(12) UK Patent Application (19) GB (11) 2628860 (13) A

(43) Date of A Publication 09.10.2024

(21) Application No: 2305672.4

(22) Date of Filing: 18.04.2023

(30) Priority Data:
(31) 63492624 (32) 28.03.2023 (33) US

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(51) INT CL:
C12P 3/00 (2006.01) ***E21B 43/00*** (2006.01)
E21B 43/29 (2006.01)

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Int J Hydrogen Energy, Vol 47, 2022, MJ Veshareh et al, "The light in the dark: In-situ biorefinement of crude oil to hydrogen using typical oil reservoir Thermotoga strains", 5101-5110

(58) Field of Search:
Other: **SEARCH-PATENT**

(54) Title of the Invention: **Process and plant**
Abstract Title: **Process and plant for the microbial production of hydrogen from the site of hydrocarbonaceous deposit**

(57) Process and plant for the microbial production of hydrogen from the site of hydrocarbonaceous deposit, the process comprising modifying the composition of the deposit through the introduction into or into the vicinity of the deposit of at least one hydrogen producing microorganism, wherein the at least one hydrogen producing microorganism or at least one microbiological condition conducive to the thriving of the microorganism is selected, or its selection is aided, by means of core flood methodology, the plant comprising means in the form of core flood methodology apparatus for selecting at least one hydrogen producing microorganism and/or for selecting at least one microbiological condition conducive to the thriving of the microorganism; and means for supplying the at least one hydrogen producing microorganism into the hydrocarbonaceous deposit.

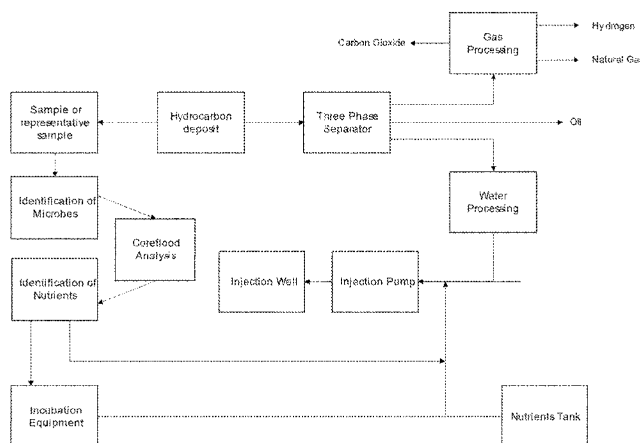

FIG. 1

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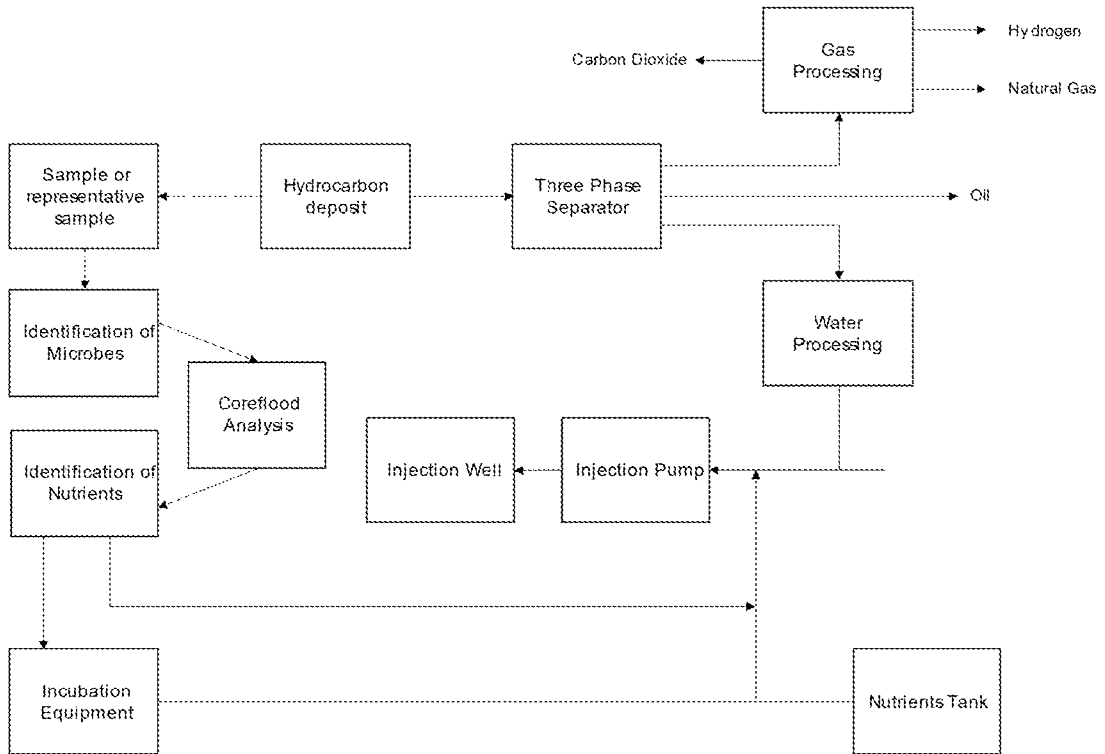

FIG. 1

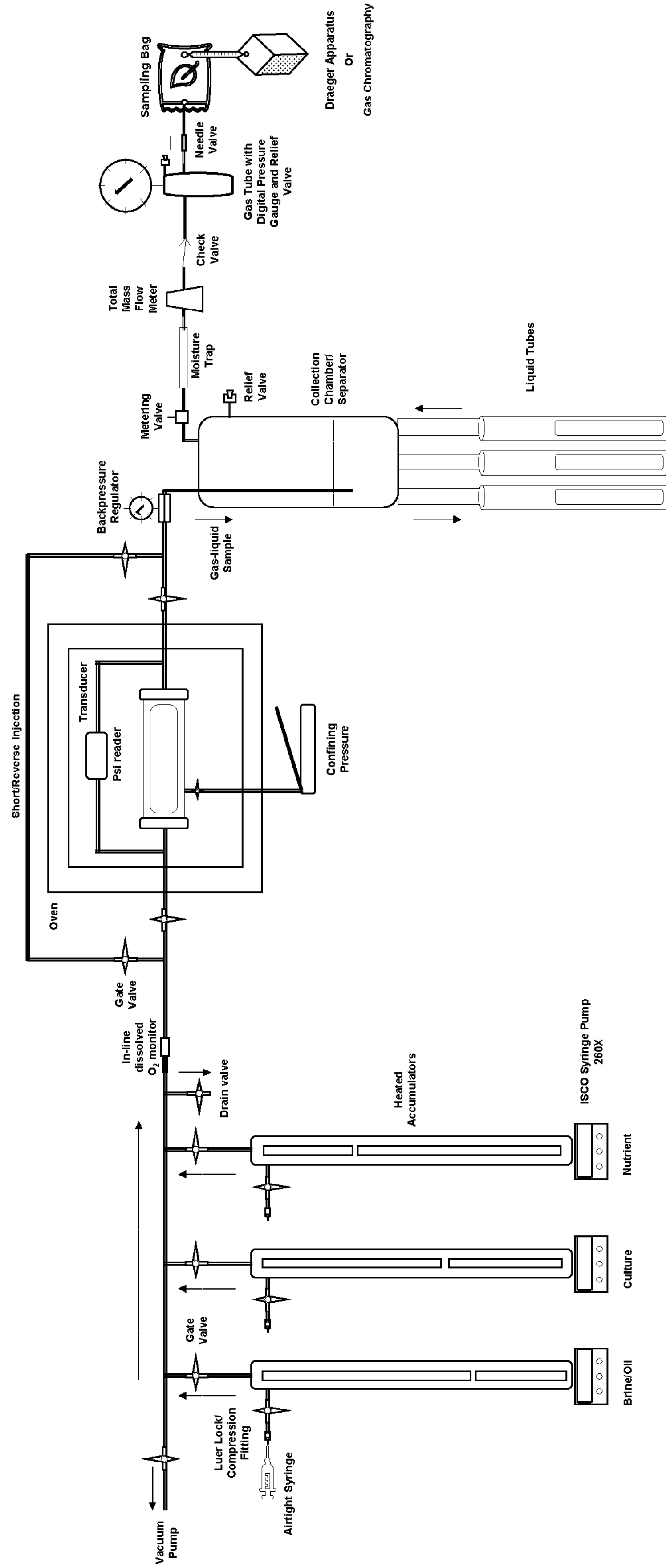

FIG. 2

PROCESS AND PLANT

FIELD

[0001] The present invention concerns a process and plant for the microbiological production of hydrogen from a hydrocarbonaceous deposit, especially a subterranean deposit, employing core flood methodology for the purposes of selecting one or more hydrogen-producing microorganisms for delivery into or into the vicinity of the hydrocarbonaceous deposit.

BACKGROUND

[0002] Hydrogen is an important fuel and chemical process substrate. It is known in the art to use microbes to produce hydrogen from hydrocarbon substrates.

[0003] WO2005115648 describes a process for characterizing and then manipulating the environment of fermentative syntrophic microorganisms naturally present in a petroleum-bearing subterranean formation in order to promote microbial generation of hydrogen in the formation.

[0004] WO2015052806 similarly describes the use of an Fe(III) activator compound to stimulate subterranean microbial hydrogen and methane and also suggests *ex situ* cultivation and subsequent re-injection of microbes naturally occurring in the subterranean environment.

[0005] WO2005113784 describes a method for enhancing microbial production of hydrogen from a hydrocarbon rich deposit. The disclosure favors achieving this by stimulating the metabolic activities of indigenous microorganisms within the deposit, including by the introduction of exogenous (possibly genetically modified) organisms having metabolic capabilities of interest. These metabolic capabilities are not defined except insofar as their impact is to improve net hydrogen production, and contextually this seems to mean by inhibiting the consumption of hydrogen rather than by metabolization of hydrocarbons to hydrogen within the deposit. This document therefore fails to appreciate or to disclose the introduction into the deposit of further microorganisms which are non-native to the deposit and which themselves are capable of metabolizing hydrocarbons to molecular hydrogen and which serve to increase hydrogen production in the deposit by positively diversifying the microbiological abundance of microorganisms in the deposit.

[0006] WO0234931 describes a method of generating and recovering methane from solid carbonaceous deposits. This disclosure suggests to inject bacterial consortia into such deposits and recognizes that hydrogen as well as methane may be produced, but methane production is the clear objective of the disclosure and fermentative hydrogen producers are envisioned as being useful only insofar as they provide a feedstock for methanogenesis.

[0007] Our co-pending application PCTUS2022076925, the contents of which are hereby incorporated by reference, describes a process for the microbiological production of hydrogen from a hydrocarbon-rich deposit. The process comprises modifying the composition of the deposit by the introduction of hydrogen producing microorganisms selected to diversify the microbiological abundance of hydrogen-producing microorganisms in the deposit and for the preferential production of hydrogen over methane.

[0008] WO2011098770 describes a method and a system for predicting the effect of microbes injected into an oil-bearing reservoir using computer-implemented modeling based on simulating the effect of injecting microbes into a multiple core flood apparatus.

[0009] Singh et al., "Overview of Carbon Capture Technology: Microalgal Biorefinery Concept and State-of-the-Art", *Frontiers in Marine Science*, 6, 2019, details an overview of carbon capture technology, and in particular microalgal biorefineries, as a means to combat climate change. Singh et al. detail how microalgae can be used to convert raw materials into high and low value products and fuels derived from biomass.

[0010] Barnhart et al., "Enhanced coal-dependent methanogenesis coupled with algal biofuels: Potential water recycle and carbon capture", *International Journal of Coal Geology*, 171, 2017, 69-75, details methods for stimulating the production of methane from coal bed methanogenesis by introducing further additives to the coal bed to stimulate the activity of the native microorganisms.

[0011] Davis', "Organic amendments for enhancing microbial coalbed methane production", *Montana State University*, 2017, details the use of organic amendments, i.e. the addition of microbes and/or additives, to enhance the microbial processes for coal-to-methane produced coalbed methane, a form of natural gas found in subsurface coal beds wherein the methane is generated by native microbes to the coal bed. The process detailed therefore focuses on the addition of additives to enhance an already natural process.

[0012] In the exemplified prior art examples, the primary focus concerns the manipulation of indigenous microbial populations or their environment, in some cases with the aid of other microbes which inhibit hydrogen consumption or which are themselves methanogenic. Little attention has been paid to the practical difficulties of selecting on-site microbiological reagents, especially in circumstances where it is desirable to select, adapt or engineer such reagents for optimization of their hydrogen producing efficacy at the site in question.

SUMMARY OF THE INVENTION

[0013] According to a first aspect of the present invention there is provided a process for the microbial production of hydrogen from the site of hydrocarbonaceous deposit, the process comprising modifying the composition of the deposit through the introduction into or into the vicinity of the deposit of at least one hydrogen producing microorganism, wherein the at least one hydrogen producing microorganism or at least one microbiological condition conducive to the thriving of the microorganism is selected, or its selection is aided, by means of core flood methodology.

[0014] The core flood methodology may comprise extracting a material sample from the site or selecting a material sample representative of a material from the site and subjecting the sample to analysis determinative of its response to microbiological conditions.

[0015] Preferably the sample extraction or sample selection is conducted under anaerobic conditions. Preferably the extracted or selected sample is then maintained under anaerobic conditions in any interim period between sample extraction or selection and its subjection to core flood methodology, which also preferably takes place under anaerobic conditions. These precautions can help to ensure that the microbiological material(s) extracted from the site or otherwise selected are not degraded, or not excessively degraded, following extraction or selection and during exploratory investigation by means of core flood methodology.

[0016] The material sample may comprise a geological or mineralogical sample (for example rock, porous rock, sand, shale, clay) and/or a hydrocarbonaceous sample (for example oil, natural gas or coal). The geological or mineralogical sample may be extracted from the site of the hydrocarbonaceous deposit or it may be otherwise selected to be representative – in at least one of its geochemical or geomineralogical characteristics - of on-site material. For example, when the site is characterisable by the geological presence of sandstone material the process of the invention may be

realized by selecting a standard geological or geomineralogical core sample – such as Berea sandstone – and subjecting that selected sample to analysis by means of core flood methodology in order to determine suitable conditions for the sustainability or enhancement of microbiological activity with respect to hydrogen production of hydrogen-producing microorganism(s) within the sample.

[0017] The material sample may be subjected to determinative analysis on or off the site of the hydrocarbonaceous deposit.

[0018] The determinative analysis may comprise maintaining the sample under desirable conditions of temperature, pressure and/or chemical environment (e.g. salinity) and determining a response of the sample to one or more microbiological conditions.

[0019] The desirable conditions may at least to some extent replicate one or more of the those conditions (of temperature, pressure and/or chemical environment) of the site location from which the sample is extracted.

[0020] The at least one hydrogen producing microorganism may be a non-native microorganism. By "non-native" is meant that the microorganism does not occur naturally at the site, or does not occur naturally in abundance at the site. An "abundance" may be defined as comprising, in a sample taken from the site, over 10%, over 5% or over 1% w/w of all microorganisms in the sample.

[0021] The hydrogen producing microorganism or at least one microbiological condition conducive to the thriving of the microorganism may be selected by means of the core flood methodology positively to diversify the microbial abundance of hydrogen-producing microorganisms in the deposit when charged thereto, and optionally also for the preferential production of hydrogen over methane. This will especially be the case when the hydrogen producing microorganism is a non-native hydrogen producing microorganism.

[0022] According to a second aspect of the present invention there is provided plant for the microbial production of hydrogen from a hydrocarbonaceous deposit comprising: means in the form of core flood methodology apparatus for selecting at least one hydrogen producing microorganism and/or for selecting at least one microbiological condition conducive to the thriving of the microorganism; and means for supplying the at least one hydrogen producing microorganism into the hydrocarbonaceous deposit.

[0023] Preferably the means for supplying the at least one hydrogen producing microorganism into the hydrocarbonaceous deposit comprise means for also providing into the deposit the at least one microbiological condition conducive to the thriving of the microorganism.

[0024] The core flood methodology apparatus may be provided on or off the site of the hydrocarbonaceous deposit.

[0025] The plant may additionally comprise means for extracting from the hydrocarbonaceous deposit a product stream comprising at least hydrogen gas generated by the microbiological action in the deposit of the at least one hydrogen producing microorganism selected by means of core flood methodology.

[0026] The core flood methodology may be used to identify the most suitable microorganisms for the deposit, which therefore improve the efficiency of the overall process and improve the yields of hydrogen produced for the deposit.

[0027] The plant provides an effective means of converting hydrocarbon deposits in situ. Once a target well or other site containing such hydrocarbon deposits has been identified its geological and/or geochemical characteristics and/or its responsiveness to microbiological conditions are assessed by means of core flood methodology. In this manner a suitable microbiological agent (or a consortia of microbial agents) may be identified for the most efficacious extraction of hydrogen from that particular site.

[0028] In one aspect of the invention the at least one microbiological agent(s) identified by means of core flood methodology may be charged to a transportable microbiological incubator, optionally together with suitable nutrients and/or adjuvants. The incubator may be maintained under conditions effective for functional maintenance of the microbiological agent(s), and transported in such condition to the site whereupon it can be established by means of suitable connective infrastructure as a "plug and play" unit feeding the microbiological agent(s) and any associated materials directly into or into the vicinity of the hydrocarbon deposits, this being the subject of our co-filed application P13140US.

[0029] The present invention provides a significant advantage over the existing state of the art because core flood analysis allows the response of the geological material to treatment with different microorganisms and nutrient conditions with regards to the efficacy of hydrogen generation from the

material to be effectively explored, improving the overall efficiency of a hydrogen extraction process. Through integration core flood analysis with a process converting a hydrocarbonaceous deposit to hydrogen using microorganisms, a more efficient and versatile conversion of hydrocarbon deposits to hydrogen can be achieved.

DETAILED DESCRIPTION

[0030] In the process and plant of the invention the assessment of the geological, geochemical and/or geo-biochemical characteristics, in particular the response of the geological material to treatment with different microorganisms and nutrient, adjuvant or salinity conditions with regards to the efficacy of hydrogen generation from the material, is effected by means of core flood analysis.

[0031] The technique of core flooding is a method wherein a hydrocarbonaceous and/or mineralogical sample from a given location, or a comparable selected material, is placed under in situ reservoir conditions at least to some extent replicative of those occurring at the given location, and the responsiveness of the sample to a variety of reservoir conditions is explored under laboratory conditions. So, for example, the technique may comprise a method where a sample of a hydrocarbon or rock deposit is removed from a subterranean reservoir or an outcrop, and is then placed under the same *in situ* reservoir conditions for testing in a laboratory setting. Single core flood experiments are well known in the crude oil recovery industry and are analysed in order to give an indication of the effect of reservoir treatments at the laboratory scale..

[0032] In core flood analysis a geological sample from the site is maintained, in the core, under conditions of high pressure and temperature replicative of the *in situ* conditions of the hydrocarbon deposit. The response of the sample to different microbial populations and conditions may be assessed and the most suitable reagents determined for a given deposit. Once that determination has been made the microbial reagents and associated nutrient or adjuvant package can be injected into a hydrocarbon deposit. In the present invention this technique is used to predict the effect of microorganisms injected into an hydrocarbon deposit.

[0033] In some embodiments of the present invention, the selected microorganisms may be charged to a mobile fermentation unit and shipped to site for injection into the deposit.

[0034] The core flood analysis may be carried out at a high pressure, to mimic the in situ conditions of the deposit. The core flood may be carried out at pressures of, up to 2,000 psi, up to 4,000 psi, up to 6,000 psi, up to 8,000 psi, or in most preferable embodiments up to 10,000 psi.

[0035] Core flood analysis also allows for the determination of the propagation behavior of microbes in porous media, which will give us some insight on field implementation. This testing is important for risk mitigation as well as for inching closer to testing under real world conditions.

[0036] The core flood analysis system of the present invention comprises the fluid injection, core flood testing, and fluid analysis.

[0037] The system assesses how high-pressure high-temperature (HPHT) conditions affect fermentation through analysis of factors such as reaction behavior, rates, volumes, side products and precipitation. Core flood analysis also assess the efficiency of the culture in propagating through long distances within the rock formation, and whether cultures can be recycled. More broadly, core flood analysis also allows the assessment of fluid flow through pores, and the effect on flow on the efficiency of fermentation.

[0038] As core flood analysis permits the assessment of the in situ conditions of a hydrocarbon deposit, it informs how the conditions are scaled up to provide full field production metrics, including reserves, production rates and best injection scenarios.

[0039] In the fluid injection stage, fluids are maintained under anaerobic conditions. The fluid injection system may comprise multiple heated accumulators containing brine, oil, microorganism cultures, and/or nutrients. The heated accumulators may be connected to a common line to the core flood chamber by gate valves to regulate the flow to the core flood. Vacuum pumps and airtight syringes may be used to add anaerobic microbes into pump systems. It is important that the dead volume is limited and that connections are easily replaceable. A dissolved oxygen monitor may be used to detect oxygen levels within injection system to ensure anaerobic conditions. The system may further comprise a drain valve. The system may further comprise a vacuum pump to maintain the system under pressure.

[0040] In some embodiments, the flow range may be between 0.001 and 1 ml/min, 0.001 and 10 ml/min, or 0.001 and 107 mL/min.

[0041] In a further particular embodiment, the maximum vacuum pump pressure may be 10,000 psi.

[0042] In the core flood testing stage, a core holder is contained within an oven, and may be made of HASTELLOY C276, a Nickel-chromium-molybdenum wrought alloy that is highly corrosion resistant. The core holder holds the core, in which the sample is contained. In some embodiments the core holder may hold 12 in. length and 1.5 ± 0.1-inch diameter cores. The fluids may be injected into the core, and subjected to high-temperature and pressure conditions. Following a core flood process, the fluid samples pass through a line, which may be controlled by valves, to the fluid sampling and analysis stage.

[0043] In the fluid analysis stage, the gas-liquid sample from the core passes unto a liquid separator collection chamber, which may further comprise liquid collection tubes. The collection chamber collects all gas for discrete or continuous measurements. The liquid collection tubes may be used to trap liquids under anaerobic conditions for further analysis.

[0044] Samples are collected from the collection chamber or separator and pass through a moisture trap to sampling bags. Samples may be analysed by a Draeger apparatus or by gas chromatography to assess different parameters. In some embodiments the measurements made are; liquid volumes (oil/water) vs time, gas flow rate and cumulative mass, the concentration of ATP or side products, pH, gas composition (batch/continuous), the culture adsorption on rocks, and/or emulsion or phase separation.

[0045] In some embodiments, metering valves may be used to regulate flow. In further embodiments, moisture traps may be added to remove humidity and obtain more accurate measurements.

[0046] The hydrogen producing microorganism may be:

a. a microorganism not naturally present in the hydrocarbonaceous deposit; and/or
b. of a strain of microorganisms not naturally present in the hydrocarbonaceous deposit; and/or
c. of a species of microorganisms not naturally present in the hydrocarbonaceous deposit; and/or

d. of a genus of microorganisms not naturally present in the hydrocarbonaceous deposit;
e. a microorganism naturally present in the hydrocarbonaceous deposit; and/or
f. a microorganism naturally present in the hydrocarbonaceous deposit but genetically modified to increase (relative to the naturally present microorganism) its propensity for hydrogen production by the metabolization by that microorganism of one or more hydrocarbons contained within the deposit.

[0047] The at least one hydrogen producing microorganism may be one of a plurality of different hydrogen producing microorganisms, strains of microorganisms, species of microorganisms, genera of microorganisms and/or naturally occurring but genetically modified organisms introduced into the deposit. Genetic manipulation of microorganisms naturally present in the deposit to form non-native species may be effected by directed evolution or other form of synthetic biology. The plurality may be greater than two, greater than three, greater then four, greater than five and/or greater than ten.

[0048] The hydrogen producing microorganism(s) may have a propensity to metabolize one or more hydrocarbons contained within the deposit to molecular hydrogen (preferably in preference to methane) such that the yield of production of molecular hydrogen (H_2) from the metabolization is higher than the yield of production of methane by at least 1%, by at least 10%, by at least 100% and/or by at least 1000%.

[0049] The hydrogen producing microorganism(s) may be introduced into the deposit and accompanied during, after or upon its introduction by at least one nutrient selected to promote the growth of said microorganism and introduced into the deposit for that purpose, optionally wherein the nutrients are supplied from a nutrient reservoir.

[0050] The at least one nutrient may be selected, or its selection aided, by means of core flood methodology.

[0051] The at least one nutrient may be selected preferentially to promote the growth of the said microorganism in preference to at least one, to at least some or to all of any native microorganisms in the deposit.

[0052] The nutrient may comprise one or more of:

a. one or more salts selected from:
    i. phosphates; and/or
    ii. halides; and/or
    iii. nitrates, ammonium salts, nitrogenous salts; and/or
b. one or more carbohydrates selected from:
    i. sugars; and/or
    ii. starches; and/or
c. one or more vitamins; and/or
d. complex nutrients, optionally comprising yeast extracts; corn steep liquor; biomass; bacterial an/or algal biomass.

[0053] As will be apparent from Example 1 below it is particularly advantageous to include at least one carbohydrate and/or complex nutrient in the at least one nutrient.

[0054] The hydrogen producing microorganism may be introduced into the deposit and accompanied during, after or upon its introduction by at least one pH regulator selected to regulate the pH environment in which the microorganism resides in the deposit and introduced into the deposit for that purpose. The pH regulator may be selected to regulate the pH of the hydrogen producing microorganism environment in the deposit to a pH within the range of from about 5 to about 9, from about 6 to about 8 and/or from about 6 to about 7.

[0055] The pH regulator may optionally also serve as a nutrient – for example, phosphate can acts as both a nutrient and as a buffering agent.

[0056] The hydrogen producing microorganism may be introduced into the deposit and accompanied during, after or upon its introduction by at least reducing agent which may or may not be included as part of the nutrient package. Suitable reducing agents include thioglycolic acid (and salts such as sodium thioglycolate), cysteine HCl, Na2S, FeS, dithiothreitol, sodium dithionite, ascorbic acid, oxalic acid, sodium sulfite, sodium metabisulfite, 2-mercaptoethanol, sodium pyruvate, glutathione and compatible mixtures of two or more thereof.

[0057] The hydrocarbonaceous deposit is preferably a liquid hydrocarbonaceous deposit, e.g oil/bitumen/heavy oil.

[0058] The at least one hydrogen producing microorganism may have a genus of Syntrophobacter, Syntrophus, Syntrophomonas, Thermoanaerobacter, Thermotoga, Pseudothermotoga, Thermoanaerobacterium, Fervidobacterium, Thermosipho, Haloanaerobium, Acetoanaerobium, Anaerobaculum, Geotoga, Petrotoga, Thermococcus, Pyrococcus, Clostridium, Enterobacter, Klebsiella, Ethanoligenens, Pantoea, Escherichia, Bacillus, Caldicellulosiruptor, Pelobacter, Caldanaerobacter, Marinitoga, Oceanotoga, Defluviitoga, Kosmotoga, Caloranaerobacter or a combination or mixture thereof.

[0059] The hydrogen producing microorganism may express at least one protein selected from hydrogenases, dehydrogenases, hydroxylases, carboxylases, esterases, hydratases and acetyltransferases having an amino acid sequence at least 95% identical to a sequence expressed by an upregulated or downregulated gene selected from mth (EC 1.12.98.2), mrt, hycA (ID: 45797123), fdhF (ID: 66346687), fhlA (ID: 947181), ldhA (ID: 946315), nuoB (ID: 65303631), hybO (ID: 945902), fdh1, narP, ppk or Pepc by expressing a non-native protein expressing nucleotide sequence, wherein an amount of hydrogen produced or protein produced by the hydrogen producing microorganism is greater than that produced relative to a control microorganism lacking the non-native protein expressing nucleotide sequence.

[0060] The hydrogen producing microorganism may be a recombinant microorganism.

[0061] The recombinant microorganism may express at least one Coenzyme M reductase and or dehydrogenase protein having a gene sequences at least 95% identical to SEQ ID NO. [mmg:MTBMA_c15480], [mth:MTH_1015], [mmg:MTBMA_c15520], [mmg:MTBMA_c15490], [mth:MTH_1166], [mth:MTH_1167], [eco:b4346], [eco:b4345], [ag:AAA22593], [mea:Mex_1p4538, [mea:Mex_1p4535], [ag:ACS29499], [ag:CAH55641], [mrd:Mrad2831_0508], by expressing a non-native Coenzyme M reductase and or dehydrogenase expressing nucleotide sequence.

[0062] Preferably, an amount of hydrogen produced or protein produced by the hydrogen producing microorganism is greater than that produced relative to a control microorganism lacking the non-native protein expressing nucleotide sequence.

[0063] The environment of the hydrocarbonaceous deposit and the introduced hydrogen producing microorganism may constitute an enclosed bioreactor, being a bioreactor subterranean formation, a bioreactor landfill enclosure, or a combination thereof.

[0064] In this case there is provided in accordance with the aforesaid first aspect of the invention and any or each of its described variants a method of increasing hydrogen production from an enclosed bioreactor (as constituted by the environment of the hydrocarbonaceous deposit and the introduced hydrogen producing microorganism) comprising: providing a baseline reaction mixture in the enclosed bioreactor, wherein the baseline reaction mixture includes a hydrocarbon, water, and a baseline amount of at least one microorganism; producing baseline microorganism data on an identity and a baseline percentage of the at least one microorganism, relative to a baseline total percentage of microorganisms in the baseline reaction mixture, by performing DNA and/or RNA sequencing of a baseline microorganism sample from the baseline reaction mixture; measuring a baseline amount of hydrogen in a baseline gas sample of gasses collected from the enclosed bioreactor; increasing hydrogen production from the enclosed bioreactor by forming a synthetic reaction mixture including at least one hydrogen producing microorganism selected by means of core flood methodology, and harvesting the hydrogen from the enclosed bioreactor at a hydrogen harvesting rate by separating the hydrogen from other gasses and transferring the hydrogen into a hydrogen storage container.

[0065] The synthetic reaction mixture is formed by: adding at least one hydrogen producing microorganism selected by means of core flood methodology until a percentage of the hydrogen producing microorganism in the synthetic reaction mixture is at least 20% of a total amount of microorganisms in the synthetic reaction mixture.

[0066] The method may further comprise after providing the baseline reaction mixture, but before forming the synthetic reaction mixture, producing baseline environmental data from the baseline reaction mixture. The baseline environmental data may include one or more of the following measurements of a baseline environmental sample from the baseline reaction mixture: pH; temperature; water analysis; oxidation-reduction potential; pressure; dissolved oxygen; hydrocarbon concentrations; volatile fatty acids concentrations; cation concentration; anion concentration; concentration of gases (such as one or more of NH_3, CO_2, CO, H_2, H_2S and CH_4); salt concentration; and metal concentration. Core flood methodology may be used to investigate any one or more of these parameters.

[0067] The baseline microorganism sample and the baseline environmental sample may be the same or different.

[0068] The hydrogen harvesting rate may be at least about 0.1 L/hr, or at least about 1 L/hr, or at least about 10 L/hr, or at least about 100 L/hr. The hydrogen harvesting rate may be up to about 10^6 L/hr, or up to about 10^5 L/hr, or up to about 10^4 L/hr, or up to about 10^3 L/hr. The hydrogen harvesting rate may be from about 0.1 L/hr to about 10^6 L/hr, or from about 0.1 L/hr to about 10^3 L/hr, or from about 10^3 L/hr to about 10^6 L/hr.

[0069] The subterranean formation may include a natural formation, non-natural formation, a hydrocarbon-bearing formation, a natural gas-bearing formation, a methane-bearing formation, a depleted hydrocarbon formation, a depleted natural gas-bearing formation, a wellbore, or a combination thereof.

[0070] The bioreactor landfill enclosure may include a landfill that is enclosed by a building material. The building material may include at least one of a brick, a cement, a plastic, a non-natural rubber, a geomembrane of any kind, concrete, steel, a glass, or a combination thereof.

[0071] The hydrogen producing microorganism may be supplied to the deposit in combination with a hydrogen production enhancer, for example a biocidal inhibitor, a methanogenesis inhibitor, a sulfate reduction inhibitor, a nitrate reduction inhibitor, an iron reduction inhibitor, or any suitable combination thereof.

[0072] The biocidal inhibitor may be glutaraldehyde, a quaternary ammonium compound, formaldehyde, a formaldehyde releaser such as 3,3'-methylenebis[5-methyloxazolidine], dibromonitrilopropionamide, tetrakis hydroxymethyl phosphonium sulfate, chlorine dioxide, peracetic acid, tributyl tetradecyl phosphonium chloride, methylisothiazolinone, chloromethylisothiazolinone, sodium hypochlorite, dazomet, dimethyloxazolidine, trimethyloxazolidine, N-bromosuccinimide, bronopol, or 2-propenal, or a mixture thereof.

[0073] The methanogenesis inhibitor may be bromethane sulfonic acid, an aminobenzoic acid, 2-bromoethanesulfonate, 2-chloroethanesulfonate, 2-mercaptoethanesulfonate, lumazine, a fluoroacetate, nitroethane, or 2-nitropropanol, or a mixture thereof.

[0074] The sulfate reduction inhibitor may be a molybdate salt, a nitrate salt, a nitrite salt, a chlorate salt, or a perchlorate salt or a mixture thereof.

[0075] The nitrate reduction inhibitor may be sodium chlorate, a chlorate salt, or a perchlorate salt, or a mixture thereof.

[0076] The method of the invention may further comprise producing carbon dioxide from the enclosed bioreactor and optionally processing the carbon dioxide in a useful manner, for example by providing the same as feedstock for a biomass-producing reactor as described in our co-pending USSN 63364275, the contents of which are hereby incorporated by reference, for example.

[0077] The method may further comprise harvesting hydrogen from the enclosed bioreactor at a hydrogen harvesting rate, and separating the hydrogen from other gasses by filtering the hydrogen through a hydrogen-selective membrane filter and transferring the hydrogen into a hydrogen storage container.

[0078] Forming the synthetic reaction mixture may comprise adding the at least one hydrogen producing microorganism until a percentage of the hydrogen producing microorganism in the synthetic reaction mixture is at least about 10% or at least about 20% of a total amount of microorganisms in the synthetic reaction mixture.

[0079] The enclosed bioreactor may have a volume of at least about 100 m3, or at least about 103 m3, or at least about 104 m3, or at least about 105 m3. The enclosed bioreactor may have a volume of up to about 4 x 109 m3, or up to about 4 x 108 m3, or up to about 4 x 107 m3, or up to about 4 x 106 m3. The enclosed bioreactor may have a volume of from about 100 m3 to about 4 x 109 m3, or from about 100 m3 to about 4 x 106 m3, or from about 4 x 106 m3 to about 4 x 109 m3.

[0080] The hydrogen storage container may be a gas tank, a hydrogen subterranean formation, or a hydrogen artificial enclosure.

[0081] The hydrogen subterranean formation may include a natural formation or non-natural formation.

[0082] The hydrogen artificial enclosure may be made of one or more building materials. The building materials may include a cement, a plastic, a non-natural rubber, a geomembrane of any kind, concrete, a metal or metal alloy (such as steel), or a combination thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0083] The invention will now be more particularly described with reference to the following examples and figures, in which;

[0084] Figure 1 is a schematic flow diagram of a process operating in accordance with one aspect of the invention.

[0085] Figure 2 is a schematic illustration of a core flood analysis system suitable for use with the process of Figure.

[0086] The plant, as illustrated by Figure 1, comprises:

a. a hydrocarbonaceous deposit;
b. means for extracting a material sample from the deposit or selecting a material sample representative of a material from the site;
c. core flood methodology apparatus for determining the responsiveness of that sample to a variety of physical, chemical and/or microbiological conditions;
d. equipment for incubating at least one microorganism selected by means of the core flood methodology for efficacious hydrogen production from the deposit;
e. means for supplying the selected microorganism into the hydrocarbonaceous deposit; and
f. means for extracting produced hydrogen from the deposit.

[0087] The hydrocarbon rich deposit may contain crude oil, natural gas or coal. The deposit may comprise a porous rock formation.

[0088] The three phase separator separates water, oil and gas components collected from the hydrogen-rich deposits. The gaseous components are collected and are provided to a gas processing station. The liquid hydrocarbon components are collected and may be subject to further processing, or sold as an end product. The aqueous components are collected and may be provided to a water processing unit, or disposed of.

[0089] The gas processing station is used to process the gaseous products collected from a deposit, and may be used to separate hydrogen, natural gas, and carbon dioxide. In some embodiments of the

present invention, the carbon dioxide may be collected usefully re-processed. The gas processing station also provides a means for cleaning the product gases for further use, or for sale as an end product.

[0090] The water processing unit may be responsible for cleaning the water collected by the three phase separator. In some embodiments of the present invention, undesirable volatile fatty acids (VFAs) may be removed in the water processing unit. The water collected by the three phase separator may further be used as a supply to the injection pump. An advantage of recycling the water from the extraction stages is that waste water is reduced.

[0091] The incubation equipment contains the at least one hydrogen producing microorganism capable of modifying the composition of the hydrogen-rich deposit. The incubation equipment may comprise at least one bioincubator responsible for producing the hydrogen producing microorganisms. In some embodiments, the incubation equipment may be supplied with water from the water processing unit.

[0092] The nutrient tank may contain the nutrients or adjuvants required by the hydrogen producing microorganisms. In preferred embodiments of the present invention, the incubation equipment and the nutrient tank may be housed together.

[0093] The flow of microbes, nutrients from the incubation equipment and water passes to an injection pump, which injects the reaction mixture into an injection well, which is the deposit wherein the microbial production of hydrogen from a deposit occurs.

[0094] The core flood methodology is described more particularly below in Example 3 with reference to Figure 2.

[0095] For the avoidance of doubt, all features relating to the method of the present invention also relate, where appropriate, to the plant of the present invention and *vice versa*.

[0096] It should be apparent that any of the embodiments of the invention, and each or any of their described variants, may be provided in combination with the first or second aspects of the invention and each or any of its described variants and/or in combination with any one or more of each other.

EXAMPLES

Example 1

[0097] Schematically illustrated (for a single well) in Figure 1, two low producing oil wells are stimulated in a huff-n-puff application to increase microbial hydrogen production. A Berea sandstone core is conditioned under anaerobic conditions with an oil representative of an oil sample extractable from the well. Its indigenous microbiological content is determined, with the results set out in Tables 1 and 2 below:

Table 1 – Sample 1 – Indigenous microbial population:

Halanaerobium praevalens DSM 2228	18.1%
Acinetobacter johnsonii	13.4%
Desulfohalobium retbaense DSM 5692	12.1%
Halanaerobium hydrogeniformans	7.4%
Methanohalophilus halophilus	6.0%
Methanohalophilus mahii DSM 5219	4.7%
Escherichia coli	2.0%
Halobacteroides halobius DSM 5150	2.0%
Azospirillum thiophilum	1.3%
Keratinibaculum paraultunense	1.3%

Table 2 – Sample 2 – Indigenous microbial population:

Methanohalophilus halophilus	13.2%
Methanohalophilus mahii DSM 5219	11.0%
Halanaerobium praevalens DSM 2228	7.3%
Desulfohalobium retbaense DSM 5692	6.8%
Halanaerobium hydrogeniformans	3.7%
Acinetobacter johnsonii	3.2%
Petrotoga mobilis SJ95	3.2%
Halothermothrix orenii H 168	2.3%
Flexistipes sinusarabici DSM 4947	2.3%
Pelobacter acetylenicus	1.8%
Methanotorris igneus Kol 5	1.4%

Bacillus mycoides	1.4%

[0098] In the first sample, nutrients are blended as described below in Table 3 into 500bbls of produced water in a frac tank.

Table 3: Nutrient package mixed into the 500bbls:

Reagent	**[g/L]**
K_2HPO_4	1.044
NH_4Cl	1.5
Sucrose	1.41
Yeast extract	1.5
Tween 80	0.081

[0099] The nutrient mix is injected down the annulus of the well (from which sample 1 is representative) and an additional 500bbls of produced water is pumped down the annulus on top of the nutrient mixture. In the second well (of which sample 2 is representative), the same process occurs with the exception that a consortium of microbes capable of producing hydrogen from hydrocarbon fermentation, and the nutrient conditions capable of ensuring thriving of that consortia, is selected by means of core flood methodology and added to the first 500bbls of produced water along with the nutrient package.

[0100] The consortium is prepared by combining hydrogen producing microorganisms selected by means of core flood methodology to be different from the indigenous microbial populations, and for their capability to digest hydrocarbons to yield hydrogen in preference to methane, in the proportions identified in Table 4:

Table 4 – Well 2 – Exogenous microbial population:

Pseudothermotoga elfii	~20%
Pseudothermotoga hypogea	~20%
Thermotoga petrophila	~20%
Petrotoga mobilis	~20%
Caldanaerobacter tengcongensis	~20%

[0101] The exogenous microbes are maintained in anaerobic liquid culture and nurtured for 2 months under nitrogen (100% N2) at 150 F (65.56degC) , with fresh media inoculated every 3-4 days. The selected media is an ATCC 2114 medium modified for preferential culturing of extremophiles.

[0102] Approximately 400L of microbial culture consisting of approximately 10^8 cells/mL is added to the 500bbls.

[0103] Following addition of the nutrient package (Well 1) and the nutrient/microbial consortium package (Well 2), the two wells are shut-in for 4 days. After the four-day shut-in period the wells are opened and samples are collected off the gas flow line for analysis with respect to H2 content on a gas chromatograph, with the results presented in Table 5 below:

Table 5: Gas Chromatography characterization of samples:

Well	**Baseline H2 (ppm)**	**After shut-in H2(ppm)**
1 (nutrients only)	<112 (LOD)	1761
2 (nutrients and microbes)	<112 (LOD)	13251

[0104] The gas chromatography is carried out using a standard protocol as follows: 10 milliliter gas samples are extracted from culture bottles using 10 milliliter plastic luer lock syringes. Field gas samples are collected in multi-layer foil gas sampling bags connected via tygon tubing to a sampling valve directly off the of wellhead flow line. Gas samples are injected immediately into the inlet port of an SRI 8610C Gas Chromatograph. The sample is analyzed using a Flame Photometric Detector (FPD), a Flame Ionization Detector (FID), an FID with a large methanizer (FIDM), and a Thermal Conductivity Detector (TCD).

[0105] The samples are passed through an 18-inch HayeSep D Packed Column, a 3-foot Molecular Sieve 5A Packed Column, and then into the TCD and FIDM detectors following relay G injection. When relay F is turned on the samples are run through a 6-foot HayeSep D Column and a 60-meter MXT-1 Capillary Column before being analyzed using the FID and FPD. The G relay is turned on at time 0.020 minutes and is turned off at 1.000 minutes, while the F relay is turned on after 4.500 minutes. The initial temperature is set for 50° C and held for 6 minutes before ramping to 270°C at a rate of 30°C per minute. The temperature is held at 270°C for 6.500 minutes to remove excess sample from the columns.

[0106] Any peak areas produced are converted into ppm values using the trend lines of calibration curves derived from standards of various concentrations.

[0107] It will be seen from the results in Table 5 that modifying the composition of the well by the introduction into the well of a nutrient package and of consortium of hydrogen producing microorganisms selected by means of core flood methodology positively to diversify the microbiological abundance of hydrogen-producing microorganisms in the well and for the preferential production of hydrogen over methane increases hydrogen production from the well by two orders of magnitude with respect to baseline H2 production, and by an order of magnitude with respect to introduction of the nutrient package alone.

Example 2: Microbe Laboratory Data

[0108] The consortium of microbes described in Example 1 and capable of producing hydrogen from hydrocarbon fermentation is used to inoculate 6 different synthetic seawater blends in triplicate as described below in Table 6.

Table 6: Synthetic seawater blends:

Brine	**Description**
A	Synthetic seawater
B	Synthetic seawater with oil
C	Synthetic seawater with nutrients
D	Synthetic seawater with nutrients and oil
E	Synthetic seawater with enhanced nutrients
F	Synthetic seawater with enhanced nutrients and oil
G	Synthetic seawater with algae biomass and oil

[0109] Synthetic seawater is a simple reproducible representative of produced water brines. It is produced using NeoMarine aquarium salts by Brightwell Aquatics. The oil used in this example is a sweet west Texas crude blend (API 25-35). 4mL of the oil is used in 100mL synthetic seawater sample. The nutrient packages employed are as follows in Tables 7, 8 and 9:

Table 7: Synthetic seawater with nutrients:

Reagent	**[g/L]**

Aquarium Salts	35.40290621
K_2HPO_4	0.348
KH_2PO_4	0.227
NH_4Cl	0.5
Wolfes Vitamin solution	10mL
Reducing agent	1
Resazurin solution	~1mL
dH_2O	989mL
Combine, pH to desired 6.5 +- 0.5), filter sterilize	

Table 8: Synthetic seawater with enhanced nutrient package:

Reagent	**[g/L]**
Aquarium Salts	35.40290621
K_2HPO_4	0.348
NH_4Cl	0.5
Glucose	0.47
Yeast extract	0.5
Tween 80	0.027
Reducing agent	1
Resazurin solution	~1mL
dH_2O	999mL
Combine, pH to desired 6.5 +- 0.5), filter sterilize	

Table 9: Synthetic seawater with algae biomass nutrient package:

Reagent	**[g/L]**
Aquarium Salts	35.40290621
K_2HPO_4	0
NH_4Cl	0
Glucose	0
Yeast extract	0
Chlorella algae powder	0.5
Tween 80	0.027
Reducing agent	1
Resazurin solution	~1mL

dH_2O	999mL

[0110] A 100mL sample of each brine A-E is prepared anaerobically in glass bottles and sealed. Following inoculation, the bottles are incubated at 65C for 48 hours along with abiotic controls for each brine.

[0111] At 48 hours, samples are taken for ATP analysis (microbial enumeration) and gas analysis, the results of which are shown in Table 10.

Table 10: ATP Analysis:

		Abiotic Control		Inoculated	
Brine	Description	H2 Concentration (ppm)	Microbial enumeration (cells/mL)	H2 Concentration (ppm)	Microbial enumeration (cells/mL)
A	Synthetic seawater	0	6.92E+03	0	1.51E+06
B	Synthetic seawater with oil	0	2.00E+04	82.33	7.54E+06
C	Synthetic seawater with nutrients	0	1.40E+03	119	7.55E+06
D	Synthetic seawater with nutrients and oil	0	7.67E+03	1406.7	2.58E+07
E	Synthetic seawater with enhanced nutrients	0	9.80E+03	62.33	3.04E+07
F	Synthetic seawater with enhanced nutrients and oil	0	2.95E+04	2735.33	2.07E+07
G	Synthetic sea water with algae biomass and oil	0	1.18E+07	2365.5	1.01E+08

[0112] In sample E, the enhanced nutrient package used causes rapid microbial growth at 24 hours and all of the carbon source is consumed which leads to a lower reading at 48 hours when no oil is present to maintain microbial activity, which rationalizes the lower H_2 concentration observed for this sample relative to comparative sample C.

[0113] The test kit used for the determination of ATP is the Luminultra QGO-M which is compliant with ASTM Standard E2694 for the measurement of ATP in Metalworking Fluids and D7687 for the measurement of ATP in fuels, fuel/water mixtures and fuel-associated water.

Example 3: Core Flood Methodology

[0114] The microbial and nutrient package selected from Example 2 that can produce hydrogen from hydrocarbon fermentation is used to run dynamic and continuous injection studies at high pressure and temperature with core flood and sandpack equipment (Fig. 2).

[0115] Rock, sand, oil, and brine samples can be obtained from a potential well. The rock and sand sample can also be procured from outcrops or vendor sources that closely resemble the mineralogical and petrophysical properties of subsurface formations.

[0116] The components of these systems were procured from different suppliers. Some of the parts were customized to fit the requirements of the test.

[0117] All the components in the system are pressure tested for leakages. The system was ensured to be leakproof before starting an experiment.

[0118] The rock or sand sample is added to the reactor and closed on both sides. Vacuum pressure is applied to the reactor to remove any trapped air. Nitrogen gas is then injected into the reactor for a few hours to establish anaerobic conditions.

[0119] The pore pressure, confining pressure, and reservoir temperature are established using regulators and a convection oven. The representative rock core or sand is brought to representative fluid saturations by injecting anaerobic brine in the forward direction into the samples in the forward direction at high pressure and temperature. Live or dead crude oil is then injected into the rock or sand in the reverse direction at high pressure and temperature. If the rock or sand are already at representative fluid saturations, they will be used as is without modification.

[0120] The samples can be "aged" at reservoir pressure and temperature to replicate wettability conditions in the subsurface.

[0121] Brine is then injected into the rock or sand in the forward direction to establish fluid pressure. Effluent samples are run through a separator and then collected in separate evacuated collection chambers. The fluid samples can be analyzed discretely or continuously through in-line sensors or

external measurement devices. Some of the parameters that would be analyzed include but not limited to microbial cell count, volatile fatty acids, effluent hydrocarbon composition, gas composition, gas generated volume, liquid volume, and surface adsorption.

[0122] Once the brine pressure is established, the reactors are inoculated by injecting microbes and nutrients into the brine stream in the forward direction at predetermined concentrations.

[0123] When sufficient inoculation is completed, the reactors may be shut-in for a period for microbial growth (otherwise known as a “Huff n’ Puff” lab test). In continuous injection or a “waterflooding” lab test, there will be no shut-in.

[0124] After the shut-in period in the Huff n’ Puff lab test, the flow lines are opened, and brine is injected into the reactor in the reverse direction. Fluid samples are continuously collected in separate evacuated collection chambers. The gas and liquids are then analyzed discretely or continuously.

[0125] In a waterflooding lab test, brine is continuously injected into the rock or sand. Microbes and nutrients can be added as a pill or continuously. Effluent fluid samples are continuously collected in separate evacuated collection chambers. They are then analyzed discretely or continuously.

[0126] The pressure drop across the reactor is continuously measured during the test.

[0127] The end of the test is predetermined based on injection volumes, injection time, soaking time, and data collection metrics.

[0128] Upon completing the test, the rock or sand samples are removed from the reactor and immediately stored in evacuated bottles for further DNA sequencing analysis. They are also analyzed for pore structure or sand surface analysis.

[0129] The reactors, flow lines, and collection chambers are then cleaned thoroughly with solvents and deionized water. They are made ready for the next round of testing.

CLAIMS

1. A process for the microbial production of hydrogen from the site of hydrocarbonaceous deposit, the process comprising modifying the composition of the deposit through the introduction into or into the vicinity of the deposit of at least one hydrogen producing microorganism, wherein the at least one hydrogen producing microorganism or at least one microbiological condition conducive to the thriving of the microorganism is selected, or its selection is aided, by means of core flood methodology.

2. A process according to claim 1 wherein the core flood methodology comprises extracting a material sample from the site or selecting a material sample representative of a material from the site and subjecting the sample to analysis determinative of its response to microbiological conditions.

3. A process according to claim 2 wherein the material sample comprises a geological, mineralogical and/or a hydrocarbonaceous sample.

4. A process according to claim 3 wherein sample is extracted from the site of the hydrocarbonaceous deposit or otherwise selected to be representative – in at least one of its geochemical or geomineralogical characteristics - of on-site material.

5. A process according to any one of claims 2 to 4 wherein the material sample is subjected to determinative analysis on or off the site of the hydrocarbonaceous deposit.

6. A process according to any one of claims 2 to 5 wherein the determinative analysis comprises maintaining the sample under desirable conditions of temperature, pressure and/or chemical environment and determining a response of the sample to one or more microbiological conditions.

7. A process according to claim 6 wherein the desirable conditions at least to some extent replicate one or more of the those conditions (of temperature, pressure and/or chemical environment) of the site location from which the sample is extracted.

8. A process according to claim 6 or claim 7 where in the desirable conditions comprise a pressure of up to about 2,000 psi, up to about 4,000 psi, up to about 6,000 psi, up to about 8,000 psi, or up to about 10,000 psi.

9. A process according to any one of claims 2 to 8 wherein the sample extraction or sample selection is conducted under anaerobic conditions.

10. A process according to claim 9 wherein the extracted sample is maintained under anaerobic conditions in any interim period between sample extraction or selection and its subjection to core flood methodology.

11. A process according to any one of claims 1 to 10 wherein the core flood methodology takes place under anaerobic conditions.

12. A process according to any one of claims 1 to 11 wherein the hydrogen producing microorganism is selected by means of core flood methodology positively to diversify the microbial abundance of hydrogen-producing microorganisms in the deposit when charged thereto.

13. A process according to any one of claims 1 to 12 wherein the hydrogen producing microorganism is selected by means of core flood methodology for the preferential production of hydrogen over methane.

14. A process according to any of claims 1 to 13, wherein the at least one hydrogen producing microorganism is:
    a. a microorganism not naturally present in the hydrocarbonaceous deposit; and/or
    b. of a strain of microorganisms not naturally present in the hydrocarbonaceous deposit; and/or
    c. of a species of microorganisms not naturally present in the hydrocarbonaceous deposit; and/or
    d. of a genus of microorganisms not naturally present in the hydrocarbonaceous deposit;
    e. a microorganism naturally present in the hydrocarbonaceous deposit; and/or
    f. a microorganism naturally present in the hydrocarbonaceous deposit but genetically modified to increase (relative to the naturally present microorganism) its propensity

for hydrogen production by the metabolization by that microorganism of one or more hydrocarbons contained within the deposit.

15. A process according to any of claims 1 to 14, wherein the at least one hydrogen producing microorganism is one of a plurality of different hydrogen producing microorganisms, strains of microorganisms, species of microorganisms, genera of microorganisms and/or naturally occurring, optionally genetically modified, organisms introduced into the deposit.

16. A process according to claim 15, wherein the plurality is greater than two, greater than three, greater then four, greater than five and/or greater than ten.

17. A process according to any of claims 1 to 16 wherein the at least one hydrogen producing microorganism is introduced into the deposit and accompanied during, after or upon its introduction by at least one nutrient selected to promote the growth of said microorganism and introduced into the deposit for that purpose, optionally wherein the at least one nutrient is are supplied from a nutrient reservoir

18. A process according to claim 17 wherein characteristics of the at least one nutrient are determined at least in part by core flood methodology.

19. A process according to any of claims 1 to 18, wherein the at least one hydrogen producing microorganism is introduced into the deposit and accompanied during, after or upon its introduction by at least one pH regulator selected to regulate the pH environment in which the microorganism resides in the deposit and introduced into the deposit for that purpose.

20. A process according to claim 19 wherein characteristics of the at least one pH regulator are determined at least in part by core flood methodology

21. A process according to claim 19 or claim 20, wherein the pH regulator is selected to regulate the pH of the hydrogen producing microorganism environment in the deposit to a pH within the range of from about 5 to about 9, from about 6 to about 8 and/or from about 6 to about 7.

22. A process according to any one of claims 19 to 21, wherein the pH regulator also serves as a nutrient.

23. A process according to any of claims 1 to 22, wherein the hydrogen producing microorganism is introduced into the deposit and accompanied during, after or upon its introduction by at least one reducing agent.

24. A process according to any of claims 1 to 23, wherein the hydrocarbonaceous deposit is a liquid hydrocarbonaceous deposit.

25. A process according to any of claims 1 to 24, wherein the at least one hydrogen producing microorganism has a genus of *Syntrophobacter, Syntrophus, Syntrophomonas, Thermoanaerobacter, Thermotoga, Pseudothermotoga, Thermoanaerobacterium, Fervidobacterium, Thermosipho, Haloanaerobium, Acetoanaerobium, Anaerobaculum, Geotoga, Petrotoga, Thermococcus, Pyrococcus, Clostridium, Enterobacter, Klebsiella, Ethanoligenens, Pantoea, Escherichia, Bacillus, Caldicellulosiruptor, Pelobacter, Caldanaerobacter, Marinitoga, Oceanotoga, Defluviitoga, Kosmotoga, Caloranaerobacter* or a combination or mixture thereof.

26. Plant for the microbial production of hydrogen from a hydrocarbonaceous deposit comprising: means in the form of core flood methodology apparatus for selecting at least one hydrogen producing microorganism and/or for selecting at least one microbiological condition conducive to the thriving of the microorganism; and means for supplying the at least one hydrogen producing microorganism into the hydrocarbonaceous deposit.

27. Plant according to claim 26 wherein the means for supplying the at least one hydrogen producing microorganism into the hydrocarbonaceous deposit comprise means for also providing into the deposit the at least one microbiological condition conducive to the thriving of the microorganism.

28. Plant according to claim 26 or claim 27 wherein the core flood methodology apparatus is provided on or off the site of the hydrocarbonaceous deposit.

29. Plant according to claim any one of claims 26 to 28 additionally comprising means for extracting from the hydrocarbonaceous deposit a product stream comprising at least

hydrogen gas generated by the microbiological action in the deposit of the at least one hydrogen producing microorganism selected by means of core flood methodology.

30. Plant adapted and arranged to operate the process of any one of claims 1 to 25.

Intellectual Property Office

Application No:	GB2305672.4	**Examiner:**	Dr Patrick Purcell
Claims searched:	1-30	**Date of search:**	26 October 2023

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
Y	1	WO02/34931 A (GUYER & SCOTT) see whole document
Y	1	WO2005/113784 A (LUCA TECHNOLOGIES, LLC) see whole document
Y	1	Int J Hydrogen Energy, Vol 47, 2022, MJ Veshareh et al, "The light in the dark: In-situ biorefinement of crude oil to hydrogen using typical oil reservoir Thermotoga strains", 5101-5110 see whole document, available online at https://www.sciencedirect.com/science/article/pii/S0360319921045067
Y	1	US2012/0255726 A (LOMANS) see whole document, esp. para 0050, Example
Y	1	US8868392 B (BEATTIE ET AL) see whole document, esp. column 10, lines 41-53
Y	1	US8658412 B (CHOBAN ET AL) see whole document, esp. Examples 9 and 20
Y	1	US7484560 B (LAL ETA L) see whole document, esp. Example 1
Y	1	US2018/0237683 A (CONNELL ET AL) see whole document, esp. paras 0585-0587, 0598-0624
A	-	WO2005/115648 A (UNI NEWCASTLE UPON TYNE ET AL)

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X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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Field of Search:

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SEARCH-PATENT

International Classification:

Subclass	Subgroup	Valid From
C12P	0003/00	01/01/2006
E21B	0043/00	01/01/2006
E21B	0043/29	01/01/2006