



## Description

### Field of the Invention

**[0001]** This invention relates to a method for recovering oil and other hydrocarbons from a subterranean formation.

### Background of the Invention

**[0002]** The primary production of oil and other hydrocarbons from a subterranean reservoir employs that reservoir's natural energy or initial pressure. When the reservoir's own energy is insufficient to maintain oil production, enhanced (secondary or tertiary) oil recovery methods may be utilized to treat production wells and subterranean formations in order to increase petroleum, gas, oil or other hydrocarbon production. These methods are broadly classified into three major categories: thermal injection, chemical injection, and gas injection. And the effectiveness of such methods in oil recovery (Rf) is broadly described by a given method's contribution to macroscopic oil displacement - determined by both horizontal and vertical sweep efficiency - and microscopic oil displacement.

**[0003]** The injections of gases into subterranean formations - to displace oil in the field and to effectively push the oil to a collector point with the purpose of maintaining reservoir pressures, avoiding condensation in retrograde reservoirs and thereby stabilizing production levels. A variety of gases - such as nitrogen, oxygen, carbon dioxide (CO<sub>2</sub>), C<sub>1</sub>-C<sub>4</sub> alkanes and flue gases - have been used in this context, with each having advantages and disadvantages depending on reservoir and operation conditions. The present application is directed to gas injection operations in which nitrogen is used together with CO<sub>2</sub>.

**[0004]** Given that CO<sub>2</sub> is both stable and non-toxic, CO<sub>2</sub> flooding has been commonly used to recover oil from reservoirs in which the initial pressure has been depleted through primary production and possibly water-flooding. As the CO<sub>2</sub> is forced into the reservoir via injection wells a zone of miscible CO<sub>2</sub> and light hydrocarbons forms a front. Production is from an oil bank that forms ahead of the miscible front: as that miscible front is soluble in the oil, it causes a reduction in the viscosity of the oil and also oil-swelling which renders it easier to move the displacement front towards the production wells. As reservoir fluids are produced through production wells, the CO<sub>2</sub> reverts to a gaseous state and provides a "gas lift" similar to that of the original reservoir natural gas pressure.

**[0005]** Despite its utility, certain disadvantages of using carbon dioxide have been identified. Firstly, CO<sub>2</sub> may either not be available in sufficient volumes or not be economically transferred to the oil bearing formation. Secondly, capillary pressures within the reservoir can cause water to be drawn into the zone saturated with CO<sub>2</sub>, both

from above and below: the resultant lowering of the CO<sub>2</sub> in said zone lowers its mobility, and therefore decreases the distance the gas can penetrate into the reservoir before gravity segregation moves it to the top of the formation, the macroscopic sweep efficiency of CO<sub>2</sub> thus being diminished. Thirdly, individual stratum within facies can possess highly variable permeability to CO<sub>2</sub> flooding and, consequently, CO<sub>2</sub> may tend to channel through higher permeability strata. Further, carbon dioxide in the presence of water forms carbonic acid, which can negatively affect the injectivity of CO<sub>2</sub> over time - particularly in carbonate rock formations - due to mineral scale deposition from the injection waters; the carbonic acid may also have a corrosive effect on reservoir equipment.

**[0006]** Nitrogen is beneficially an inert gas that has no corrosive effect on borehole piping. When nitrogen is injected into an oil-bearing reservoir at a sufficiently high pressure, in excess of 345 Bar (5000 psi), it forms a miscible front by vaporizing lighter oil components. The nitrogen gas, now enriched to some extent, continues to move away from the injection wells, contacting new oil and vaporizing more components, thereby enriching it still further. As this action continues, the leading edge of this gas front becomes so enriched that it goes into solution in the reservoir oil. At this time, the interface between the oil and gas disappears, and the fluids blend as one. The continued injection of nitrogen moves the bank of displaced oil toward the production wells.

**[0007]** Whilst nitrogen has a lower solubility in oil and a lower impact on oil properties than CO<sub>2</sub>, the behaviour of nitrogen is similar to that of CO<sub>2</sub> in the sense that both are not first contact miscible. This renders nitrogen as a suitable replacement for CO<sub>2</sub> where that gas is not available in sufficient volumes or where the corrosive effects of the CO<sub>2</sub> must be mitigated. That said, the efficacy of nitrogen flooding as an oil recovery method is improved when specific conditions exist or are approached in a candidate reservoir: the reservoir oil must be rich in C<sub>2</sub>-C<sub>6</sub> hydrocarbons, often characterized as "light oils" having an API gravity higher than 35°; the residual oil should have a high formation-volume factor, that is the capability of absorbing the added gas under reservoir conditions; and, the oil should be under saturated or low in methane (C<sub>1</sub>).

**[0008]** Given the attendant advantages and disadvantages of carbon dioxide and nitrogen flooding independently, there is an attendant need to optimize any gas injection process in which they are both employed. To do so requires the operative to assess how and when a reservoir must be re-stimulated: that is, for example, how and when to respond to injectivity declines and to variations in the movement of oil displacement fronts within facies; and, how and when to use nitrogen to displace a CO<sub>2</sub> slug and its oil bank. Where a decision to re-stimulate a well is made, the operative must also decide on the amount of gas to be injected, the rate of injection, the pressure of injection and so forth. Whilst desirable injection parameters can be set by extrapolating phase equi-

librium models, for instance, the commitment of those parameters to practice may not however be feasible: the *in situ* availability of gases may be limited; and, the quality of the available fluids may not be suitable for injection.

### Statement of the Invention

**[0009]** In accordance with a first aspect of the present invention, there is provided a method for the recovery of oil or other hydrocarbon deposits from a subterranean formation below a surficial formation, said method comprising the steps of: a) separating an air stream into an oxygen-rich stream and a nitrogen-rich stream; b) pressurizing said nitrogen-rich stream and injecting said pressurized nitrogen stream into the subterranean formation; c) collecting hydrocarbons displaced from the subterranean formation by injected fluid; d) combusting at least a portion of the collected hydrocarbons and generating a carbon dioxide-rich stream from the products of said combustion; and, e) pressurizing said carbon dioxide-rich stream and injecting said pressurized carbon dioxide stream into the subterranean formation, wherein in said method at least a portion of the oxygen-rich stream is used in step d).

**[0010]** The nitrogen rich stream will usually be injected into said subterranean formation either prior to and / or subsequent to the injection of said carbon dioxide rich stream, with a cyclic injection of the two gas streams being preferred. The simultaneous injection of the nitrogen rich stream and said carbon dioxide rich stream into said subterranean formation - at one or more times during the performance of the method or a given injection cycle thereof - is not precluded by the invention. However, as co-injected nitrogen and carbon dioxide may separate out in the formation due to density differences - causing nitrogen to move to the top of the reservoir - any such simultaneous injection is preferably performed at a molar ratio by of  $N_2$  to  $CO_2$  of less than 1:10, preferably less than 1:20.

**[0011]** The steps of air separation a) and combustion d) may all be performed proximate to the site of gas injection(s). The effective provision of *in situ* sources of carbon dioxide and nitrogen injectants obviates the need to transport these gases over long distances. Process steps a) and d) can also be controlled to modify the available gas volumes at a given time in the injection or oil recovery regime.

**[0012]** The combustion step d) will release energy and generate water as products in addition to carbon dioxide. Importantly, energy so released should be used for at least one of: said air separation step a); pressurization of said nitrogen rich stream; and, pressurization of said carbon dioxide rich stream. Additionally, that energy may be employed to control the temperature of the nitrogen, oxygen and carbon-dioxide rich streams.

**[0013]** In an embodiment, the method may further comprise the step of injecting an aqueous fluid into said subterranean formation. That aqueous fluid injectant may

advantageously be derived by dilution of production water brought to the surface during said hydrocarbon collection step c), that dilution serving to lower the production water's salinity. And water condensed from the combustion products of step d) may optimally be used to dilute that production water. Making use of production water and / or the condensed water can obviate the need to transport water for injection over substantial distances.

**[0014]** In accordance with a second aspect of the invention there is provided a system for use in the above defined method, said system comprising: an air separation unit; a fuel combustion unit; and, at least one injector unit for introducing injectants under pressure into a subterranean formation.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0015]**

Figure 1 is a schematic illustration of a method in accordance with the present invention.

Figure 2 shows one embodiment of a system for use in a method in accordance with the present invention.

Figure 3 shows a further embodiment of a system for use in a method in accordance with the present invention.

Figure 4 shows a system for controlling the method of the present invention.

Figure 5 depicts a number of examples of flow profiles for the injected gases that may be employed in the method of the present invention.

### DETAILED DESCRIPTION OF THE INVENTION

#### Definitions

**[0016]** As used herein, the terms "comprises," "comprising," "includes," "including," "has," or "having" are intended to cover a non-exclusive inclusion.

**[0017]** The use of "a" or "an" to describe the various elements herein should be read to include one or at least one of said elements; the singular also includes the plural unless it is obvious that it is meant otherwise.

**[0018]** As used herein, the terms "nitrogen-rich" and "carbon dioxide-rich" are intended to denote mixtures which comprise at least 50 mol.%, usually at least 75 mol.% or at least 90 mol.% of nitrogen (as  $N_2$ ) and carbon dioxide (as  $CO_2$ ) respectively.

**[0019]** As recognised in the art, salinity is a measure of the amount of dissolved particles and ions in water.

**[0020]** As described by Collins, A. G. in *Geochemistry of Oilfield Waters*, Elsevier, New York 1975, most oil and gas wells produce a saline solution, or brine, in addition to the desired oil and gas. Such saline solutions / brines generally have moderate to high salinities - for example from 5,000 to 270,000 mg/L dissolved solids - and their major solutes are sodium and calcium chlorides, which are accompanied by a wide range of other solutes at

lower concentrations. As strictly speaking, the term "brine" means water with more than 35,000 mg/L total dissolved solids (Hem, J. D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 264), the term "production water" is used herein to denote the chloride-rich waters found in sedimentary environments and brought to the surface during oil and gas production and will thus incorporate variously oil-field brines, oil-and-gasfield brines, sedimentary-basin brines, and saline formation water often found in the art.

[0021] The salinity values given herein define the compositions of the production water at the time it was sampled at the surface. As production water may have undergone a number of changes during accumulation in the well bore, travel to the surface, and sampling, this may not reflect the salinity of the brine at depth in the reservoir rocks.

[0022] As used herein, the term "cyclic injection" refers to gas injection which occurs in batches into a single well, "shutting it in" after every injection. The shut-in time, sometimes referred to as soaking time, permits gas migration into the reservoir and the interaction between the injected gas and the oil-in-place. Production resumes after the shut-in period. A cycle, by-definition, begins with gas injection and ends when the production rate has dropped to below an economic limit.

### The Nitrogen-Rich Injectant

[0023] The nitrogen which is to be injected to the subterranean formation is, in the present invention, derived at least in part from an air stream which is fed into a suitable air separation unit. These units may utilize air separation technologies including but not limited to cryogenic distillation, ambient temperature adsorption and membrane separation to form the desired oxygen-rich and nitrogen-rich streams from the inputted air stream. Suitable and optimal conditions under which these units may be operated or under which these technologies may be performed can be easily established by person of ordinary skill in the art and are thus not critical to the present invention in its broadest sense.

[0024] The thus separated nitrogen-rich stream is in whole or in part compressed - using a suitable compressor - to generate a pressurized nitrogen stream. Without intention to limit the present invention, the pressure at which the nitrogen injectant will typically be injected into the underground reservoir at a pressure of at least 80 Bar, preferably at least 100 Bar e.g., 140 or 200 Bar.

[0025] The nitrogen rich stream from the air separation unit may comprise gases, such as argon, in addition to N<sub>2</sub>. Further, to form the nitrogen rich injectant, the stream from the air separation unit may be mixed with one or more non-condensable gases - including but not limited to natural gas, C1-C4 alkanes, ethylene, hydrogen sulfide, carbonyl sulfide, air, combustion flue gas, argon and mixtures thereof - intended for co-injection into the

reservoir. Of these, natural gas, C1-C4 alkanes, (supplementary) argon and combustion flue gas are preferred as they may be sourced *in situ*, either directly from the recovered hydrocarbons, by combustion of a fraction of recovered hydrocarbons or by air separation processes.

[0026] Furthermore, as is known the art, the nitrogen-rich injectant may comprise additives, typically in an amount up to 5 wt. %, based on the weight of the injectant, said additives including, but not limited to, surfactants, corrosion inhibitors, co-surfactants, scale inhibitors, and mixtures thereof.

[0027] Whilst it is preferred that at least 75% by volume, preferably at least 80% by volume of any nitrogen (as N<sub>2</sub>) to be injected into the subterranean formation should be derived from the air separation process, the use of alternative nitrogen sources is not precluded. In an embodiment, up to 25% by volume of the injected nitrogen (N<sub>2</sub>) can be derived from a nitrogen recovery or rejection unit (NRU) whereby nitrogen recovered from the reservoir together with natural gas and natural gas liquids is separated from those hydrocarbons by cryogenic processing, pressure swing absorption (PSA) and the like. Advantageously, this additional source of nitrogen may be disposed proximate to a production well and / or an injection well.

### The CO<sub>2</sub>-Rich Injectant

[0028] The physical state of CO<sub>2</sub> varies depending on pressure and temperature; it can exist as a solid, liquid, vapor (gas) or a supercritical fluid. Carbon dioxide is in a liquid phase when subjected to a pressure of about 1,000 psi (68.9 Bar) and a temperature below about 31°C. In addition, the carbon dioxide can transition to a supercritical phase when, at a pressure of about 1,000 psi (69 Bar), the temperature rises above 31°C.

[0029] In embodiments of the present disclosure, the carbon dioxide rich injectant is injected, through wells, into the reservoir formation under conditions of pressure and temperature wherein the carbon dioxide may be in either a supercritical phase or a liquid phase. As used herein, the term "dense phase" is a collective term for CO<sub>2</sub> when it is in either the supercritical or liquid states. For most oil recovery projects, economics will drive the need for any transport of CO<sub>2</sub> to the injection wells to be in its dense phase since vapor phase transmission would require considerably larger diameter pipelines for the same mass flow rate. As the injected dense phase carbon dioxide descends in the wellbore, it is heated by a naturally increasing temperature, causing it to become more gas-like within the wellbore or in the formation in the immediate vicinity of the wellbore.

[0030] The dense phase carbon dioxide may be co-injected with one or more non-condensable gases including but not limited to natural gas, C1-C4 alkanes, ethylene, hydrogen sulfide, carbonyl sulfide, air, combustion flue gas, and mixtures thereof. Of these, nitrogen, natural gas, C1-C4 alkanes, argon and combustion flue gas are

preferred as they may be sourced *in situ*, either directly from the recovered hydrocarbons or by combustion of a fraction of recovered hydrocarbons.

[0031] Furthermore, as is known the art, the second fluid may comprise additives, typically in an amount up to 5 wt.%, based on the weight of the second fluid injectant, said additives including, but not limited to, surfactants, corrosion inhibitors, co-surfactants, scale inhibitors, and mixtures thereof.

### Optional Aqueous Fluid Injectant

[0032] As noted above, the process of the invention may further include the injection of an aqueous fluid into the subterranean formation. It is preferred if this aqueous fluid is at least in part sourced locally to the injection site. More preferably the aqueous fluid injectant is derived from production water.

[0033] Good results have been obtained when the aqueous fluid injectant is derived by lowering the salinity of that production water by: demineralization, for which suitable demineralization equipment may be provided by Industrial Water Equipment Ltd; and / or dilution with one or more lower salinity aqueous fluids.

[0034] The diluting fluid is not intended to be limited. It may for instance be distilled water, demineralised water and / or de-ionized water. Equally, and for marine operations in particular, seawater or treated seawater - which has been subjected to at least one of filtration, de-oxygenation or a biocidal treatment to remove algae and other microbes - may be employed where the salinity of the production water is sufficiently high. In other circumstances, water from freshwater lakes, rivers or aquifers - which may be similarly treated to remove particulates, microbes and oxygen - may provide a source of water for lowering the salinity of seawater or production water. Still further, the diluting liquid may comprise or consist of water condensed from the reaction products of an *in situ* combustion process of recovered hydrocarbons.

[0035] The aqueous fluid injectant has a lower salinity than the production water. In a preferred but not limiting embodiment, average dissolved salt content of the injected aqueous fluid is less than 10,000 ppm total dissolved solids (TDS), preferably less than 5,000 ppm TDS, more preferably less than 2,000 ppm TDS. Alternatively or additionally, the injectant aqueous fluid should have a multivalent cation content lower than 0.02 mol %, preferably less than 0.005 mol %.

[0036] As is known in the art, the processed aqueous fluid to be injected into the subterranean formation may further comprise chemical additives, of which surfactants, polymers such as polyacrylamides, alkylpolyglycosides (APG), alkalis, polypeptides, enzymes, microbes and nano-materials may be mentioned.

[0037] The choice of any included surfactants is not intended to be limiting on the present invention. Suitable surfactants are disclosed in, for instance: US Patent No. 4,113,011; US Patent No. 4,380,266; US Patent No.

4,502,538; US Patent No. 4,739,831; US Patent No. 5,363,915; and, US Patent No. 5,502,538. These disclosures are incorporated herein by reference. As taught in US Patent No. 4,860,828 (Oswald et al.), the aqueous fluid may also include at least one solubilizing component in an amount effective to increase the brine tolerance of the surfactant composition.

[0038] The pH of the aqueous fluid injectant may be any which will function in the process of this invention, but will typically be from 3 to 10 and should preferably be from 5 to 10. The un-dissolved solids content - that is the content of particulates and fines - of the aqueous fluid injectant should be less than 2000 ppm, preferably less than 1000 ppm and more preferably less than 500 ppm.

### Illustrative Embodiments of the Invention

[0039] Figure 1 schematically shows the method according to the invention as applied to a subterranean formation in which oil and / or other hydrocarbons are retained. The subterranean formation will typically have a temperature of from 40°C to 130°C. The subterranean formation may be either a single or multi-layer system wherein individual layers are distinguished by their permeability. In the latter case, each layer may be in communication with layers above or below it, in that, depending on the permeability of those adjacent layers, fluids may migrate from one layer into the other through the interface there-between.

[0040] By injecting the nitrogen rich injectant (2), as defined above, into the formation (1), oil is displaced through the formation in the displacement direction indicated by the arrows. Similarly, the second gaseous injectant (3) here introduced simultaneously with the nitrogen rich stream will also displace the oil therein. A displacement front (4) is generated, the progress of which should be monitored. Oil from the formation (1) is pushed towards the one or more production pipes (5); an extraction pump (not shown) will draw the oil into the pipes and transport it upwards towards the surface (6). Where the nitrogen rich injectant (2) and the second injectant comprising carbon dioxide (3) are injected sequentially, this will generate two independent displacement fronts. The progress of these fronts should preferably be controlled and kept within predetermined limits, dependent on the parameters of a specific field.

[0041] Although Figure 1 shows vertical pipes, the injection and production wells may also be disposed at an angle to the vertical, as is known in the art.

[0042] Figure 2 shows a system (20) that can be used for the supply of injectants for the method described in Figure 1. The system comprises an air separation unit (21) that separates incoming air (22) into its main components, nitrogen gas (23) and oxygen (24). The nitrogen gas may then be used as an injectant. The oxygen (24) is transported to a combustion unit (25) that combusts fuel (26) that may itself comprise oil and gas derived from an oil production method, in particular the method as de-

scribed in figure 1. The combustion unit (25) produces energy (27), as well as carbon dioxide (28) and water (29), which may both be processed for use as injectants in the method described in Figure 1. For example, the carbon dioxide (28) may be subject to: compression or decompression to achieve the desired injection pressure; cooling or heating to achieve the desired injection temperature; and, optionally mixture with other injectants. Moreover, the water (29) may be mixed with production water to lower the salinity of that production water and thus form an aqueous liquid injectant, which may in turn be further processed to its desired injection temperature and pressure.

**[0043]** Figure 3 shows a method (30), wherein an air separator unit (31) separates air (32) into nitrogen gas (33) and oxygen (34). The oxygen is used in a combustion unit (35) to combust fuel (36), yielding energy (37), water (38) and carbon dioxide (39) as main products. The water (38) from the combustion unit (35) is lead to a first injector unit (40). In the injector unit (40), the water is brought to the desired temperature and pressure and is mixed with production water (41) and, optionally other liquids and/or flow-affecting compounds such as surfactants. Subsequently, the derived aqueous liquid (42) is injected into the formation (43) to displace oil and/or gas therefrom. The carbon dioxide (39) and nitrogen gas (33) are independently transportable to a second injector unit (44): in this injector unit (44), the gases are either independently or in admixture brought to the desired temperature and pressure for injection. Optionally, additional gases (45) are added from external sources, such as additional carbon dioxide, nitrogen gas and / or C<sub>1</sub>-C<sub>4</sub> alkanes. The gaseous injectants (46) are then injected into the formation (43) to displace oil and/or gas.

**[0044]** The oil and/or gas so displaced from the formation is then collected at a distance from the injector positions through one or more oil wells (47) connected to a collector unit (48). The thus recovered hydrocarbons are then processed to derive a fraction which is lead to the combustion unit (35) for use as fuel (36). It is preferred that this combusted fraction consists of gaseous hydrocarbon products.

**[0045]** To attain the gases, the recovered hydrocarbons may be passed through a single or multiple stage horizontal separator, a cyclone or another suitable device which can at least segregate the gaseous components from the liquid / solid components. Prior to its combustion, the resultant gaseous hydrocarbon stream may then be further subjected to acid gas removal by which - through contacting the gas stream with either a solvent such as monoethanolamine, diethanolamine, methyldiethanolamine, diisopropylamine and diglycolamine, or commercial products such as Selexol (R) and Rectisol (R) - hydrogen sulphide, water vapour and acid gases including carbon dioxide may be removed and recovered. A further acid gas removal method is disclosed in US2009/0220406A1, the disclosure of which is herein incorporated by reference.

**[0046]** A liquid product stream can be derived by further subjecting the liquid / solid components to one or more of settling, centrifugation and filtration. As residue, these steps should not produce solids *per se* but rather a concentrated slurry of solids in which some liquid hydrocarbon portion is retained. The main liquid product stream from these steps will contain production water or brine which can itself be separated off from the liquid hydrocarbons by gravity, chemical reaction or a combination thereof. And at least a portion of this separated production water (41) can then be led off from the collector unit (48) to the injector unit (40) for mixture with water (38) from the combustion unit.

**[0047]** Separated solid and liquid hydrocarbon streams, and any gas not combusted in the process of the invention, may be transported away as produced gas and/or oil (49).

**[0048]** The method of the present invention is applied to a subterranean, oil-bearing permeable formation penetrated most usually by at least one injection well and at least one spaced-apart production well. The injection well and production well are perforated to establish fluid communication with a substantial portion of the formation.

**[0049]** While oil recovery may most usually be carried out by employing only two wells, the present invention is not limited to any particular number of wells. Purposively, a field will incorporate a planned distribution of gas-injection wells to maintain reservoir pressure and effect an efficient sweep of recoverable liquids; the present invention may thus be practiced using a variety of patterns such as an inverted five spot pattern in which an injection well is surrounded with four production wells, an in-line drive using a series of aligned injection wells and a series of aligned production wells or, conversely, a singular well where a cyclic injection regime ("huff-and-puff") is viable. Further well patterns are illustrated in US Patent No. 3,927,716 (Burdyn et al.). The physical characteristics of a formation - namely its thickness, width, fracture gradient, and vertical and horizontal permeability-should determine both well spacing and any injection rate.

**[0050]** The depth within the formation at which the nitrogen gas injectant, the carbon dioxide and further injectants are injected is not intended to be limited. For instance, all injectants may be introduced at the same depth. Alternatively, they may be introduced at different depths; the carbon dioxide rich injectant might favourably be introduced at the base of a crude oil-bearing facies and the nitrogen rich injectant at a reduced depth, particularly where that crude oil-bearing facies is overlain by a facies containing natural gas or natural gas liquids.

**[0051]** As discussed in TABER et al. EOR Screening Criteria Revisited - Part 1: Introduction to Screening Criteria and Enhanced Recovery Field Projects, SPE Reservoir Engineering, August 1997, immiscible flooding of the oil bearing reservoir with carbon dioxide and nitrogen can be affected by injecting the gases at depth of 550m (1800ft). However, in that preferred embodiment where the nitrogen is injected so as to be miscible with the oil

in place, the nitrogen should preferably be injected at a depth below 1830m (6000 ft). Similarly, in that preferred embodiment where the carbon dioxide is injected so as to be miscible with the oil in place, the carbon dioxide should preferably be injected at a depth below 760m (2500ft).

**[0052]** The injection rate through a given injection well is limited by the pressure at which the reservoir will hydraulically fracture. The "hydraulic fracturing pressure" or "hydraulic fracture pressure" may be determined by a number of methods known in the art: a "mini-frac" or "step-rate" fluid injection test may be mentioned here as a non-limiting Example thereof.

**[0053]** The pressure at which any gas is injected to the formation should be within a range which is below the formation fracturing pressure but above the bubble point pressure of the oil. Moreover, the gas injection pressure should ideally not raise the formation pressure more than about 5% above the formation pressure prior to gas injection or pressure pulsing may arise.

**[0054]** As both miscible and immiscible processes are envisaged as being within the scope of the present invention, the carbon dioxide and nitrogen may be introduced at a pressure respectively above or below the minimum miscibility pressure (MMP) of the injection gas in the oil in place. The minimum miscibility pressure (MMP) is defined as the pressure at which the interfacial tension between the oil and a gas approximates zero at their contact point: the disclosures of Yellig et al "Determination and Prediction of CO<sub>2</sub> Minimum Miscibility Pressure," J. of Pet. Tech., Jan. 1980, pp. 160-168, and Chung et al. Phase Behaviour and Minimum Miscibility Pressures for Nitrogen Miscible Displacement, Department of Energy Report No. NIPER-226, 1986 are hereby incorporated by reference in its entirety.

**[0055]** Factors considered in selecting the actual gas injection pressure also include the incremental oil recovery which can be achieved for a given pressure, the required volume of gas, and the energetic or material cost of compressing gas to a given pressure. This energetic cost can be mitigated in the present invention by using the energy (27, 37) released by combustion of a portion of the recovered hydrocarbons.

**[0056]** The nitrogen rich stream and the carbon dioxide rich stream are generally each injected into the formation for a period of from 0.1 to 500 days duration. Whilst the present method may be terminated after a single injection of each fluid, the fluids are preferably injected repeatedly, the duration of each injection step being independently selected from the aforementioned period of from 0.1 to 500 days. The injection of the nitrogen-rich injectant and of the carbon dioxide rich injectant need not be consecutive but may be punctuated by the injection of one or more alternative fluid injectants. A shut-in or soaking time may be employed between each fluid injection step within the injection regime and may be of the order of from 0.1 to 50 days, preferably from 1 to 10 days e.g. from 2 to 8 or 3 to 6 days.

**[0057]** Figure 4 schematically depicts a system (50) for controlling a method as shown in Figures 1 and 3, and more particularly to control the progress of hydrocarbon displacement in producing layer(s). A control unit (51) receives input from monitoring sensors of the first injector (52) that regulates the injection of a first gaseous or liquid injectant into a given layer, and a second injector (53) that regulates the injection of a second gaseous or liquid injectant into that layer or a distinct, second layer. Optionally, the control unit (51) also receives external monitoring data (54), for instance pressure changes (drops) from the production, injection and / or surveillance wells and/or seismic monitoring data.

**[0058]** The control unit (51) compares the progress of the injectants in the layer(s). Where the progress of the injectants fails to fall within certain thresholds - as described above - the control unit (51) instructs an adjusting unit (55) to adjust *inter alia* the injection ratio of the first injector (52) and the second injector (53). It will be understood that this system (50) can be extended to control run for more than 2 injectors (52, 53) simultaneously.

**[0059]** The level of oil recovery is a major determinative of the duration and volume of each fluid injection sequence: for instance, where the level of oil recovery resulting from the nitrogen injection peaks and then declines, at some predetermined point on the decline curve, the injection sequence for that particular fluid may be terminated and the injection sequence for a second fluid begun. In the present invention, the operative can quickly respond to any decline in oil recovery using very short duration injection cycles and can - in addition or alternatively - rapidly change the composition of the injected fluid using compounds and processes available *in situ*. Figure 5 describes examples of flow profiles that may be used in the present method and which are reflective of the flexibility thereof.

**[0060]** Figure 5a shows a sequential injection profile, schematically showing the injected volumes of injectants over time. The time scale for this method is typically weeks, months or years. The upper line (60) shows the first nitrogen-rich injectant, whereas the lower line (61) shows the second, carbon-dioxide rich injectant. In this profile the injectants are injected intermittently but for equivalent volumes and durations according to a predetermined sequence.

**[0061]** Figure 5b shows a simultaneous injection profile of which the upper line (62) relates to the injected volume of nitrogen gas over time, and the lower line (63) the injected volume of carbon dioxide gas over time. Again here the injectants are injected for equivalent durations and at equal volumes.

**[0062]** In Figure 5c and 5d only a single line (64, 65) is depicted which is to represent schematically the volume injected into the formation over time of either carbon dioxide or nitrogen gas introduced independently or alternatively of an introduced mixture of these gases. In the profile of Figure 5c, the volumes of the injectant are varied for given interval of injection. In the profile of Figure

5d, the interval of injection and the shut-in or soaking time are varied over time.

**[0063]** It will be recognized that these illustrated injection profiles are not mutually exclusive but over time one or more of these profiles may be employed. These injection profiles are further independent of the physico-chemical properties - including for instance the temperature and composition - of the first and second injectants as used at a given time.

**[0064]** Importantly, the injected volumes of the nitrogen, carbon dioxide and optionally further fluids of the present method are monitored by *inter alia* pumps, meters and check valves as is known in the art. In a preferred embodiment of the present invention, the ratio by volume of total injected nitrogen gas (as N<sub>2</sub>) to the total injected carbon dioxide (as CO<sub>2</sub>) is in the range from 0.05:1 to 1:1, preferably from 0.2:1 to 1:1.

**[0065]** Where the process of the present invention further includes the injection of water into the subterranean formation, the ratio by volume of total injected aqueous fluid and total injected gas in a single injection cycle - the WAG or SWAG ratio - is in the range from 0.8: 1 to 5:1. It also within the scope of the present invention to employ "tapering" of the WAG ratio - that is increasing the WAG ratio e.g. from 1:1 to 2:1 to 3:1, at decreased gas slug size - in order to decrease the required gas production and therefore improve the overall economics of the process.

**[0066]** The process of the present invention should typically be continued until the amount of oil recovered from the formation via the production well renders it unfavorable. Without intention to limit the present invention, practical durations for the production to be operative well are from 7 to 20 months, 9-18 months or from 11-16 months.

**[0067]** The principle of the invention and the preferred embodiments contemplated for applying that principle have been described. It is to be understood that the foregoing is illustrative only and that other means and techniques can be employed without departing from the scope of the invention defined in the following claims.

## Claims

1. A method for the recovery of oil or other hydrocarbon deposits from a subterranean formation below a surficial formation, said method comprising the steps of:

- a) separating an air stream into an oxygen-rich stream and a nitrogen-rich stream;
- b) pressurizing said nitrogen-rich stream and injecting said pressurized nitrogen stream into the subterranean formation;
- c) collecting hydrocarbons displaced by the injected fluid;
- d) combusting at least a portion of the collected

hydrocarbons and generating a carbon dioxide-rich stream from the products of said combustion; and,

e) pressurizing said carbon dioxide-rich stream and injecting said pressurized carbon dioxide stream into the subterranean formation,

wherein in said method at least a portion of the oxygen-rich stream is used in step d).

2. The method according to claim 1, wherein said nitrogen rich stream is injected into said subterranean formation at a pressure of at least 80 Bar, preferably at least 100 Bar.
3. The method according to claim 1 or claim 2, wherein a gaseous hydrocarbon product stream is separated off from said collected hydrocarbons and at least a portion of that gaseous hydrocarbon product stream is combusted in step d).
4. The method according to claim 3, wherein said gaseous hydrocarbon product stream is first subjected to acid gas removal prior to said portion thereof being combusted.
5. The method according to any one claims 1 to 4, wherein energy released in the combustion of step d) is used for at least one of: said air separation step a); pressurization of said nitrogen rich stream; and, pressurization of said carbon dioxide rich stream.
6. The method according to any one of claims 1 to 5, wherein said carbon dioxide-rich stream is injected into the subterranean formation at a pressure of at least 80 Bar, preferably at least 100 Bar.
7. The method according to any one of claims 1 to 6, wherein said nitrogen rich stream and said carbon dioxide rich stream are injected simultaneously into said subterranean formation.
8. The method according to any one of claims 1 to 6, wherein said nitrogen rich stream is injected into said subterranean formation either prior to and / or subsequent to the injection of said carbon dioxide rich stream.
9. The method according to any one of claims 1 to 8, wherein said nitrogen rich stream and said carbon dioxide rich stream are injected cyclically.
10. The method according to any one of claims 1 to 9, further comprising the step of injecting an aqueous fluid into said subterranean formation.
11. The method according to claim 10, wherein said injected aqueous fluid is derived by dilution of produc-



tion water brought to the surface during said hydrocarbon collection step c).

12. The method according to claim 11, wherein water condensed from the products of combustion of step d) is used to dilute said production water. 5
13. The method according to any one of claims 1 to 12, wherein the progression of a front of displacement of oil or other hydrocarbons is monitored through seismic or volumetric methods. 10
14. A system for use in the method according to any one of claims 1 to 13, said system comprising: 15
- an air separation unit (31);  
a fuel combustion unit (35); and,  
at least one injector unit (40, 44) for introducing injectants under pressure into a subterranean formation. 20
15. The system according to claim 14 further comprising a collector unit (48) for hydrocarbons displaced from said subterranean formation, said collector unit (48) being in operative contact with the combustion unit (35). 25

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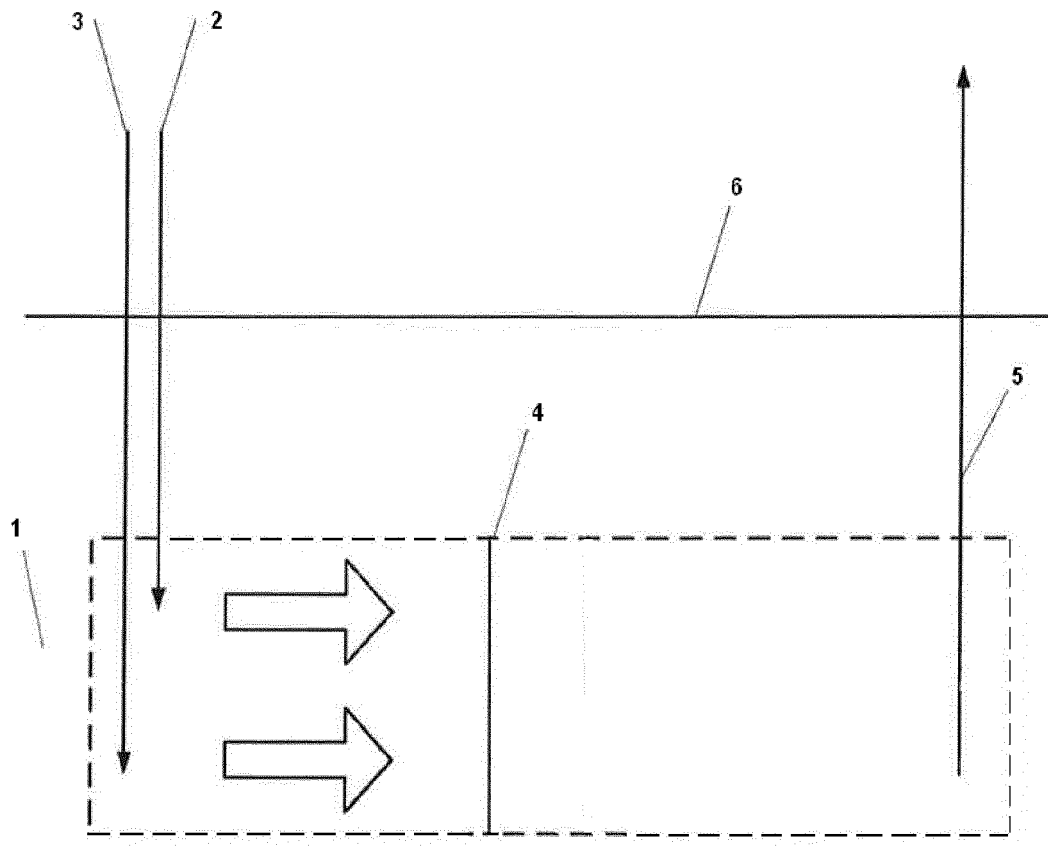


Fig. 1

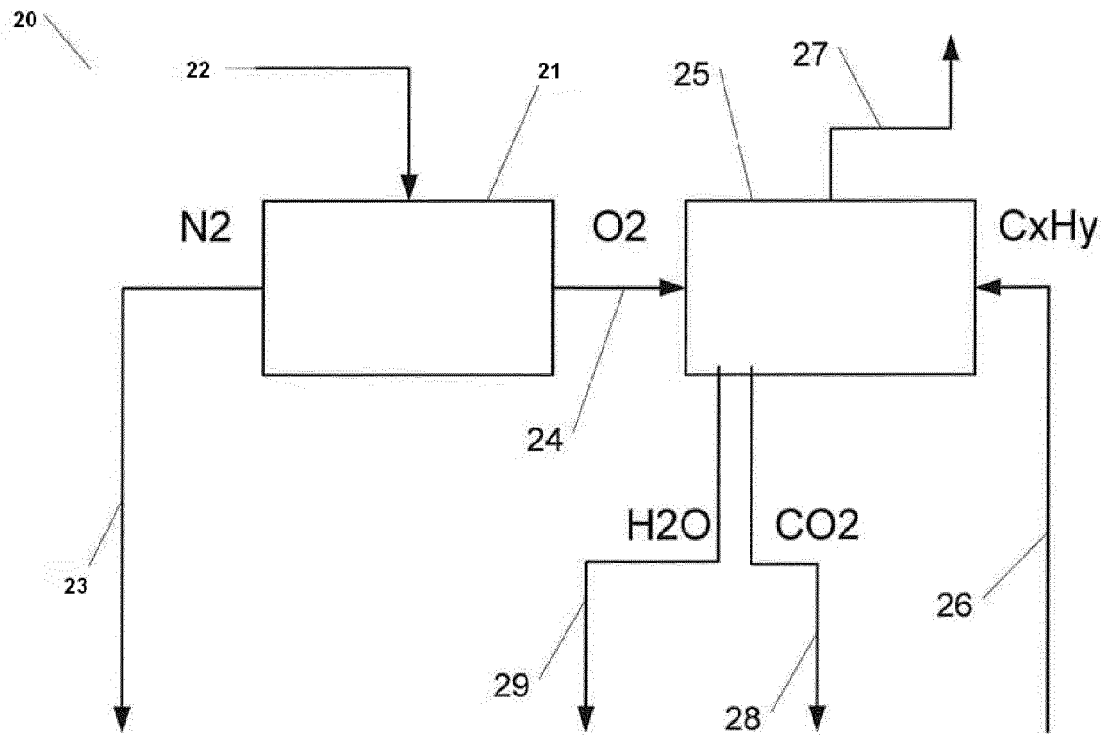


Fig. 2

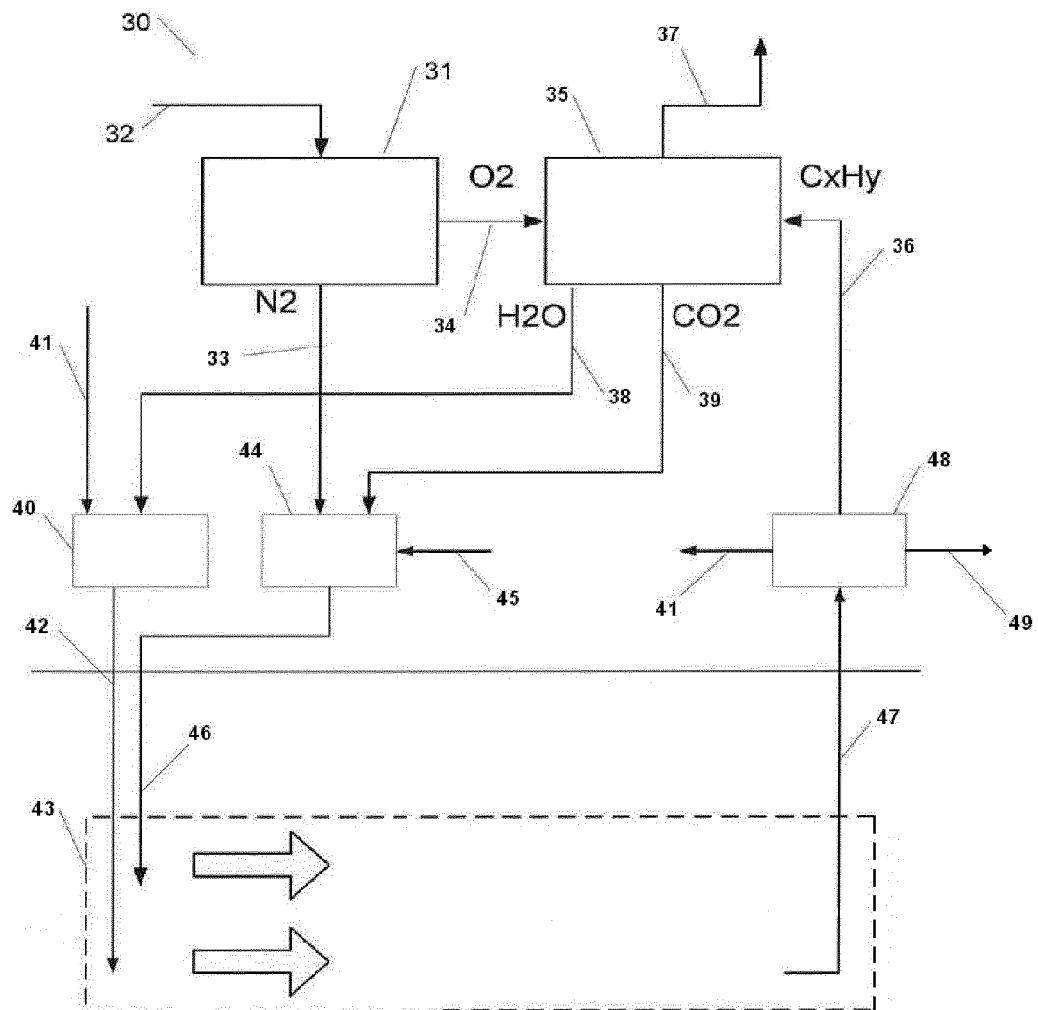


Fig. 3

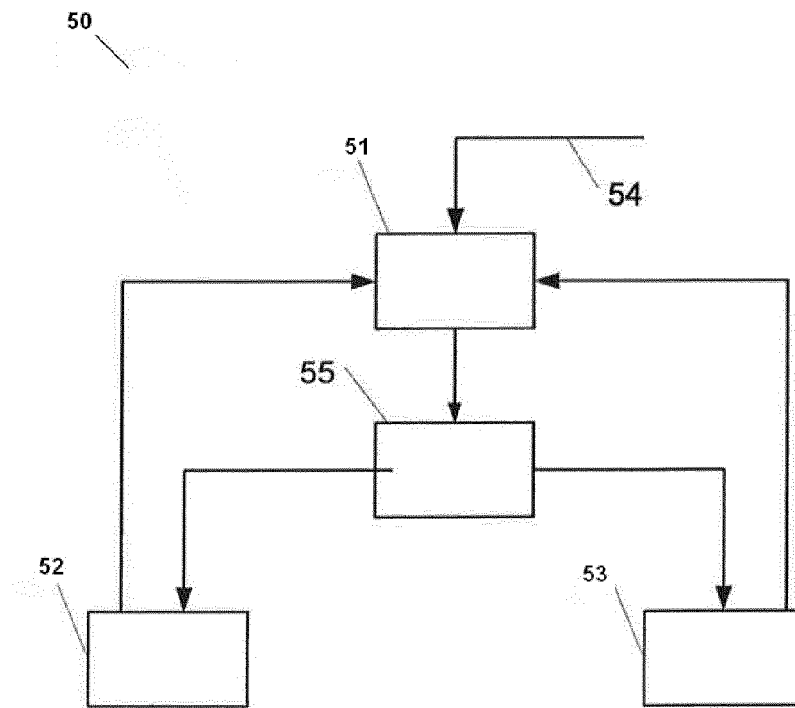
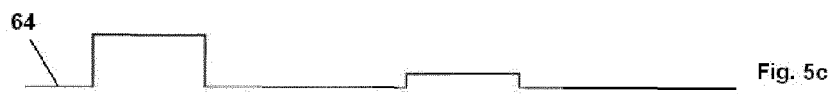
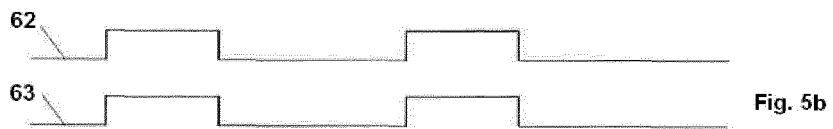
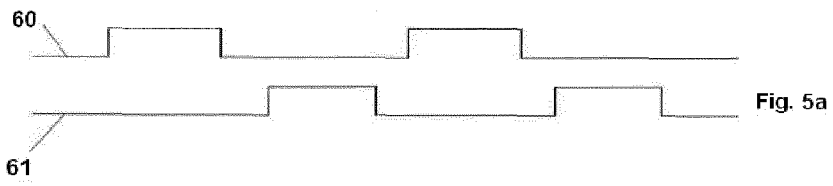


Fig. 4





## EUROPEAN SEARCH REPORT

Application Number  
EP 12 18 7689

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2011/146978 A1 (PERLMAN ANDREW [US]) 23 June 2011 (2011-06-23)	1-12, 14, 15	INV. E21B43/16
Y	* paragraphs [0094] - [0097], [0215]; claim 1 *	13	F25J3/04
Y	----- US 2003/220750 A1 (DELHOMME JEAN-PERRE [FR] ET AL DELHOMME JEAN-PIERRE [FR] ET AL) 27 November 2003 (2003-11-27) * paragraph [0083] * -----	13	
			TECHNICAL FIELDS SEARCHED (IPC)
			E21B
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 23 January 2013	Examiner Bellingacci, F
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... &amp; : member of the same patent family, corresponding document</p>			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 12 18 7689

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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23-01-2013

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