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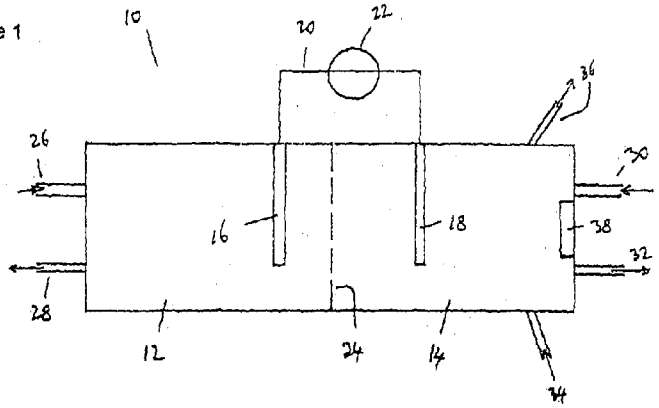
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(54) **Title**: PRODUCTION OF METHANOL OR METHANOL DERIVATIVES

Figure 1



(57) **Abstract**: A process for producing methanol or a methanol derivative from methane comprises the steps of providing a bio-electrochemical system having a bioanode and a cathode, causing oxidation at the bioanode, providing an aqueous medium to the cathode to produce a reactive oxygen species at the cathode; and reacting the reactive oxygen species with methane to form methanol or a methanol derivative.

PRODUCTION OF METHANOL OR METHANOL DERIVATIVES

FIELD OF THE INVENTION

The present invention relates to a process for the production of methanol or methanol derivatives.

BACKGROUND TO THE INVENTION

CO_2 and methane are the most ubiquitous greenhouse gases known. The emission of both compounds due to increased anthropogenic activity causes global climate change (IPCC report 2008). Therefore, increasing attention is focused on either decreasing the emission of these compounds or capturing them.

Decreasing the emissions is possible via decreased usage of fuels and non-renewables that lead to their production, or by immediate conversion of the compounds before discharge. The latter can be achieved by e.g. incinerating methane originating from landfills to generate the much less potent greenhouse gas CO_2. During such a process, electricity and/or heat are generated, both of which are difficult to store.

It is known that reactive oxygen species can be used to oxidise methane to methanol in fuel cells (Tomita et al Angew. Chem. Int. Ed. 2008, 47, 1462 –1464), at moderate temperatures and a catalyst such as $Sn_{0.9}In_{0.1}P_2O_7$. In this process, methane was obtained from natural gas.

Anaerobic digestion is a key process for the production of biogas, which is highly enriched in methane. Biogas typically contains methane, carbon dioxide and some reduced sulphur compounds, such as H_2S. At present, methane produced in biogas is converted to electricity and heat by combustion. The methane is generally converted immediately after creation as it cannot be stored economically, and only in exceptional cases it is transported. A strategy to liquefy methane under the form of methanol could therefore be highly advantageous.

Hydrogen peroxide is a potent oxidant with many industrial applications. Besides being used as a disinfectant, it is used for pulp and paper bleaching, detergents, wastewater treatment, chemical syntheses, metallurgy, in the textile industry and in the electronics industry (Fierro et al., Angew. Chem. Int. Ed. 2006, 45, 6962-6984). On a large scale, hydrogen peroxide is predominantly produced using the anthraquinone autooxidation process (AO process) or Riedl–Pfleiderer process. In this process the anthraquinone is reduced with hydrogen gas and subsequently oxidised again with oxygen. During the oxidation step hydrogen peroxide is formed. The resulting net reaction is:

$$H_2 + O_2 \rightarrow H_2O_2 \qquad \text{(equation 1)}$$

The AO process is by far the most applied technology for the production of hydrogen peroxide and accounts for over 95% of the worldwide hydrogen peroxide production (Fierro et al., Angew. Chem. Int. Ed. 2006, 45, 6962-6984). However, alternative approaches also exist. One of the alternative approaches is the hydrogen peroxide production through conventional electrochemical processes. Of these conventional electrochemical processes two main approaches exist: (i) the electrolyser type approach (e.g., Foller and Bombard, J. Appl. Electrochem. 1995, 25, 613-627), and (ii) the fuel cell type approach (e.g., Yamanaka, Angew. Chem. Int. Ed. 2003, 42, 3653-3655). The electrolyser approach is based on a chemically catalyzed anode that generates oxygen:

Anode (acid conditions): $H_2O \rightarrow 0.5\ O_2 + 2\ H^+ + 2\ e^-$ (equation 2a)

Anode (alkaline conditions): $2\ OH^- \rightarrow 0.5\ O_2 + H_2O + 2\ e^-$ (equation 2b)

The fuel cell approach is based on a chemically catalyzed anode that consumes hydrogen:

Anode (acid conditions): $H_2 \rightarrow 2\ H^+ + 2\ e^-$ (equation 3a)

Anode (alkaline conditions): $H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2\ e^-$ (equation 3b)

In both approaches the anode is coupled to a chemically catalyzed cathode that reduces oxygen to form hydrogen peroxide.

Cathode (acid conditions): $O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$ (equation 4a)

Cathode (alkaline conditions): $O_2 + H_2O + 2e- \rightarrow HO_2^- + OH^-$ (equation 4b)

Unfortunately, both approaches require significant energy inputs. The electrolyser approach requires significant energy inputs due to the large electricity consumption; the fuel cell approach requires significant energy inputs due to the large hydrogen consumption. This renders these processes expensive and often not economically viable.

Recently, bioelectrochemical systems, such as microbial fuel cells and microbial electrolysis cells, have emerged as potentially interesting technology for the production of energy and products from aqueous waste streams (e.g., wastewater). Industrial, agricultural and domestic waste waters typically contain dissolved organics that require removal before discharge into the environment. Bioelectrochemical systems are based on the use of electrochemically active microorganisms, which transfer the electrons to an electrode (anode) while they are oxidising (and thus removing) (in)organic pollutants in aqueous waste streams (e.g., wastewater). Bioelectrochemical wastewater treatment can be accomplished by electrically coupling such a biocatalysed anode to a counter electrode (cathode) that performs a reduction reaction. As a result of this electrical connection between the anode and the cathode, the electrode reactions can occur and electrons can flow from the anode to the cathode. The bioelectrochemical system may operate as a fuel cell (in which case electrical energy is produced) or as an electrolysis cell (in which case, electrical energy is fed to the bioelectrochemical system). Examples of bio-electrochemical systems are microbial fuel cells for electricity production (Rabaey and Verstraete, Trends Biotechnol. 2005, 23, 291-298) and biocatalyzed electrolysis for the production of hydrogen gas (Patent WO2005005981A2). It was recently described that bio-electrochemical systems can also be used for the production of hydrogen peroxide (Australian provisional patent application number 2008905337, International patent application number PCT/AU2009/001355; Rozendal et al Electrochem. Commun. 2009, 11, 1752-1755). Australian provisional patent application number 2008905337 and International patent application number PCT/AU2009/001355 in the name of the present

applicant describes a process for producing hydrogen peroxide in a bioelectrochemical system.

Methanol is an interesting molecule as potential stepping stone to larger chain hydrocarbons. For example, it has been described that methanol can be converted to hydrocarbons over a fresh SAPO-34 catalyst at elevated temperatures (Shahda, Shahda, M.1; Dengchao, Y.1; Huixin, W.1, Petroleum Science and Technology, Volume 26, Number 16, January 2008 , pp. 1893-1903). More specifically, Song et al (Weiguo Song, James F. Haw, John B. Nicholas, and Catherine S. Heneghan. Methylbenzenes Are the Organic Reaction Centers for Methanol-to-Olefin Catalysis on HSAPO-34. J. Am. Chem. Soc., 2000, 122 (43), pp 10726–10727) described the conversion of methanol to olefins at 673K using a similar catalyst. Dahl and Kolboe (On the reaction mechanism for propene formation in the MTO reaction over SAPO-34, 1993, Catalysis letters 20(3-4): 329-336) reported that propene is the main reaction product of direct methanol conversion on SAPO-34.

BRIEF DESCRIPTION OF THE INVENTION

In one aspect, the present invention provides a process for producing methanol or a methanol derivative from methane comprising the steps of:

- providing a bioelectrochemical system having a bioanode and a cathode;
- causing oxidation at the bioanode,
- providing an aqueous medium to the cathode to produce a reactive oxygen species at the cathode; and
- reacting the reactive oxygen species with methane to form methanol or the methanol derivative.

In another aspect, the present invention provides a process for producing methanol or a methanol derivative from methane comprising the steps of:

- providing a bioelectrochemical system having a bioanode and a cathode;
- causing oxidation at the bioanode,

- having a power supply in an electrical circuit connecting anode and cathode,
- applying a voltage with the power supply,
- providing an aqueous medium to the cathode to produce a reactive oxygen species at the cathode, and;
- reacting the reactive oxygen species with methane to form methanol or the methanol derivative.

To increase the rate of production of the reactive oxygen species, the anode and cathode may be connected to each other in short circuit, i.e., without the extraction of electrical energy. Alternatively, or further, to speed up the process even further, an external power supply can optionally be connected between the anode and the cathode. Using this power supply, an external voltage may be applied to the system, which speeds up the electrode reactions and increases the production rate of reactive oxygen species. The voltage applied with the power supply between the anode and the cathode may be between 0 and 2.5 V, preferably between 0 and 1.5 V, more preferably between 0 and 1.0 V. This may result in a volumetric current density in the bioelectrochemical cell of between 0 and 10,000 A/m^3 of bioelectrochemical cell, preferably between 10 and 5,000 A/m^3 of bioelectrochemical cell, more preferably between 100 and 2500 A/m^3 of bioelectrochemical cell and/or an area specific current density of between 0 and 1,000 A/m^2 membrane surface area, preferably between 1 and 100 A/m^2 membrane surface area, more preferably between 2 and 25 A/m^2 membrane surface area.

In one embodiment, the reactive oxygen species comprises hydrogen peroxide or a reactive oxygen species formed from oxygen or hydrogen peroxide in an aqueous medium. For example, hydrogen peroxide can break down in water to form water and a reactive oxygen species in accordance with the following equation:

$$H_2O_2 \rightarrow H_2O + O^* \qquad \text{(equation 5)}$$

in which O* refers to an reactive oxygen species.

Other examples of reactive oxygen species are OH^-, O_2^- and ozone.

In one embodiment, the methanol is further converted to hydrocarbons using a catalyst. Examples of hydrocarbons to which the methanol can be converted include olefins such as propene and other hydrocarbons as known to a person skilled in the art. An example of a catalyst is SAPO-34, a zeolite based compound. The methanol conversion can occur inside the cathode compartment or in a separate vessel, the latter being particularly necessary in case the conversion occurs at elevated temperatures.

In one embodiment the cathode is supplied with a gas flow containing oxygen. Examples of such gas flows include air or boiler off gases. The latter may be the result of biogas combustion. Alternatively, the aqueous medium provided to the cathode contains appreciable levels of dissolved oxygen.

In one embodiment, the bioanode is supplied with a waste stream, such as a wastewater stream, which contains organic and/or inorganic material. The organic material in the waste stream may be oxidised at the bioanode to provide a supply of electrons to the cathode. The waste stream may comprise an effluent stream from an anaerobic digester.

In another embodiment, the bioanode is supplied with a biogas or a combination of biogas and a waste stream. The biogas may contain reduced sulphur compounds and the reduced sulphur compounds will be oxidised at the bioanode. In addition, the methane may be oxidised to carbon dioxide at the anode. The methane may pass through the anode and cause turbulence, before being passed to the cathode.

In a further embodiment, the bioanode is supplied with a waste stream containing reduced sulphur compounds and the reduced sulphur compounds are oxidised at the bioanode.

The bioanode will also contain microorganisms that can facilitate oxidation of material at the bioanode. These microorganisms are known by the person skilled in the art of bioelectrochemical systems and are typically referred to as electrochemically active

microorganisms. The microorganisms will typically comprise a microbial culture. The microbial culture may comprise a mixed microbial culture.

Oxidation of material at the bioanode results in the liberation of electrons. These electrons will travel through appropriate electrical connections in the bioelectrochemical system and to the cathode. The bioelectrochemical system also includes a membrane or a passage that allows electrical charge to flow between the bioanode and the cathode in order to complete the electrical circuit in the bioelectrochemical system. The membrane may comprise a bipolar membrane, an anion exchange membrane, a proton exchange membrane or a cation exchange membrane. In some embodiments, the membrane may comprise a gas permeable membrane. In some embodiments, the membrane can be a porous structure, such as microporous PVC.

In the process of the present invention, an aqueous stream is provided to the cathode. Water and/or protons from the aqueous material react with oxygen and the electrons at the cathode to form hydrogen peroxide (the reactions are set out in equations 4a and 4b above). The thus-formed hydrogen peroxide can then react with methane to form methanol or a methanol derivative, such as formate or propene. The reaction that takes place in this regard is as follows:

$$CH_4 + H_2O_2 \rightarrow CH_3OH + H_2O \qquad \text{(equation 6)}$$

In one embodiment, methane is added to the cathode, where it reacts with the hydrogen peroxide. This results in an overall reaction equation at the cathode:

Cathode (acid conditions): $CH_4 + O_2 + 2\ H^+ + 2\ e^- \rightarrow CH_3OH + H_2O$ (equation 7a)

Cathode (alkaline conditions): $CH_4 + O_2 + H_2O + 2e^- \rightarrow CH_3OH + 2\ OH^-$ (equation 7b)

In another embodiment, methane is mixed with the reactive oxygen species (such as hydrogen peroxide) in a separate compartment to the cathode. In another embodiment,

the methanol is further converted to a hydrocarbon over a catalyst, which can either be in the cathode, in a separate vessel where the reactive oxygen species reacts with methane (in embodiments where the reactive oxygen species reacts with the methane in a separate vessel to the cathode compartment), or in yet another vessel.

Methane may be mixed with the reactive oxygen species by bubbling or sparging methane containing gas through a liquid containing the reactive oxygen species. In one embodiment, methane is bubbled or sparged through the liquid in the cathode compartment of the bioelectrochemical system. In another embodiment, a methane-containing gas may be fed to the anode compartment of the bioelectrochemical system and the bioelectrochemical system may be provided with a gas permeable membrane between the anode compartment and the cathode compartment, with the methane passing from the anode compartment through the gas permeable membrane and into the cathode compartment.

In another embodiment, a methane-containing gas may be fed to the anode compartment of the bioelectrochemical system and the bioelectrochemical system may be provided with a passage that allows transport of the gas exiting the anode to the cathode or to another vessel where the methane in the gas can react with hydrogen peroxide. In a further embodiment of this, the gas exiting the external vessel can be recirculated to the anode chamber.

It may be necessary to provide a catalyst to catalyse the reaction between the methane and the hydrogen peroxide in order to form the methanol or methanol derivative. Any catalyst known to be suitable to the person skilled in the art may be used in this regard. An example of such a catalyst is di-iron-substituted silicotungstate, γ-$SiW_{10}(Fe(OH_2))_2O_{38}$ as shown by Mizuno et al. (Mizuno et al. J. Catal. 1999. 184, 550-552, Aqueous Phase Oxidation of Methane with Hydrogen Peroxide Catalyzed by Di-iron-Substituted Silicotungstate).

Alternatively, the catalyst may be part of the cathode so that direct oxidation of methane

to methanol takes place (equation 7a and 7b). An example of such a cathode catalyst is Palladium/Carbon (such as 10wt% Pd) as shown by Tomita et al (Tomita et al. Angew. Chem. Int. Ed. 2008, 47, 1462-1464, Direct Oxidation of Methane to Methanol at Low Temperature and Pressure in an Electrochemical Fuel Cell).

In one embodiment of the invention, an oxygen containing gas flow is introduced in the cathode chamber. The cathode chamber is partially or wholly surrounded by or surrounding a reaction compartment through which biogas or a methane containing gas is supplied (or, alternatively, the cathode may partially or wholly surround the reaction compartment). The cathode is separated from this compartment by a membrane that allows passage of the reactive oxygen species (such as hydrogen peroxide) and/or methanol. Examples of such membranes include anion exchange membranes, non selective membranes (e.g., Teflon, silicone) or other membranes known to a person skilled in the art. The reaction compartment may contain a catalyst that allows reaction between methane and hydrogen peroxide, leading to the formation of methanol. The catalyst can be coated on a three dimensional structure or can be associated to the membrane. The reaction chamber can be humidified or filled with aqueous medium or solution.

In another embodiment of the present invention, the cathode compartment comprises a gas diffusion layer, allowing diffusion of gas, such as oxygen, methane, biogas or air, from a gaseous phase into the cathode fluid. In a further embodiment, the cathode compartment contains a gas diffusion electrode, as known to a person skilled in the art.

In one embodiment of the present invention, the process of the present invention is operated as a complementary system to an anaerobic digester. In the anaerobic digester, an effluent stream or a waste stream is digested under anaerobic conditions to form a biogas. The biogas will typically include methane, carbon dioxide and some reduced sulphur compounds (such as hydrogen sulphide, H_2S). This biogas may be provided as a feed to the bioanode of the bioelectrochemical system. In the bioanode, the reduced sulphur compounds are oxidised. A gas permeable membrane may be provided between

the bioanode and the cathode. The methane gas can pass through the gas permeable membrane and therefore can move from the bioanode to the cathode. As the reduced sulphur compounds in the biogas have been oxidised at the bioanode, the gas passing through the gas permeable membrane to the cathode has been largely purified and this gas can react with the hydrogen peroxide generated at the cathode to form methanol or methanol derivatives. The step of oxidising the reduced sulphur compounds is advantageous in that sulphur compounds can poison catalysts commonly used to catalyse the reaction of methane with hydrogen peroxide. However, oxidising the reduced sulphur compounds in the bioanode can result in the formation of elemental sulphur, which removes the sulphur compounds from the gas stream. Consequently, the gas passing through the gas permeable membrane does not contain sulphur compounds (or, if it does, those compounds are at a level that is below the level at which significant catalyst poisoning occurs).

As an additional benefit to this process, elemental sulphur is also produced as one of the products of the process. Elemental sulphur has economic value in its own right.

A biogas may also be used as a feed stream to the anode compartment of the bioelectrochemical system in other embodiments of the present invention that use other membranes besides gas-permeable membranes. In these embodiments, the treated biogas leaving the anode may be captured and sent to the cathode by external piping or it may simply be vented.

In another embodiment of the present invention, a waste stream, such as a digester effluent or a wastewater stream, is supplied as a feed to the bioanode. Organic materials in the waste stream are oxidised to provide at least part of the energy required to form hydrogen peroxide at the cathode. Alternatively, carbon rich leachate from solid waste systems or lagoons could provide the feed stream to the anode. In this embodiment, methane gas, such as methane gas derived from a biogas, may also be provided to the cathode.

In another embodiment, a reactive oxygen species (e.g. hydrogen peroxide) is generated at the cathode and is removed from the cathode. The reactive oxygen species may be contacted with methane in a separate compartment or vessel.

In yet another embodiment, the cathode at which the reactive oxygen species are produced is a gas diffusion electrode that is directly exposed to an oxygen containing gas (e.g. air) (as described in Rozendal et al, Electrochem. Commun. 2009, 11, 1752-1755).

In another aspect of the present invention, a biogas containing reduced sulphur compounds may be fed to an anode in order to oxidise the reduced sulphur compounds to elemental sulphur or another oxidized sulfur species. This removes reduced sulphur compounds from the biogas and the biogas may then be mixed with a reactive oxygen species, optionally in the presence of a catalyst, to thereby form methanol or methanol derivatives. In this aspect of the present invention, the anode need not necessarily be a bioanode. Rather, the electrochemical system can be a conventional electrochemical cell. Accordingly, in this aspect, the present invention provides a process for producing methanol or methanol derivative comprising the steps of providing an electrochemical cell having an anode and a cathode, supplying a biogas containing methane and reduced sulphur compounds to the anode, oxidising the reduced sulphur compounds at the anode to form elemental sulphur and to remove sulphur compounds from the gas phase, removing a methane containing gas from the anode, providing an aqueous feed to the cathode to thereby form a reactive oxygen species at the cathode, and mixing the reactive oxygen species with the methane containing gas removed from the anode to thereby form methanol or methanol derivative.

In another embodiment of the present invention the anode is supplied with a waste stream and a methane containing gas. The membrane separating anode and cathode allows liquid to pass through but limits crossover of organic constituents. Examples of such membranes are a reverse osmosis membrane, a microfiltration membrane, a nanofiltration membrane, an ultrafiltration membrane, or a dialysis membrane. The liquid and gaseous effluents of the anode are separated at the end of the anode or in another compartment,

for example via a gas exchange membrane. The gas flow is sent to the cathode or a separate reaction vessel, as previously described.

In another embodiment of the present invention the reaction compartment where methanol is produced is operated at temperatures above 30°C, preferably above 50°C, even more preferably above 100°C. This will cause the methanol to be in the gaseous form. The effluent of the reaction compartment is sent through a distillation column to separate the methanol from the product stream.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic diagram of an apparatus suitable for use in one embodiment of the present invention;

Figure 2 shows a schematic diagram of an apparatus suitable for use in another embodiment of the present invention;

Figure 3 shows a schematic diagram of an apparatus suitable for use in another embodiment of the present invention;

Figure 4 shows a schematic diagram of an apparatus suitable for use in another embodiment of the present invention;

Figure 5 shows a schematic plan view of another embodiment of the present invention;

Figure 6 shows a schematic view of a further embodiment of the present invention; and

Figure 7 shows a schematic view of a further embodiment of the present invention.

DETAILED DESCRIPTION OF THE DRAWINGS

It will be appreciated that the drawings have been provided for the purposes of illustrating preferred embodiments of the present invention. Therefore, it will be understood that the present invention should not be considered to be limited solely to the features as shown in the attached drawings.

The description of the drawings also makes reference to the reactive oxygen species being hydrogen peroxide. However, the present invention also encompasses the use of other reactive oxygen species that may be formed at the cathode.

Figure 1 shows an apparatus suitable for use in one embodiment of the present invention. The apparatus shown in figure 1 comprises a bioelectrochemical system 10 having an anode compartment 12 and a cathode compartment 14. The anode compartment 12 has an anode 16 and the cathode compartment 14 has a cathode 18. An electrical circuit, comprising wiring 20 and an electrical load or an electrical power source 22, is used to electrically connect the anode 16 to the cathode 18. An ion permeable membrane 24 separates the anode compartment 12 from the cathode compartment 14 and allows ionic species to pass through the membrane 24 to thereby close the electrical circuit and maintain charge balance in the bioelectrochemical system.

The anode compartment 12 includes a liquid inlet 26 and a liquid outlet 28. A waste stream, such as a wastewater or an effluent from an anaerobic digester is fed to the anode compartment 12 via the liquid inlet 26. In the anode compartment 12, the waste stream is subject to oxidation by virtue of the presence of microorganisms in the anode compartment 12. The microorganisms oxidise organic material in the anode compartment 12 and transfer electrons to the anode 16. Treated waste is removed from the liquid outlet 28 of the anode compartment 12.

The cathode compartment 18 has a liquid inlet 30 and a liquid outlet 32. An aqueous material, such as water, is supplied to the cathode compartment 14 via liquid inlet 30. The cathode compartment 18 also includes a gas inlet 34 and a gas outlet 36. Oxygen or oxygen containing gas (such as air) may be supplied to the cathode compartment 14 via

gas inlet 34. In the cathode compartment, the aqueous material reacts with the oxygen at the cathode to form hydrogen peroxide. Alternatively, oxygen or oxygen containing gas may be mixed with the aqueous stream entering the cathode compartment via liquid inlet 30.

The gas inlet 34 may also be used to supply methane gas to the cathode compartment 14. The methane gas reacts with the hydrogen peroxide formed in the cathode compartment to form methanol or a methanol derivative. To facilitate reaction between hydrogen peroxide and the methane, a catalyst 38 may be provided in the cathode compartment 18. The catalyst 38 may, for example, be deposited on a high surface area substrate or it may be deposited on an inner wall of the cathode compartment. Alternatively, the catalyst 38 may be a finely-divided catalyst that is suspended in the liquid material in the cathode compartment 14.

A mixed product stream containing water and methanol is removed via liquid outlet 32.

Figure 2 shows another embodiment of the present invention. In figure 2, those features that are common with the features of figure 1 are denoted by similar reference numerals, except that a "1" has been added to the front of the reference. For example, anode compartment 112 in figure 2 corresponds to anode compartment 12 in figure 1. These features of figure 2 that are common to the features shown in figure 1 needs not be described further.

In the apparatus shown in figure 2, the anode compartment 112 is provided with a gas inlet 140. A biogas containing methane, reduced sulphur compounds (such as H_2S) and carbon dioxide, is supplied to the anode compartment 112 via gas inlet 140. The biogas may comprise a biogas generated from an anaerobic digester.

The biogas supplied to the anode compartment 112 reacts with the electrochemically active microorganisms present in the anode compartment to cause oxidation of the reduced sulphur compounds. This results in the formation of elemental sulphur (which

will typically be formed as solid sulphur) at the anode 116. Electrons are transferred to the anode 116 and travel via the electrical circuit to the cathode 118.

The apparatus 110 shown in figure 2 also includes a gas permeable membrane 124. The gas permeable membrane 124 allows gas to travel from the anode compartment 112 to the cathode compartment 114. As the sulphur compounds present in the biogas that is supplied to the anode compartment 112 have been oxidised to elemental sulphur, the gas that flows through the gas permeable membrane 124 comprises essentially methane and carbon dioxide. Essentially no sulphur compounds are present in the gas that travels through the gas permeable membrane 124. This is important because many catalyst that catalyse the reaction of hydrogen peroxide with methane are poisoned by sulphur compounds.

In the cathode compartment 114, oxygen or an oxygen-containing gas is supplied via gas inlet 134. An aqueous medium, such as water, is provided via liquid inlet 130. Hydrogen peroxide is formed at the cathode and this hydrogen peroxide reacts with the methane that passes through the gas permeable membrane 124 into the cathode compartment to form methanol or a methanol derivative. Excess oxygen and carbon dioxide are removed from the cathode compartment 114 via gas outlet 136. The gas leaving the gas outlet 136 may be treated to separate any unreacted methane therefrom. The unreacted methane may be mixed with the biogas stream entering the anode compartment 112 via gas inlet 140.

Figure 3 shows a schematic diagram of apparatus suitable for use in a further embodiment of the present invention. The apparatus shown in figure 3 has a number of features in common with the apparatus shown in figure 1. For convenience and brevity of discussion, features in figure 3 that are in common with features in figure 1 will be denoted by a similar reference numeral, except that a "2" will be added to the front of the reference numeral. For example, anode compartment 12 shown in figure 1 corresponds to anode compartment 212 shown in figure 3. These features need not be described further.

Operation of the apparatus shown in figure 3 is very similar to that shown in figure 1 in that a wastewater stream is supplied as a feed material to the anode compartment 212. In the anode compartment 212, the waste stream is oxidised by electrochemically active microorganisms. Similarly, in the cathode compartment 214, hydrogen peroxide is formed as described with reference to figure 1.

Where figure 3 differs from figure 1 is that a hydrogen peroxide containing stream is removed from the cathode compartment 214 through liquid outlet 232. The hydrogen peroxide containing liquid stream is then fed to a vessel 250. Vessel 250 includes a catalyst 238. Methane is supplied to vessel 250 via methane inlet 252. A gas exhaust 254 is provided to vent excess gas from the vessel 250. In vessel 250, the methane reacts with the hydrogen peroxide to form methanol or a methanol derivative. A mixed stream containing water and methanol is removed via liquid outlet 256.

It will be appreciated that the apparatus shown in figure 2 may also be modified along a similar fashion such that reaction between methane and hydrogen peroxide occurs in a separate reaction vessel. This is shown schematically in figure 4. The apparatus shown in figure 4 has a number of features in common with the embodiment shown in figure 2. For convenience and brevity of discussion, features shown in figure 4 that are common to features shown in figure 2 shall be denoted by a similar reference numeral, except that the numeral "3" will be used at the front of the reference numeral instead of the numeral "1". For example, the anode compartment 312 of figure 4 corresponds to the anode compartment 112 of figure 2.

The embodiment shown in figure 4 is generally similar to that shown in figure 2 in that a biogas is supplied via gas inlet 342 the anode compartment 312 and elemental sulphur is produced in the anode compartment. Similarly, oxygen and an aqueous stream are provided to the cathode compartment 314 to thereby form hydrogen peroxide in the cathode compartment. However, unlike the embodiment shown in figure 2, the membrane 324 used in figure 4 is not a gas permeable membrane, but rather is an ion permeable membrane. The treated biogas having substantially no gaseous sulphur compounds in it is

removed from the anode compartment via gas outlet 360 and transferred via line 362 to vessel 370. Simply, the hydrogen peroxide containing stream is removed from cathode compartment 314 via liquid outlet 332 and line 364 and is also supplied to vessel 370. Vessel 370 has a catalyst 338 for catalysing the reaction between methane in the gas provided to the vessel 370 through gas inlet 366 and hydrogen peroxide in the liquid stream supplied to the vessel 370 via liquid inlet 368. A liquid stream containing methanol is removed from the vessel 370 via liquid outlet 372. Excess gas is vented from the vessel 370 via gas outlet 374. The gas that is being vented from the vessel 370 may be treated to separate any unreacted methane therefrom. The thus-separated methane may be returned to the anode compartment 312 via gas inlet 340.

Figure 5 shows a schematic plan view of another embodiment of the present invention. In figure 5, the cathode compartment 400 surrounds an inner chamber 402. Methane is provided to the inner chamber 402. A membrane 404 that is permeable to hydrogen peroxide separates the cathode compartment 400 from the internal chamber 402. A further membrane 406 is positioned between the cathode compartment 400 and the anode compartment (not shown). The anode compartment, although not shown in figure 5, is positioned externally to the cathode compartment 400. A catalyst layer 408 is provided in the inner chamber 402 and the catalyst layer 408 catalyses the reaction between methane and hydrogen peroxide to form methanol.

It will also be understood that the embodiment shown in Figure 5 may be arranged so that a central anode chamber is surrounded by the cathode chamber, with the reaction chamber that receives methane being external to the cathode chamber.

Figure 6 shows a schematic view of a further embodiment of the present invention. In figure 6, the apparatus 500 includes an anode chamber 502 and a cathode chamber 504. The anode chamber is provided with an anode 506 and the cathode chamber is provided with a cathode 508. The anode and the cathode are placed in electrical connection with each other via an electrical circuit (not shown, but which will be readily understood by a person skilled in the art). A membrane 510 is positioned between the anode chamber 502

and the cathode chamber 504. The membrane 510 allows for the passage of ions therethrough to thereby complete the electrical circuit in the apparatus 500. The apparatus 500 shown in figure 6 may also include means for supplying waste water or biogas to the anode compartment and means for supplying oxygen and an aqueous medium to the cathode chamber. These features may be as described with reference to the embodiments shown in figures 1 to 4. For clarity and brevity of description, these features have been omitted from figure 6.

The cathode chamber 504 is also provided with a further membrane 512. Membrane 512 allows hydrogen peroxide to pass therethrough. The membrane 512 separates the cathode chamber 504 from a further chamber 514. Further chamber 514 is arranged so that a methane containing gases can pass through chamber 514. A catalyst 516 is arranged in the chamber 514. The catalyst 516 catalyses the reaction between hydrogen peroxide and methane to form methanol.

The embodiments shown in figures 5 and 6 can be advantageously engineered as a circular system (figure 5) or as a thin stack system (figure 6).

Figure 7 shows a schematic view of a further embodiment of the present invention. In figure 7, features that are common with figure 1 are denoted using the same reference numeral, but with the addition of a "7" to the beginning of the reference numeral. For example, anode compartment 712 in figure 7 corresponds to anode compartment 12 in figure 1. These features need not be described further.

The cathode compartment 714 of figure 7 includes a gas diffusion electrode 718. This gas diffusion electrode allows gas, such as oxygen or other gases, to diffuse into cathode compartment 714. Although figure 7 shows gas inlet 734 and gas outlet 736, it will be appreciated that these may not be required if the gas diffusion electrode 718 has sufficient gas transfer capacity to enable the gas feed and gas exhaust requirements of the cathode chamber to be met.

It will also be understood that hydrogen peroxide generates reactive oxygen species. Throughout this specification, reference to hydrogen peroxide should also be taken to include references to such reactive oxygen species, especially in relation to the reaction between methane and hydrogen peroxide.

Those skilled in the art will appreciate that the present invention may be susceptible to variations and modifications other than those specifically described. It will be understood that the present invention encompasses all such variations and modifications that fall within its spirit and scope.

CLAIMS.

1. A process for producing methanol or a methanol derivative from methane comprising the steps of:
- providing a bioelectrochemical system having a bioanode and a cathode;
- causing oxidation at the bioanode,
- providing an aqueous medium to the cathode to produce a reactive oxygen species at the cathode; and
- reacting the reactive oxygen species with methane to form methanol or a methanol derivative.

2. A process for producing methanol or a methanol derivative from methane comprising the steps of:
- providing a bioelectrochemical system having a bioanode and a cathode;
- causing oxidation at the bioanode,
- having a power supply in an electrical circuit connecting anode and cathode,
- applying a voltage with the power supply,
- providing an aqueous medium to the cathode to produce a reactive oxygen species at the cathode, and;
- reacting the reactive oxygen species with methane to form methanol or the methanol derivative.

3. A process as claimed in claim 1 or claim 2 wherein the reactive oxygen species comprises hydrogen peroxide or a reactive oxygen species formed from hydrogen peroxide or oxygen in an aqueous medium, $OH^{\cdot}$, O_2^{-} or ozone, or mixtures of two or more thereof.

4. A process as claimed in any one of claims 1 to 3 wherein the cathode is supplied with a gas flow containing oxygen or the aqueous medium provided to the cathode contains dissolved oxygen.

5. A process as claimed in any one of claims 1 to 4 wherein the bioanode is supplied with a waste stream which contains organic and/or inorganic material.

6. A process as claimed in any one of claims 1 to 4 wherein the bioanode is supplied with a biogas or a combination of biogas and a waste stream.

7. A process as claimed in claim 6 wherein the biogas contains reduced sulphur compounds and the reduced sulphur compounds are oxidised at the bioanode.

8. A process as claimed in claim 6 or claim 7 wherein the biogas contains methane and at least some of the methane is oxidised to carbon dioxide at the anode.

9. A process as claimed in any one of the preceding claims wherein the bioelectrochemical system includes a membrane or a passage that allows electrical charge to flow between the bioanode and the cathode in order to complete the electrical circuit in the bioelectrochemical system.

10. A process as claimed in claim 9 wherein the membrane comprises a bipolar membrane, an anion exchange membrane, a proton exchange membrane or a cation exchange membrane, or a a gas permeable membrane or a porous structure.

11. A process as claimed in any one of the preceding claims wherein methane is added to the cathode, where it reacts with the reactive oxygen species.

12. A process as claimed in any one of claims 1 to 10 wherein methane is mixed with the reactive oxygen species in a separate compartment to the cathode.

13. A process as claimed in any one of the preceding claims wherein the methanol is further converted to a hydrocarbon over a catalyst, said catalyst being present in the cathode, or in a separate vessel where the reactive oxygen species reacts with methane or in another vessel.

14. A process as claimed in any one of the preceding claims wherein methane is mixed with the reactive oxygen species by bubbling or sparging methane containing gas through a liquid containing the reactive oxygen species.

15. A method as claimed in claim 14 wherein methane is bubbled or sparged through the liquid in the cathode compartment of the bioelectrochemical system, or a methane-containing gas is fed to the anode compartment of the bioelectrochemical system and the bioelectrochemical system is provided with a gas permeable membrane between the anode compartment and the cathode compartment with the methane passing from the anode compartment through a gas permeable membrane and into the cathode compartment, or a methane-containing gas is fed to the anode compartment of the bioelectrochemical system and the bioelectrochemical system is provided with a passage that allows transport of the gas exiting the anode to the cathode or to another vessel where the methane in the gas can react with hydrogen peroxide.

16. A process as claimed in any one of the preceding claims wherein a catalyst to catalyse the reaction between the methane and the hydrogen peroxide in order to form the methanol or methanol derivative is provided.

17. A process as claimed in claim 15 wherein the catalyst forms part of the cathode.

18. A process as claimed in any one of the preceding claims wherein the reaction compartment where methanol is produced is operated at temperatures above 30°C, preferably above 50°C, even more preferably above 100°C.

19. A process as claimed in any one of the preceding claims wherein a voltage is applied to the cell amd the voltage applied between the anode and the cathode is between 0 and 2.5 V, preferably between 0 and 1.5 V, more preferably between 0 and 1.0 V and the cell has a volumetric current density of between 0 and 10,000 A/m^3 of bioelectrochemical cell, preferably between 10 and 5,000 A/m^3 of bioelectrochemical

cell, more preferably between 100 and 2500 A/m^3 of bioelectrochemical cell and/or an area specific current density of between 0 and 1,000 A/m^2 membrane surface area, preferably between 1 and 100 A/m^2 membrane surface area, more preferably between 2 and 25 A/m^2 membrane surface area.

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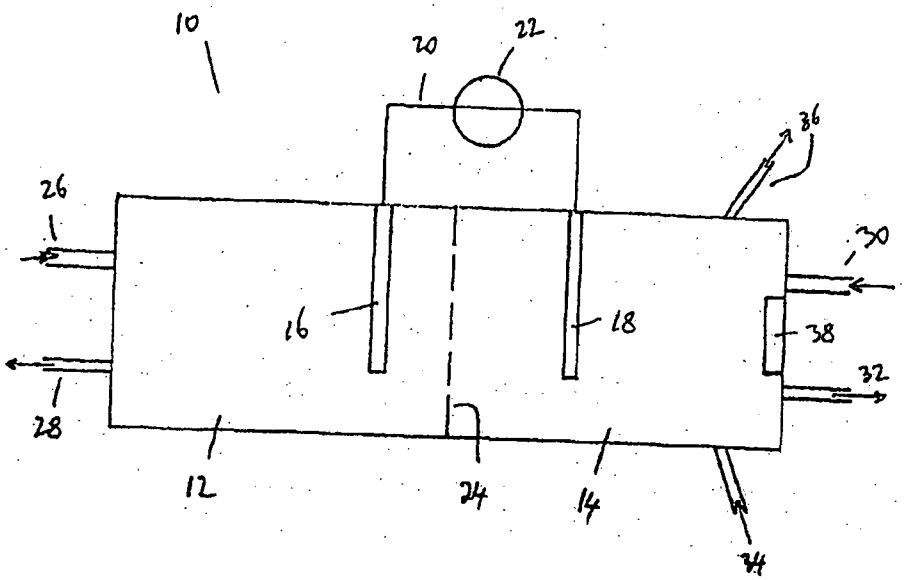


Figure 1

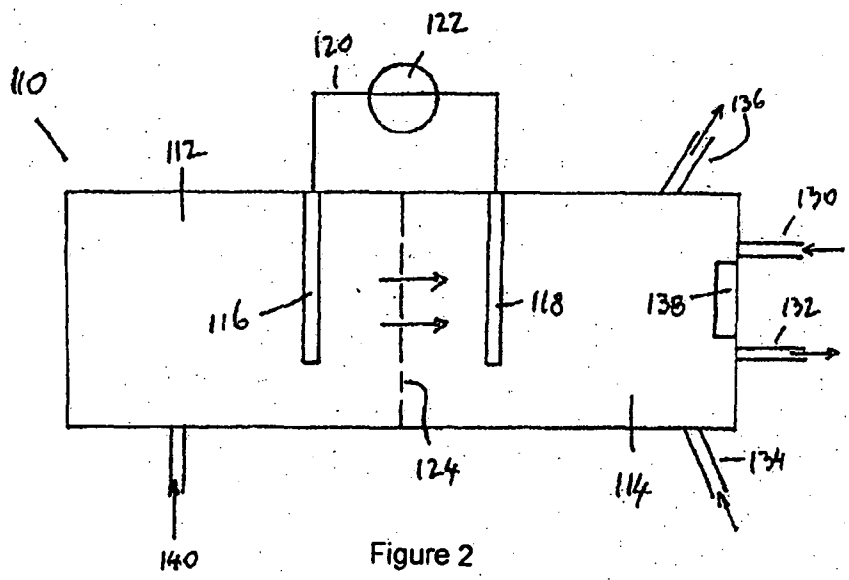


Figure 2

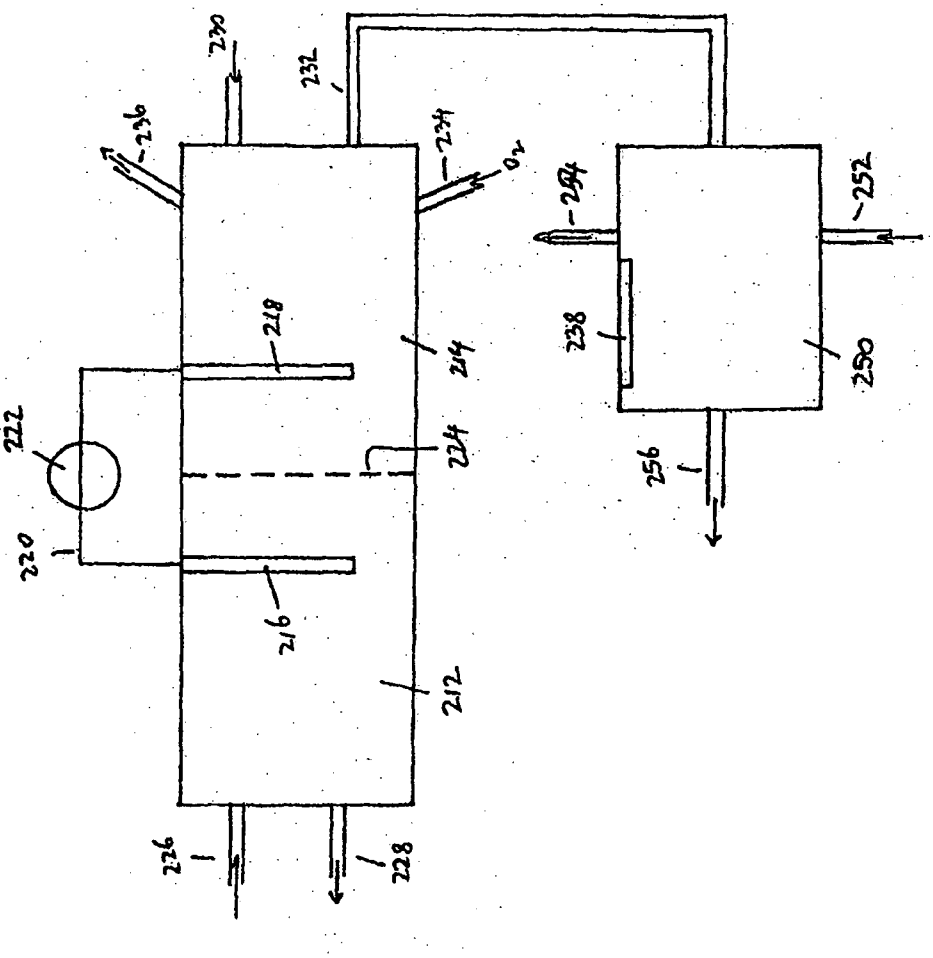

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Figure 3

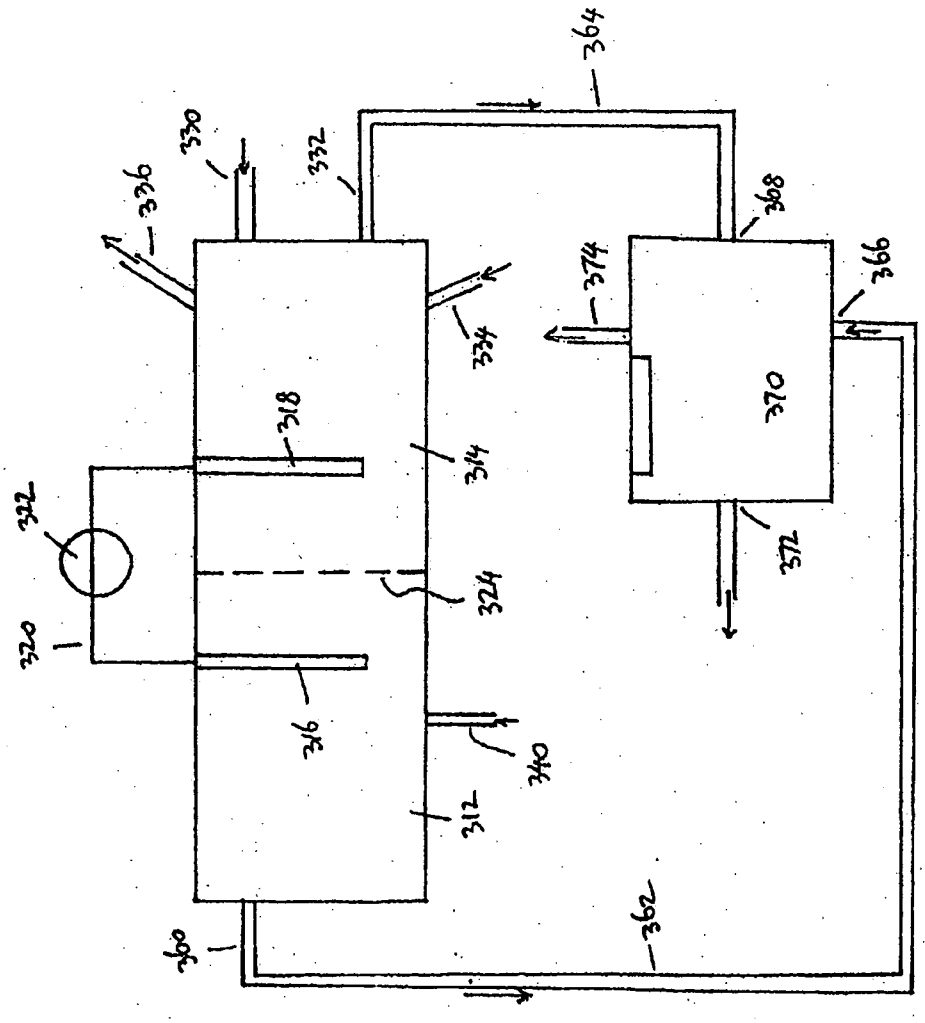

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Figure 4

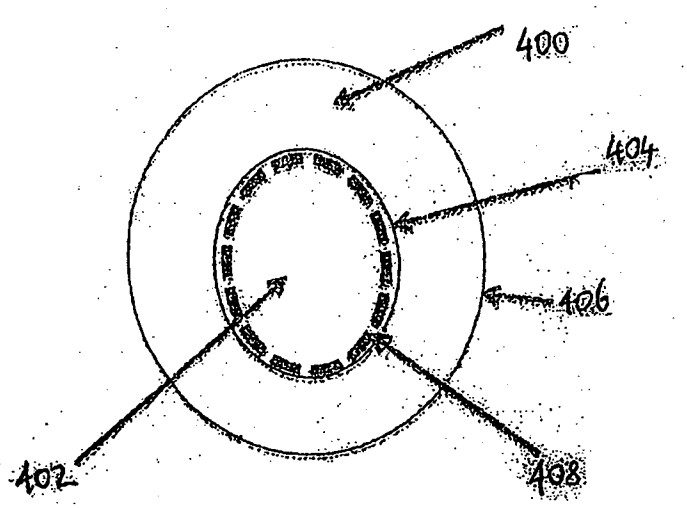


Figure 5

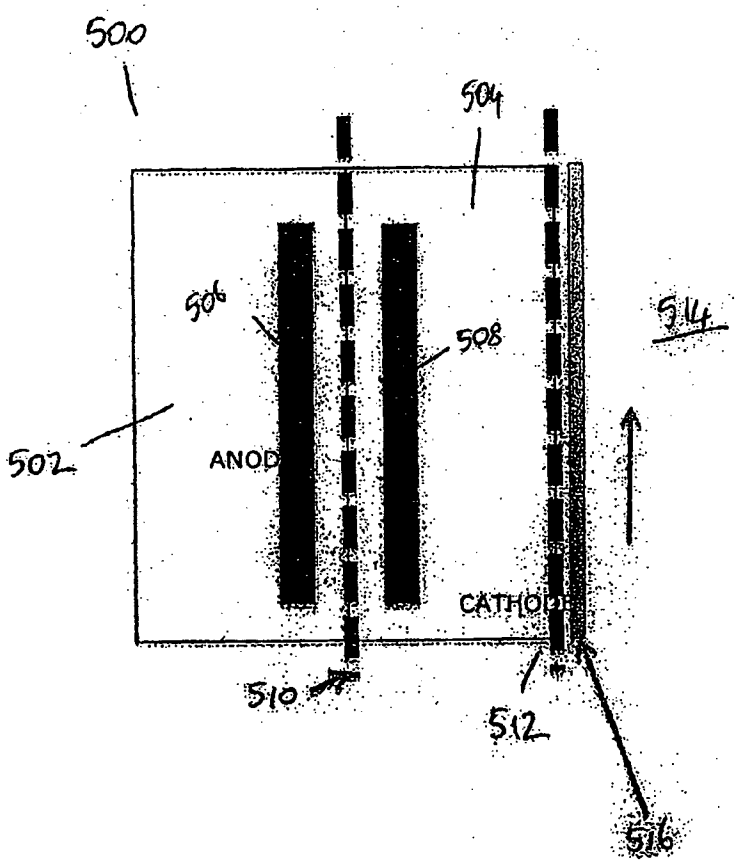


Figure 6

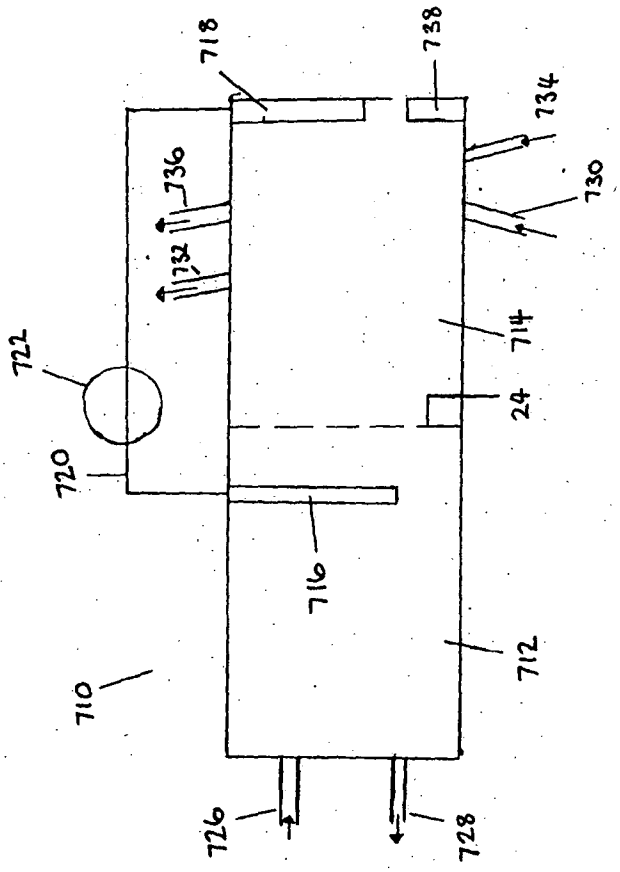


Figure 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2009/001629

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C07C 31/04 (2006.01) *C25B 3/02* (2006.01) *C25B 5/00* (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI, EPODOC, CAPLUS, AGRICOLA, WPIDS: Keywords (biomass, algae, microorganism, biogas, anode, electrochemistry, fuel cell, bioanode, peroxide, oxygen, methane, production and like terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ASTIER, Y. et al., 'Cofactor-independent oxygenation reactions catalyzed by soluble methane monooxygenase at the surface of a modified gold electrode', European Journal of Biochemistry 2003, vol. 270, pages 539-544 Abstract and page 540, column 1, lines 1-4 and column 2, lines 1-5	1-4, 9, 11, 14-16
A	TOMITA, A. et al., 'Direct Oxidation of Methane to Methanol at Low Temperature and Pressure in an Electrochemical Fuel Cell' Angew. Chem. Int. Ed. 2008, vol. 47, no. 8, pages 1462-1464	1-19
A	CLAUWAERT, P. et al., 'Minimizing losses in bio-electrochemical systems: the road to applications', Applied Microbiology and Biotechnology 2008, vol. 79, pages 901-913	1-19

☐ Further documents are listed in the continuation of Box C ☐ See patent family annex

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 February 2010	12 FEB 2010
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **Jocelyn Chan** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6283 2914