing through the throat portion T. The inlets 123 are provided at spaced apart locations around a circumference of the throat
15 portion T, neighbouring inlets 123 being substantially equidistant from one another. In the embodiment shown twelve inlets 123 are provided. Other numbers of inlets 123 and other arrangements of inlets 123 may also be useful.

In use, liquid passing through the Venturi portion 121 is arranged to cause shear of gas
20 bubbles forming in liquid passing through the generator portion 120. The bubbles form as gas is injected through the inlets 123. Shear of the bubbles causes a reduction in size of the bubbles compared with an equilibrium size of gas bubbles formed in stagnant liquid. A microbubble generator portion 120 of the type shown in FIG. 2 has been found to be highly effective in producing a stable flow of microbubbles in the converter portion 115.

25

Ultrasonic energy generator

The converter portion 115 is configured in use to deliver a flow of liquid with microbubbles of process gas entrained therein from the microbubble generator portion 120 to the ultrasonic
30 generator portion 140.

The ultrasonic generator portion 140 is shown in more detail in FIG. 3. FIG. 3(a) shows the ultrasonic generator portion 140 in side view whilst FIG. 3(b) shows the ultrasonic generator portion 140 as viewed along axis A from above. The ultrasonic generator portion 140
35 includes two linear arrays of whistle devices 141AA, 141AB, respectively. Each array has four pairs of whistle devices 141, one device of each pair being mounted above a

substantially horizontal gas feed line GA, GB whilst the other is mounted below it. Gas flowing along each feed line GA, GB is forced to flow through the whistle devices 141, the gas being exhausted to liquid within the column 125.

5 With reference to FIG. 4, each whistle device 141 has a portion in the form of a chamber 141C that also provides a whistle body. A nozzle member 141N and a receptor member 141R are coupled to the whistle body 141C. The whistle body 141C is arranged to support the receptor member 141R in a substantially fixed spaced apart and substantially coaxial relationship with the nozzle member 141N. The nozzle member 141N is shown coupled to a
10 gas supply head 141GH that forms part of the respective gas feed line GA, GB.

The nozzle member 141N is arranged to direct a flow of process gas through an opening 141RO of the receptor member 141R into an open cavity 141RC defined by the receptor member 141R. The receptor member 141R is arranged to be screwed into a tapped
15 aperture in the whistle body 141C thereby to couple the receptor member 141R to the whistle body 141C. The receptor member 141R is thus arranged to close one end of the chamber 141C. Flow of gas from the nozzle member 141N to the cavity 141RC results in the generation of ultrasonic energy in the manner of a Hartmann-type whistle device. Other whistle devices may also be useful.

20

A distance between the opening 141RO of the receptor member 141R and nozzle 141N may be adjusted by means of the screw thread by rotation of the receptor member 141R.

In some arrangements a depth D of the cavity 141RC defined by the receptor member 141R
25 may be adjusted. In some arrangements the adjustment is by means of a further screw adjustment, for example by adjusting a position of a screw defining at one end an interior basal surface of the cavity 141RC. This feature has the advantage that an amount of sound energy produced by the device 141 may be optimised. A frequency of sound energy (i.e. a frequency of sound waves generated by the device 141) may be adjusted by adjustment of
30 the depth D in some embodiments.

The whistle body 141C provides a substantially tubular sleeve coaxial with the nozzle member 141N and receptor member 141R, the sleeve having a pair of apertures 141A formed therein to accommodate flow of gas from the nozzle member 141N out from the
35 body 141C and into liquid in the column 125. The whistle devices 141 thereby act as gas delivery devices, delivering a flow of gas into liquid in the column. The gas rises in the liquid,

causing pumping of liquid through the converter portion 115 by gas lift.

The gas used to drive the ultrasonic generator may be referred to as a drive gas. The drive gas may be of the same type and optionally from the same source as the process gas.

5 Alternatively the drive gas may be a different gas.

In some embodiments, the process gas may be the product of a combustion reaction. The process gas may comprise around 13-14% carbon dioxide or other amount depending on the combustion conditions, the balance being nitrogen, sulphur oxides (SO_x), and nitrous
10 oxides (NO_x). For example the process gas may be delivered from a coal, oil or gas-fired powerstation. In some embodiments the process gas may be ship's flue gas. Other sources of gas containing carbon dioxide are also useful such as exhaust gas from an internal combustion engine.

15 In some alternative embodiments, the apparatus is arranged such that drive gas is not exhausted into liquid in the column. In some embodiments the drive gas may be repressurised and recirculated through the whistle devices 141.

Conversion reaction

20

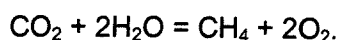
It is understood that exposure of microbubbles of carbon dioxide to ultrasonic energy in the column 125 of the converter portion 110 causes the bubbles to collapse, causing rapid and extreme heating of the gas and the generation of free radicals. This is believed to result in the conversion of carbon dioxide to methane and oxygen by the equation below.

25

The reaction may be represented by the following equation:



30 or, alternatively,



In some embodiments, a catalyst may be provided for catalysing the reaction. The catalyst
35 may be provided in particulate form, particles of catalyst being suspended in liquid medium in the tank 110. In some embodiments, the catalyst particles contain iron or an oxide

thereof. Particles of hematite or a hematite-bearing particle are useful in some embodiments.

5 Embodiments of the present invention have the feature that one or more gases that may be harmful to the environment such as carbon dioxide may be converted to useful forms in a relatively straightforward manner and by means of an energy efficient process. The generation of ultrasonic energy by means of a flow of pressurised gas enables a relatively robust and resilient apparatus to be provided compared with other methods of generating ultrasonic energy, such as electrical transducer devices.

10 Embodiments of the present invention are useful in converting carbon dioxide present in combustion gases emitted by power stations to be converted into oxygen and methane gas. Oxygen gas generated in some embodiments of the present invention may be released to the environment or stored in oxygen gas containers and used or sold, for example as an industrial process gas.

The methane gas generated may be used as a fuel, or for any other suitable purpose such as in processing of chemicals.

20 It is to be understood that in some embodiments, recirculation of gas that has passed through the column 125 is not performed. In some embodiments, the gas is supplied to the separator 190 without recirculation. In some embodiments gas that has passed along the column 125 is not delivered to a separator 190. In some embodiments the gas is stored in a storage tank.

25 It is to be understood that gas conversion apparatus according to some embodiments of the present invention may be operated by means of electrical energy generated by a renewable energy source such as solar energy. It is to be understood that in some embodiments, process gas may be supplied to the apparatus at a pressure sufficiently high to enable whistle devices of the ultrasonic energy generator to be operated without a requirement to compress the process gas, such that compressor 105 is not required. Furthermore, the process gas may be supplied at a pressure sufficiently high to enable powering of a compressor for compressing gas undergoing recirculation through the column 125 after being drawn from the head space 110H, such that little or substantially no additional power is required to operate the compressor 105.

In some embodiments, gas collecting in the head space 110H, being a mixture of methane and oxygen at least, in some embodiments, may be in a form that may be used as a fuel or in an industrial process without a requirement to separate methane and oxygen. In embodiments in which residual carbon dioxide process gas is present in the head space
5 110H, the concentration of carbon dioxide may be reduced by recirculation of gas through the compressor 105 until the concentration is sufficiently low that the gas is useful as a fuel or in a particular industrial process. Other arrangements may also be useful.

In some alternative embodiments of the present invention, a different microbubble generator
10 and/or a different ultrasonic energy generator may be employed.

One alternative embodiment of the converter portion is shown at 215 in FIG. 5. The converter portion 215 of FIG. 5 has a different microbubble generator 220 and a different ultrasonic energy generator 240. Like features of the embodiment of FIG. 5 to those of the
15 embodiment of FIG. 1 are shown with like reference numerals incremented by 100.

FIG. 5 shows the converter portion 215 as viewed at section A-A of FIG. 5(b). FIG. 5(b) shows the converter portion 215 in plan view. The converter portion 215 has a column 225 that has at its base a liquid inlet 220L arranged to allow liquid to be drawn or pumped into
20 the column from the lower end thereof.

The embodiment of FIG. 5(a) is substantially to scale, with length L1 being around 160mm and length L2 being around 1100mm. Other dimensions may also be useful.

25 The microbubble generator 220 is provided above the inlet 220L and comprises a flange 220F1 arranged to couple the generator 220 to a corresponding flange 225F1 of the column 225. It is to be understood that the column 225 may be disposed in any desired orientation. In the present embodiment the column 225 is disposed in a substantially upright, vertical direction with a cylinder axis A of the column 225 substantially vertical. In the embodiment of
30 FIG. 5 the flange 220F1 of the microbubble generator 220 lies in a substantially vertical plane.

As shown in FIG. 6(a), the microbubble generator 220 has a gas conduit 230GB that passes through and is fixedly coupled to the flange 220F1. The conduit 230GB extends from the
35 flange 220F1 substantially normal to the flange 220F1 and coaxial therewith, and defines a boom-like structure for supporting a gas bubbler device 221 at a free end of the boom. A

pair of upstanding web portions 230W are attached to the flange 220F1 at one end, and run along and are coupled to the conduit 230GB along a substantial portion of a length of the conduit 230GB. The web portions 230W are disposed directly above and below the conduit 230GB, and serve to stiffen and strengthen the conduit 230GB. It is to be understood that
5 flow of liquid past the conduit 230GB within the column 225 may exert a not insubstantial force on the conduit 230GB. The presence of the web portions 230W therefore serves at least in part to reduce bending of the conduit 230GB. The web portions 230W are arranged to be substantially parallel to flow of liquid along a direction parallel to cylinder axis A of the column 225.

10 The bubbler device 221 has a housing 221H defining a downward-opening cavity in which is provided a hollow dome member 221D being a dome-shaped or cup-shaped member having a radiused internal shapeform. The dome member 221D is disposed above a flow of process gas into the bubbler device 221 and is arranged to assist in channeling gas that
15 flows into the bubbler device 221 downwardly towards insert member 221I as described below. The radiused internal shapeform of the dome member 221D serves to reduce eddy current generation in the housing 221H when process gas flows into the dome member 221D.

20 Process gas entering the bubbler 221 is caused to flow downwardly through the substantially cylindrical, hollow insert member 221I that is arranged to enjoy a sliding fit within the housing 221H of the bubbler 221, being introduced from below (with respect to the illustrated orientation) during assembly. The insert member 221I is provided with five swirl or vortex-inducing upstanding blade elements 221IB equally spaced around an upper
25 peripheral rim thereof. Other numbers of blade elements 221IB may also be useful. The blade elements 221IB are aligned with a longitudinal cylinder axis of the conduit 230GB such that their impingement faces are positioned directly in a flowpath of process gas passing from the conduit 230GB into the housing 221H. The blade elements 221IB are positioned in a circular symmetrical arrangement around a longitudinal axis normal to the
30 direction of gas flow of the process gas passing from the conduit 230GB into the housing 221H. Process gas entering the bubbler 221 therefore impinges directly on the faces of the blade elements 221IB which causes the process gas to begin to swirl within the bubbler 221. That is, the process gas assumes a vortex-like flowpath. The process gas is forced to flow downwardly through a fluid passage defined by the insert member 221I. The passage is in
35 the form of a cone, being tapered inwardly such that the passage narrows from an upper to a lower end thereof. Consequently, a velocity of process gas flowing downwardly and away

from the blade elements 221IB increases as a function of distance from the blade elements 221B.

At the lower end of the insert member 221I a cylindrical aperture cap member 221AP is provided that screws onto the free end of the housing 221H, retaining the insert member 221I within the housing 221H. The aperture cap member 221AP has an aperture 221APA provided in a head portion 221APH thereof, coaxial with the housing 221H. The aperture 221APA is arranged to allow flow of process gas out from the bubbler 221 and into liquid in which the bubbler 221 is immersed. The feature that process gas is caused to assume a swirl flow and subsequently forced to accelerate along the insert member 221I has the feature that gas may be injected into liquid in the column 225 at a relatively high velocity and with high intensity swirl or spin. The present applicant has discovered that gas bubbles formed by injection of gas into liquid in this manner may be caused to be of particularly small size, and less than 50 micrometres in diameter in some embodiments, enabling intimate mixing of the gas with liquid in the column 225. Furthermore, the gas bubbles have been found to be stable and to remain of substantially the same size as they are drawn or forced upwardly towards the ultrasonic energy generator 240 in the flow of liquid upwardly through the column 225.

In the embodiment of FIG. 6, the bubbler 221 is provided substantially coaxially of the column 225 such that a cylinder axis thereof (being substantially coincident with the cylinder axes of the insert member 221I and aperture cap 221AP), is substantially coincident with that of the column 225. Other arrangements may also be useful. However, it is found that by disposing the bubbler 221 such that it is substantially centred with respect to the column 225, a relatively homogeneous flow of microbubbles may be established with respect to a cross-sectional area of the column.

FIG. 7 shows the ultrasonic energy generator 240 in further detail. FIG. 7(a) is a 3D view of the generator 240 whilst FIG. 7(b) is an external view of one of nineteen whilst devices 241 that form part of the generator 240. FIG. 7(c) shows the device 241 as viewed along section B-B of FIG. 7(b) whilst FIG. 7(d) is a 3D view of the device 241. Like features of the device of FIG. 7 to that of the device of FIG. 4 are shown with like reference signs incremented by 100.

As can be seen from FIG 7(a), sixteen of the whistle devices are arranged circumferentially around the column 225 of the converter portion 215 and three are disposed at spaced apart

locations along a diameter of the column 225, facing upstream of a direction of flow of liquid through the column 225, in use. Other numbers of whistle devices and other arrangements of whistle devices are also useful. In the embodiment shown the whistle devices 241 are arranged such that substantially all fluid passing along the column 225 passes within 50mm of a portion of a body of at least one whistle device 241. This is so as to ensure exposure of microbubbles entrained in the fluid to ultrasonic radiation of sufficiently high intensity. Other distances may also be useful.

As per the whistle device 141 of the embodiment illustrated in FIG. 4, the whistle device 241 of FIG. 7 has a chamber 241C that defines a tapped whistle body. A nozzle member 241N and a receptor member 241R are coupled to the whistle body 241C by means of respective screw threads. The receptor member 241R is substantially wholly contained within the whistle body 241C in the embodiment shown, and in a substantially fixed, spaced apart and substantially coaxial orientation with respect to the nozzle member 241N. In the embodiment shown, the nozzle member 241N is integrally formed from the same component as a gas supply head coupling 241GHC. The coupling 241GHC is provided with an internal thread arranged to allow the nozzle member 241N to be coupled to a gas supply head. An external thread allows the nozzle member 241N to be coupled to the whistle body 241C.

FIG. 8 shows the nozzle member 241N and gas supply head coupling 241GHC separated from the housing 241C. FIG. 8 is drawn substantially to scale and in the present embodiment length L1 is 40mm and diameter DGHC is approximately 31mm. Other dimensions are also useful.

As shown in FIG. 8, the nozzle member 241N has a flow-splitting vane element which may also be described as a turbulator 241NT. The turbulator 241NT is a substantially flat, rectangular element arranged to divide gas flowing out from the nozzle member 241N into two halves. The presence of the turbulator 241NT has been found to enable tuning of the frequency of ultrasonic energy generated by the whistle device 241 to a substantially constant, reproducible frequency. In some embodiments the frequency is in the range from around 20kHz to around 30 kHz, optionally in the range from around 20kHz to around 26kHz. Other frequencies greater than 30kHz and/or less than 20 kHz are also useful, in addition or instead. The length LNT of the turbulator 241NT with respect to the longitudinal axis A of the nozzle member 241N (which is substantially coincident with that of the column 125 in use) is approximately 1mm. Other dimensions are also useful and a suitable value of length of the turbulator 241NT may be determined empirically by the skilled person.

The nozzle member 241N is arranged to direct a flow of gas through the nozzle member 241N into an open cavity 241RC defined by the receptor member 241R. Flow of gas from the nozzle member 241N into the cavity 241RC results in the generation of ultrasonic energy in the manner of a Hartmann-type whistle device. Gas flowing through the whistle device 241 flows out from the device through an aperture 241A in the whistle body 241C, contributing to gas lift in the column 225.

In the embodiment shown, the whistle devices 241 may be tuned to generate ultrasonic energy having a frequency in the range from 20 to around 26kHz. Higher frequencies may be useful in some embodiments as noted above. It is to be understood that the skilled person will be capable of determining an optimum gas pressure for driving the whistle devices, and an optimum distance between the nozzle member 241N and receptor member 241R, to generate ultrasonic energy of appropriate frequency and amplitude. The present applicant has determined that with the whistle devices 241 at a depth of 2m or more below the surface of fresh water and a process gas pressure of 1-4 bar, optionally in the range 1-5 bar, ultrasonic energy of suitable amplitude and frequency may be generated by suitable adjustment of the distance between the nozzle member 241N and cavity 241RC. A distance between the receptor member 141R and nozzle 141N may be adjusted by means of the screw thread by rotation of the receptor member 141R. In some embodiments, the drive gas for driving the whistle devices 241 is supplied at a pressure of around 1.5bar to whistle devices 241 at a depth of 2m below a level of liquid in the liquid storage tank 110. Higher pressures than 5 bar may be useful in some embodiments.

Embodiments of the present invention have been found to enable the highly efficient generation of microbubbles in liquid in the column of the converter portion 115, 215. When the microbubbles are subject to ultrasonic energy by the ultrasonic energy generator, cavitation of the microbubbles takes place. It is believed that, if the microbubbles contain carbon dioxide, cavitation in collapsing microbubbles results in the conversion of carbon dioxide to hydrocarbon gas and oxygen as described above.

In some embodiments, methane gas may be generated. In some embodiments, one or more other hydrocarbon compounds may be generated in addition or instead. For example, methanol and/or ethanol may be produced in some embodiments, in addition to or instead of methane. Other alkanes may be produced in some embodiments such as ethane, propane and one or more other alkanes in addition or instead. One or more catalyst materials may

be provided in the liquid in the liquid holding tank 110, 210, in order to promote the formation of particular products.

Non-hydrocarbon gases may be produced exclusively in some embodiments.

5

FIG. 9 is a schematic illustration showing a coal, oil or gas-fired power generating station 380 connected to a boiler exhaust gas conversion apparatus 300 that is configured to convert a process gas comprising carbon dioxide into methane gas and oxygen gas. The apparatus 300 has a liquid holding tank 310 in which are provided three converter portions 215 substantially as described and illustrated with respect to FIG. 5(a) to FIG. 8. Other numbers of converter portions 215 may also be useful, such as 1, 2, 4, 5, 10 or any other suitable number.

15 The apparatus 300 is arranged to receive process gas in the form of power station boiler exhaust gas and to pass the gas initially through a gas cooling scrubber 381. The scrubber 381 cools the gas by means of a water cooling system, and in addition removes particulates suspended in the gases such as soot particles. One or more other constituents of the gas may be removed in addition or instead in some embodiments, such as SO_x and/or NO_x .

20 The process gas then passes through a gas compression system 382 before being passed either directly to the converter portions 215 or to the converter portions 215 via a nitrogen separation system 383. The separation system 383 is arranged to separate nitrogen gas from the process gas. The separation system 383 may comprise a membrane separation system, optionally a hollow fibre membrane separation (HFMS) system, configured to
25 remove nitrogen. The separated nitrogen is passed to a nitrogen gas output handling system 384 by means of which nitrogen may be exhausted to atmosphere, stored, or used for one or more other purposes. Remaining gas is fed to the converter portions 215.

As described above, the holding tank has three converter portions 215 each arranged to
30 generate microbubbles of process gas in a column 225 thereof that is immersed in liquid in the holding tank 310. The converter portions 215 are arranged to subject the microbubbles to high intensity ultrasonic radiation. Gas that has passed through the column 225 of at least one of the converter portions 215 is drawn from the liquid tank 310 and fed to a gas compression system 388. The apparatus 300 is arranged to allow the gas to be fed directly
35 to the gas compression system 388 or to be fed to the gas compression system 388 via a nitrogen separation system 386. If the apparatus 300 is operated such that gas is fed to the

gas compression system 388 via the nitrogen separation system 386, nitrogen separated from the gas by the nitrogen separation system 386 is fed to a nitrogen gas output handling system 387 where nitrogen may be exhausted to atmosphere, stored, or used for one or more other purposes.

5

In some use scenarios, the boiler exhaust gas conversion apparatus 300 is arranged such that gas flowing through the system to gas compression system 388 passes through only one of the two nitrogen gas separation systems 383, 386. In some alternative scenarios, the apparatus 300 is arranged to allow gas to flow through both of the separation systems 383,

10

386. In some embodiments the apparatus 300 has only one of the two nitrogen gas separation systems 383, 386. In some embodiments the apparatus 300 may not be configured to pass the gas through any separate nitrogen separator 383, 386.

15

Gas passing through gas compression system 388 is subsequently fed to a methane separator 389 that separates methane from gas entering the separator 389. The separated methane is stored in a methane storage tank 390.

20

Gas from which methane has been separated is fed from the separator 389 to an oxygen separator 391 that separates oxygen from the gas fed to the separator 391. Separated oxygen is stored in an oxygen storage tank 392. Gas from which oxygen has been separated by the separator 391 may be subject to further treatment before being exhausted.

25

Thus, the apparatus 300 may be employed to generate and separate hydrocarbons and oxygen from power station boiler exhaust gas, in particular from carbon dioxide contained in power station boiler exhaust gas.

30

It is to be understood that the nitrogen separation systems 383, 386 may each have a compressor for compressing gas before it passes through a separator portion thereof, such as a membrane separator.

35

Separation of gases in embodiments of the present invention may be performed by any suitable separator such as a membrane separator, for example a hollow fibre membrane separator HFMS, or any other suitable separator.

In some embodiments, apparatus is provided for converting carbon dioxide to hydrocarbon fuel, the apparatus being powered by electrical energy. The primary consumers of the electrical energy are gas compressors, gas separator devices and control modules arranged to control the apparatus. The apparatus is employed to convert carbon dioxide to hydrocarbon gas, liquid or solid using electrical energy from renewable sources such as solar energy, geothermal energy, wind energy, wave or tidal energy. In the present embodiment the apparatus is arranged to convert carbon dioxide to methane. In some embodiments, the apparatus may be suitable for installation in a domestic or commercial building environment and the methane gas used to heat water or other substance when required, for example for washing or cooking. In some embodiments carbon dioxide so generated may be recovered back to the apparatus for conversion back to methane. Other arrangements may also be useful.

In some embodiments the apparatus may be provided in combination with a renewal energy capture device or apparatus such as a solar photovoltaic energy generator having a solar panel, power inverter and control electronics.

FIG. 10 is a schematic illustration showing the use of the novel microbubble generator 220 of the embodiment shown in Figures 5 and 6 in an example of a gas lift pump apparatus 450, such as that for circulating liquid in a liquid storage or ballast tank of a vessel, e.g. a ship or other water-going vessel, such as for the purpose of killing aquatic nuisance species (ANS) therein. It is to be understood that the microbubble generator 220, or other embodiments of same within the scope of this aspect of the invention defined herein, may be utilised in other embodiments and constructions of gas lift apparatus, including those disclosed in WO2013/093527 (the entire contents of which are incorporated herein by reference).

As shown in FIG. 10, the gas lift pump apparatus 450 includes the novel microbubble generator 220 as shown in FIG. 5 and shown in enlarged detail in FIG. 6, as well as sonic energy generator 400, provided in a generally vertical (in use) gas lift column 460. The sonic energy generator 400 may be any example sonic energy generator as used in other embodiments of the present invention in others of its aspects, or indeed may be a combined fluid delivery device/sonic energy generator as disclosed and illustrated in any embodiment of WO2013/093527. The column 460 is filled with a liquid, e.g. water (such as that in a ballast tank of a vessel in which the apparatus may be provided), which is pumped therethrough as a flow L thereof under the effect of gas lift.

The microbubble generator 220 is operable to inject a flow of gas P, such as carbon dioxide, into the column 460 via the bubbler 221, which output gas flow rises towards the sonic energy generator 400. Preferably the bubbler 221 is situated substantially coaxially within the column 460 (i.e. aligned along common longitudinal axis X), in order to enhance the homogeneity of the flow of gas microbubbles (with respect to the cross-sectional area D_1 of the column 460) as it exits the bubbler 221 and rises in the column 460 towards the sonic energy generator 400. The apparatus 450 is operable to pump the water or other liquid L through the column 460 from a draw tube 460H by the effect of gas lift due to the gas injected into the column via the sonic energy generator 400 as well as bubbler 221. As noted above, in some embodiments drive gas used to cause the sonic energy generator 400 to generate sonic energy may be recirculated by the apparatus 450 rather than being exhausted into the gas lift column 460.

- Gas bubbles are formed within, and ejected from, the bubbler 221 of the bubble generator 220 in the same manner as described above in relation to FIG. 6. A size of the bubbles is reduced to micron-order levels by the shear forces experienced as the gas P is injected via the conduit 230GB through the bubbler 221 and out the bottom (outlet) thereof.
- As disclosed in WO2013/093527, this example arrangement of gas lift pump apparatus shown in Figure 10, utilising the novel microbubble generator 220 (or its various other novel embodiments defined herein), is useful for the treatment of e.g. ballast water in waterborne vessels, e.g. for killing bacterial ANS as well as non-bacterial ANS.
- Although the embodiment of FIG. 10 shows the microbubble generator 220 positioned in the flowstream of liquid L from the draw tube 460H, it is to be understood that various alternative configurations of these components may be employed, as taught and disclosed for example in WO2013/093527. For instance the microbubble generator 220 may alternatively be provided at a base of a column having a closed lower end, with there being provided a dedicated separate inlet for supply of water or other liquid therein to be pumped by the apparatus, for example in a similar manner to the liquid inlet 120C of the apparatus of FIG. 1.

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", means "including but not limited to", and is not intended to (and does not) exclude other moieties,

additives, components, integers or steps.

Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is
5 used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

CLAIMS:

1. Gas conversion apparatus for converting one or more reactant chemical species comprised in a first gas to one or more product chemical species, comprising:
 - 5 means for introducing first gas into a liquid medium; and
an ultrasonic energy generator arranged to generate ultrasonic energy,
the apparatus being configured to launch ultrasonic energy generated by the ultrasonic energy generator into the liquid medium such that first gas is exposed to ultrasonic energy so as to convert one or more of the reactant chemical species to one or
10 more product chemical species,
the apparatus being arranged to allow collection of one or more of the product chemical species,
wherein the apparatus further comprises a gas lift column through which liquid medium may be pumped by gas lift; and
15 wherein the means for introducing first gas into the liquid medium comprises means for introducing first gas into the column,
the apparatus being configured to launch ultrasonic energy generated by the ultrasonic energy generator into liquid medium in the column such that first gas passing through the column by gas lift is exposed to ultrasonic energy generated by the generator.
20
2. Apparatus according to claim 1 wherein the ultrasonic energy generator is configured to generate ultrasonic energy in response to a flow of a drive gas therethrough.
3. Apparatus according to claim 2 wherein the ultrasonic energy generator comprises a
25 whistle device, the whistle device being arranged to generate the ultrasonic energy when drive gas is driven through the device.
4. Apparatus according to claim 2 or claim 3 arranged to feed the drive gas into the liquid medium after driving the gas through the ultrasonic energy generator.
30
5. Apparatus according to any one of claims 2 to 4 arranged wherein first gas provides the drive gas.
6. Apparatus according to any preceding claim wherein the means for introducing
35 process gas into the liquid medium comprises a microbubble generator, the apparatus being configured to cause microbubbles of process gas to be generated in the liquid medium and

to be subject to irradiation by ultrasonic energy generated by the ultrasonic energy generator.

7. Apparatus according to any preceding claim wherein the microbubble generator is configured to introduce microbubbles of first gas into the liquid medium in the column upstream of the ultrasonic energy generator.

8. Apparatus according to any preceding claim, wherein the gas lift column defines a longitudinal axis and the microbubble generator is positioned substantially coaxially with the longitudinal axis of the column.

9. Apparatus according to any preceding claim operable to pass gas that has been exposed to ultrasonic energy through a gas separator to separate gas molecules according to chemical species.

10. Apparatus according to any preceding claim configured to pass fluid that has been exposed to ultrasonic energy through a separator to separate at least one product chemical species from the fluid.

11. Apparatus according to claim 9 or claim 10 configured to separate hydrocarbon gases from one or more other gases.

12. Apparatus according to claim 11 configured to separate hydrocarbon gas chemical species from one or more chemical species comprised by the first gas.

13. Apparatus according to claim 12 operable to return one or more separated chemical species comprised by the first gas to the liquid medium for further exposure to ultrasonic energy.

14. Apparatus according to claim 2 or any of claim 3 to 13 depending through claim 2, configured to feed drive gas into liquid medium in the column of the gas lift device such that the drive gas is exposed to ultrasonic energy in the column.

15. Apparatus according to any preceding claim arranged wherein the first gas comprises carbon dioxide.

16. Apparatus according to any preceding claim arranged wherein the first gas comprises at least 10% carbon dioxide by volume, optionally at least 14%, further optionally at least 20%, still further optionally at least 40%, still further optionally at least 50% carbon dioxide by volume.

5

17. Apparatus according to any preceding claim arranged wherein the first gas consists essentially of carbon dioxide.

18. Apparatus according to any preceding claim configured to separate hydrocarbons from gas that has passed through the column.

10

19. Apparatus according to any preceding claim installed in a liquid storage tank.

20. Apparatus according to claim 19 wherein the liquid storage tank contains liquid.

15

21. Apparatus according to claim 20 wherein the liquid is provided with particles of a catalyst material dispersed or suspended therein.

22. Apparatus according to claim 21 wherein the catalyst particles comprise at least one selected from amongst iron and a hematite-bearing compound, or wherein the catalyst particles consist substantially of hematite.

20

23. Apparatus according to any preceding claim coupled to a power generating station or a power generating station in combination with apparatus according to any preceding claim, arranged wherein combustion gases generated by the station provide at least a portion of, optionally the whole of, the first gas of the apparatus.

25

24. A fuel burning engine in combination with apparatus according to any one of claims 1 to 22 arranged wherein combustion gases generated by the engine provide at least a portion of, optionally the whole of, the first gas of the apparatus.

30

25. A vessel comprising an engine according to claim 24.

26. A method of converting one or more reactant chemical species comprised in a first gas to one or more product chemical species comprising:
introducing first gas into a liquid medium; and

35

generating ultrasonic energy by means of an ultrasonic energy generator,

the method comprising launching ultrasonic energy generated by the ultrasonic energy generator into the liquid medium such that first gas is exposed to ultrasonic energy so as to convert one or more of the reactant chemical species to one or more product chemical species,

whereby introducing first gas into a liquid medium comprises introducing first gas into a column of a gas lift pump apparatus and causing pumping of liquid medium through the column by gas lift, and whereby launching ultrasonic energy generated by the generator into the liquid medium comprises launching ultrasonic energy into liquid medium in the column whereby first gas passing through the column is exposed to ultrasonic energy, the method further comprising collecting one or more product chemical species.

27. A method according to claim 26 whereby generating ultrasonic energy by means of an ultrasonic energy generator comprises generating ultrasonic energy in response to a flow of a drive gas through the ultrasonic energy generator.

28. A method according to claim 27 comprising generating ultrasonic energy by means of a whistle device of the ultrasonic energy generator by driving drive gas through the ultrasonic energy generator.

29. A method according to claim 27 or claim 28 comprising feeding drive gas into the liquid medium after passing the gas through a whistle device.

30. A method according to any one of claims 27 to 29 whereby the first gas provides the drive gas.

31. A method according to any one of claims 26 to 30 comprising causing microbubbles to be generated in the liquid medium and subjected to irradiation by ultrasonic energy generated by the ultrasonic energy generator.

32. A method according to any one of claims 26 to 30 comprising causing gas that has been subjected to ultrasonic energy to be separated according to chemical species by means of a gas separator.

33. A method according to claim 32 whereby causing gas to be separated comprises separating hydrocarbon gases from one or more other gases.

34. A method according to claim 33 whereby causing gas to be separated comprises separating hydrocarbon gases from first gas.

5 35. A method according to claim 34 comprising returning separated first gas to the liquid medium and subjecting the separated first gas to ultrasonic energy in the liquid medium.

36. A method according to any one of claims 26 to 35 whereby the first gas comprises carbon dioxide.

10

37. A method according to any one of claims 26 to 36 whereby the first gas comprises at least 10% carbon dioxide by volume, optionally at least 14%, further optionally at least 20%, still further optionally at least 40%, still further optionally at least 50% carbon dioxide by volume.

15

38. A method according to any one of claims 26 to 37 whereby the first gas consists essentially of carbon dioxide.

20

39. A method according to any one of claims 26 to 38 comprising separating methane from other gas that has passed through the column.

40. A method according to any one of claims 26 to 39 comprising drawing liquid medium into the column from a liquid storage tank.

25

41. A method according to any one of claims 26 to 40 whereby the liquid is provided with particles of a catalyst material dispersed or suspended therein.

30

42. A method according to claim 41 whereby the catalyst particles comprise at least one selected from amongst iron, iron oxide and a hematite-bearing compound or whereby the catalyst particles consist substantially of hematite.