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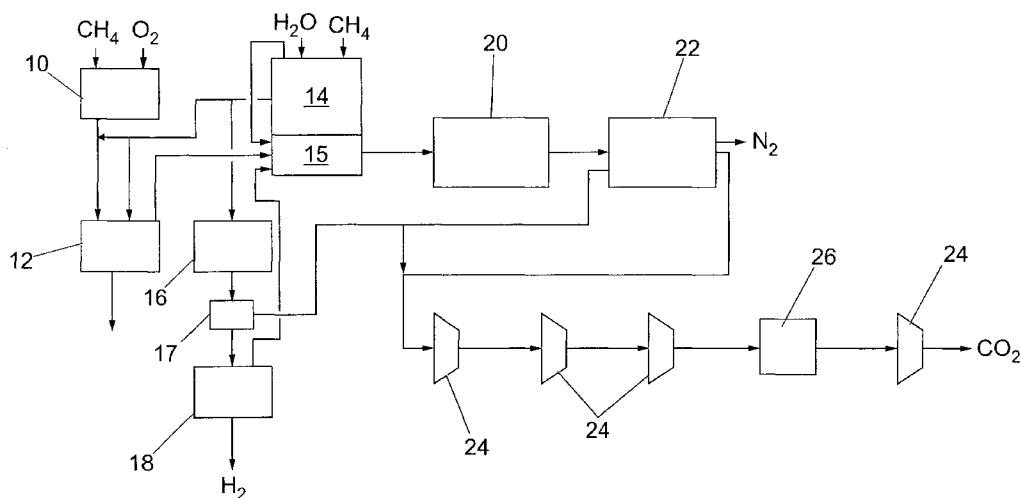
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[Continued on next page]

(54) Title: ENHANCED OIL RECOVERY PROCESS AND A PROCESS FOR THE SEQUESTRATION OF CARBON DIOXIDE



(57) Abstract: A process for the sequestration of carbon dioxide, the process comprising injecting carbon dioxide into a reservoir, the carbon dioxide derived from flue gas from a reformer, particularly from a steam methane reformer (SMR). The injected carbon dioxide may be used to enhance the recovery of oil from the reservoir. One aspect of the invention relates to a process for the recovery of hydrocarbons from a subsurface reservoir preferably in combination with the production of synthesis gas from a hydrocarbonaceous stream, comprising: (i) heating the hydrocarbonaceous stream by combustion of at least a portion of a fuel gas containing a hydrocarbonaceous source, the combustion products of said fuel gas, along with any uncombusted gas in the fuel gas, producing a flue gas containing carbon dioxide; (ii) reforming of the hydrocarbonaceous stream to produce synthesis gas; (iii) recovering hydrocarbons from a subsurface reservoir using at least a portion of the flue gas produced in step (i). In preferred embodiments, the synthesis gas produced is used in a Fischer-Tropsch process for the production of liquid hydrocarbons.

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ENHANCED OIL RECOVERY PROCESS AND A PROCESS FOR THE  
SEQUESTRATION OF CARBON DIOXIDE

This invention relates to a process for the enhanced recovery of oil (or hydrocarbons) from a subsurface reservoir by injecting a carbon dioxide containing gas into the reservoir in combination with the production of hydrocarbons from a hydrocarbonaceous stream. This  
5 invention also relates to a process for the sequestration of carbon dioxide.

Enhanced oil recovery (sometimes also called tertiary oil recovery) involves non-conventional techniques for recovering more hydrocarbons out of subsurface reservoirs than is possible by natural production mechanisms (primary oil recovery) or by the injection of water or gas (secondary oil recovery).  
10

If hydrocarbons are to move through the reservoir rock to a well, the pressure under which the hydrocarbons exist in the reservoir must be greater than that at the well bottom. The rate at which the hydrocarbons move towards the well depends on a number of features, which include the pressure differential between the reservoir and the well, permeability of the rock, layer thickness and the viscosity of the hydrocarbons. The initial reservoir pressure is usually high enough to lift the hydrocarbons from the producing wells to the surface, but as the hydrocarbons are produced, the pressure decreases and the production rate starts to decline. Production,  
15  
20  
25 although declining, can be maintained for a time by naturally occurring processes such as expansion of the gas in a gas cap, gas release by the hydrocarbons and/or the influx of water. A more extensive description of

natural production mechanisms can be found in the Petroleum Handbook, 6<sup>th</sup> edition, Elsevier, Amsterdam/New York, 1983, p. 91-97. See also Petroleum Engineering Handbook, Bradley (Ed.), Society of Petroleum Engineers, Richardson, Texas, 1992 (ISBN 1-55563-010-3), Chapter 42-47.

The hydrocarbons not producible, or left behind, by the conventional, natural recovery methods may be too viscous or too difficult to displace or may be trapped by capillary forces. Depending on the type of hydrocarbons, the nature of the reservoir and the location of the wells, the recovery factor (the percentage of hydrocarbons initially contained in a reservoir that can be produced by natural production mechanisms) can vary from a few percent to about 35 percent. Worldwide, primary recovery is estimated to produce on average some 25 percent of the hydrocarbons initially in place.

In order to increase the hydrocarbon production by natural production mechanisms, techniques have been developed for maintaining reservoir pressure. By such techniques (also known as secondary recovery) the reservoir's natural energy and displacing mechanism which is responsible for primary production, is supplemented by the injection of water or gas. However, the injected fluid (water or gas) does not displace all the hydrocarbons. An appreciable amount remains trapped by capillary forces in the pores of the reservoir rock and is bypassed. These entrapped hydrocarbons are known as residual hydrocarbons, and they can occupy from 20 to 50 percent, or even more, of the pore volume. See for a more general description of secondary recovery techniques the above-mentioned Petroleum Handbook, p. 94-96, and the Petroleum Engineering Handbook.

Many enhanced oil recovery techniques are known. They cover techniques such as thermal processes, miscible processes and chemical processes. Examples are heat generation, heat transfer, steam drive, steam soak, polymer flooding, surfactant flooding, the use of hydrocarbon solvents, high-pressure hydrocarbon gas, carbon dioxide and nitrogen. See for a more general description of secondary recovery techniques the above-mentioned Petroleum Handbook, p. 97-110, and the Petroleum Engineering Handbook.

The use of carbon dioxide for enhanced oil recovery is known. The carbon dioxide can be injected at sufficiently high pressure to enhance the recovery of the hydrocarbons. Moreover, the carbon dioxide can dissolve in the hydrocarbons and reduce its viscosity, which also enhances the recovery of hydrocarbons from the reservoir.

In the present invention, there is provided a process for enhanced oil recovery from a subsurface reservoir in combination with the production of normally liquid hydrocarbons and optionally normally solid hydrocarbons from one or more hydrocarbonaceous stream, the process comprising:

(i) combusting a fuel gas containing a hydrocarbonaceous source to produce heat, the combustion products of said fuel gas, along with any carbon dioxide already present in the fuel gas, producing a flue gas containing carbon dioxide;

(ii) heating a first hydrocarbonaceous stream together with steam using the heat generated in step (i) and reforming the mixture of the hydrocarbonaceous stream and steam to produce a first synthesis gas stream;

(iii) recovering hydrocarbons from a subsurface reservoir using at least a portion of the flue gas

produced in step (i), preferably at least a portion of the carbon dioxide in the flue gas produced in step (i);

(iv) producing a second synthesis gas stream, the second synthesis gas stream being made or obtained by partial oxidation of a second hydrocarbonaceous stream, optionally in combination with catalytic reforming; and

(v) producing normally liquid hydrocarbons, normally gaseous hydrocarbons, including liquefied petroleum gas, and optionally normally solid hydrocarbons, from the synthesis gas streams.

The first part of the process of the present invention (steps (i) and (ii)) relates to the production of synthesis gas using steam methane reforming, as part of the process of making hydrocarbons from a hydrocarbonaceous stream.

The Steam Methane Reformer (SMR) converts methane and steam at elevated temperatures to a mixture of hydrogen and carbon monoxide (i.e. synthesis gas) typically with a ratio of around 4:1 to 8:1, especially 5:1 to 6:1.

The SMR comprises a convection section and a radiant section. The convection section preheats the methane and steam whilst the radiant section has tubes with reforming catalyst, especially nickel reforming catalyst, and this is where the reforming reactions take place. Overall, the reactions are endothermic - the heat required is provided by an SMR furnace. In the process of the present invention the SMR furnace may be powered by, for example, natural gas, off gas from hydrocarbon compound synthesis, e.g. a methanol and/or DME synthesis process or a Fischer-Tropsch process, or off gas from a Pressure Swing Adsorption (PSA) unit, especially by the off gas from a Fischer-Tropsch process. This can also be designed to run on natural gas exclusively. The design of the SMR allows

operation with less than two percent oxygen (on dry basis) at the exit of the radiant section.

The flue gas produced by the combustion of the fuel gas to power the SMR contains carbon dioxide.

5 There are environmental limitations on the release of carbon dioxide into the atmosphere.

The first synthesis gas stream may contain synthesis gas with a hydrogen:carbon monoxide ratio of around 4:1 to 8:1, especially 5:1-6:1. The second synthesis gas  
10 stream typically comprises synthesis gas with a hydrogen:carbon monoxide ratio of 1.6-2.3, preferably 1.7-2.2.

The second synthesis gas stream is made or obtained by partial oxidation of a second hydrocarbonaceous  
15 stream, optionally in combination with catalytic reforming.

The hydrocarbonaceous streams to be used in the present invention may be the same or different. Suitable streams are natural gas, associated gas, coal bed methane or mixtures thereof. These gas streams usually contain at  
20 least 60 vol% methane based on the total stream, preferably at least 70%, more preferably at least 80%. The remaining compounds usually will be ethane, propane, butane and minor amounts of higher alkanes. Some inerts  
25 may be present, e.g. nitrogen and/or carbon dioxide, usually less than 10 vol% each, preferably less than 5 vol% each, based on the total stream. The second hydrocarbonaceous stream may also be coal, biomass, residual oil fractions (including tar sand oils), peat,  
30 municipal waste etc. Due to the relatively low H/C ratio of these heavy compounds, a relatively large reforming unit is required (i.e. steps (i) and (ii)), resulting in

a large flue gas stream, or, in other words, a large amount of carbon dioxide.

The source of the fuel gas is preferably off-gas from the unit which converts the synthesis gas obtained in step (ii) into liquid hydrocarbons, typically a heavy paraffin synthesis (HPS) unit.

The source of the fuel gas may be product gas from a Steam Methane Reformer. This is typically used under transient conditions only, such as during start up or during upsets.

The source of the fuel gas may be off gas from a unit adapted to remove carbon dioxide from a mixture containing hydrogen and carbon dioxide, for example a pressure swing adsorption unit (PSA).

The source of the fuel gas may be natural gas.

The source of the fuel gas may be any combination of the sources described herein.

Preferably PSA off-gas is added to the fuel gas before the combustion in step (i).

Optionally the PSA off-gas is not used as fuel gas. The PSA off-gas may be mixed with the flue gas.

The furnace is typically adapted to heat the reformer. It is typically provided as an integral part of the reformer. Preferably the furnace is a convection section of a steam methane reformer.

The combustion process of step (i) may be done with air, oxygen enriched air or pure oxygen. A (commercial) air separation unit (ASU) may be used to produce the oxygen enriched air or the pure oxygen. Preferably air is used.

The partial oxidation process (step iv) may be carried out with air, oxygen enriched air or pure oxygen. Pure oxygen (> 99 vol%) is preferred. A (commercial) ASU



may be used for the oxygen production, also membrane processes may be used. A suitable commercial process for the partial oxidation reaction is the Shell Gasification process, which process is suitable for at least natural gas, heavy residual oil and coal. The partial oxidation process may be carried out in combination with catalytic reforming. In that case steam is added to the hydrocarbonaceous stream and/or the oxygen stream, and the reaction product is directed to a reforming catalyst. A very suitable process for the combined treating is the so called autothermal reforming process. Such processes are commercially available.

The carbon dioxide content of the flue gas may be in the region of 5-20%, preferably 8-16%, more preferably 11-14%. Where PSA off-gas has been added to the fuel gas, the carbon dioxide concentration in the flue gas will be increased. In these circumstances preferably at least 8%, more preferably at least 11% of the flue gas is carbon dioxide.

Preferably the flue gas is treated to capture the carbon dioxide therein. In that way pure carbon dioxide is obtained which is very suitable for miscible flooding. Nitrogen and oxygen are to be removed as much as possible. Oxygen may result in the forming of explosive mixtures and/or may result in the growth of microbiological organisms, which could result in undesired effects as clogging of the reservoir.

The captured carbon dioxide stream contains preferably at least 80 vol% carbon dioxide, more preferably at least 90 vol% carbon dioxide, even more preferably at least 95 vol%, based on total stream.

To capture the carbon dioxide content in the flue gas, the technique of solvent extraction may be used.

The use of organic solvents or aqueous solutions of organic solvents for removing carbon dioxide from a gas stream is known. See for instance A.L. Kohl and F.C. Riesenfeld, 1974, Gas Purification, 2nd edition, Gulf Publishing Co. Houston and R.N. Maddox, 1974, Gas and Liquid Sweetening, Campbell Petroleum Series. Preferably a regenerable absorbent solvent is used in a continuous process.

On an industrial scale there are chiefly two categories of absorbent solvents, depending on the mechanism to absorb the carbon dioxide: chemical solvents and physical solvents. Each solvent has its own advantages and disadvantages as to features as loading capacity, kinetics, regenerability, selectivity, stability, corrosivity, heat/cooling requirements etc.

Chemical solvents which have proved to be industrially useful are primary, secondary and/or tertiary amines derived alkanolamines. The most frequently used amines are derived from ethanolamine, especially monoethanol amine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA).

A well-known commercial process uses an aqueous mixture of a chemical solvent, especially DIPA and/or MDEA, and a physical solvent, especially cyclotetra-methylene-sulfone.

Preferably the amines are resistant to degradation by oxygen.

The use of amines to separate carbon dioxide from a mixture of gases (such as exhaust gases) has been disclosed in a number of documents. See for example CA2265416, US6500397, EP1064980, US5904908, EP0647462, JP7100334 and JP7313840, the disclosures of which are

incorporated herein by reference in their entirety. These disclosures describe suitable amines for use in the present invention.

Physical solvents which have proved to be industrially suitable are cyclo-tetramethylenesulfone and its derivatives, aliphatic acid amides, N-methylpyrrolidone, N-alkylated pyrrolidones and the corresponding piperidones, methanol, ethanol and mixtures of dialkylethers of polyethylene glycols.

A combination of chemical and physical solvents may be used. For example see US 6051161, the disclosure of which is incorporated herein by reference in its entirety.

Another option is to use hot potassium hydroxide solution, certain heat resistant diamines and/or certain specific amino-acids. For example see JP7246315, the disclosure of which is incorporated herein by reference in its entirety.

Other methods of capturing carbon dioxide may also be used including pressure swing adsorption units, membrane separators and cryogenic separators. One cryogenic separator is the Ryan/Holmes four column process.

Typically the pressure of the flue gas is boosted before it is used to recover hydrocarbons from a subsurface reservoir. Preferably this pressure boosting is performed after the carbon dioxide content has been captured.

Preferably the pressure is boosted to a level sufficient to allow the carbon dioxide to enter the reservoir.

The flue gas, which at this stage is typically predominantly carbon dioxide, may be boosted in a series of stages, for example where flue gas at 150 bara is

required to recover hydrocarbons from a subsurface reservoir, the pressure may be progressively boosted in a first stage up to around 5 bara, in a second stage up to around 15 bara, in a further stage up to around 50 bara and in a final stage up to 150 bara. A part of the energy needed for compression may be obtained by expanding the off-gas from the hydrocarbon synthesis process (step (v)) from the reaction pressure to a pressure of 1-2 bara.

Typically the flue gas is also cooled during pressure boosting.

It is preferred to use pure CO<sub>2</sub> for the enhanced oil recovery, rather than a mixture of carbon dioxide and nitrogen and/or lower (i.e. C<sub>1</sub>-C<sub>4</sub>) hydrocarbon. Due to the different properties of these components it is more convenient to use separate components rather than mixtures. E.g. nitrogen is relatively insoluble in crude oil and is suitable to pressure the gas cap. CO<sub>2</sub> is very suitable for miscible flooding.

The hydrocarbons recovered from the subsurface reservoir may be substantially in the liquid phase optionally in combination with a mixture of light hydrocarbons, especially methane.

Some of the carbon dioxide injected can be produced with the hydrocarbons from the reservoir.

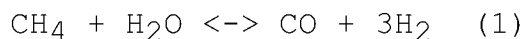
Sequestration in a subsurface formation is typically when carbon dioxide is injected into a closed off or depleted reservoir from which no further production of hydrocarbons is planned. The subsurface formation need not be a hydrocarbon reservoir since when sequestration is required without enhanced oil recovery, the carbon dioxide may be injected into an area of the subsurface formation which did or did not contain hydrocarbons.

Thus the invention also provides a process for the sequestration of carbon dioxide, the process comprising injecting carbon dioxide into a subsurface formation, the carbon dioxide derived from flue gas from a reformer, particularly from a steam methane reformer (SMR).

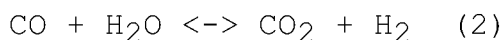
Preferably the reforming is steam methane reforming which is performed in a steam methane reformer (SMR).

The hydrocarbonaceous stream to the SMR can be natural gas, associated gas and/or coal-bed methane, or derived from residual (crude) oil fractions or coal. The SMR can operate with a range of feedstocks. The hydrocarbonaceous stream suitably is methane, natural gas, associated gas or a mixture of C<sub>1-4</sub> hydrocarbons. The stream preferably comprises mainly, i.e. more than 90 v/v%, especially more than 94%, C<sub>1-4</sub> hydrocarbons, and especially comprises at least 60 v/v percent methane, preferably at least 75%, more preferably 90%. Very suitably natural gas or associates gas is used. Suitably, any sulphur in the feedstock is removed.

In one example, the hydrocarbonaceous stream is methane from natural gas. In use, methane and steam can be introduced into the SMR which operates at an outlet temperature of 800 °C-900 °C. In the SMR, methane is typically converted into a mixture of carbon monoxide and hydrogen primarily by equilibrium reaction (1) shown below.



Some of the carbon monoxide is typically further oxidised to carbon dioxide, according to equilibrium reaction (2) below.



The net result of these reactions, and other minor reactions, is typically a product mixture having an H<sub>2</sub>/CO ratio of around 5:1 to 6:1. The mixture of hydrogen and carbon monoxide is typically referred to as synthesis gas or syngas.

This syngas can be used for a number of purposes, for example for use in a Fischer-Tropsch reactor and particularly to increase the relative hydrogen:carbon monoxide content of the syngas from a gasifier before it proceeds to a Fischer-Tropsch Reactor. Typically sufficient hydrogen is also produced for use in other units or processes which are integral or associated with the Fischer-Tropsch process, for example a hydrogenation unit.

The syngas is preferably mixed with syngas produced by partial oxidation of methane before being converted into said liquid hydrocarbons.

Preferably the syngas is converted into liquid hydrocarbons, optionally in combination with solid hydrocarbons and liquefied petroleum gas, by the Fischer-Tropsch process.

The Fischer-Tropsch process is well known to those skilled in the art and involves synthesis of hydrocarbons from a gaseous mixture of syngas, by contacting that mixture at reaction conditions with a Fischer-Tropsch catalyst.

Products of the Fischer-Tropsch synthesis may range from methane to heavy paraffin waxes. Preferably, the production of methane is minimised and a substantial portion of the hydrocarbons produced have a carbon chain length of a least 5 carbon atoms. Preferably, the amount of C<sub>5</sub>+ hydrocarbons is at least 60% by weight of the total product, more preferably, at least 70% by weight,

even more preferably, at least 80% by weight, most preferably at least 85% by weight. Reaction products which are liquid phase under reaction conditions may be separated and removed, optionally using suitable means, such as one or more filters. Internal or external filters, or a combination of both, may be employed. Gas phase products such as light hydrocarbons and water may be removed using suitable means known to the person skilled in the art.

Fischer-Tropsch catalysts are known in the art, and frequently comprise, as the catalytically active component, a metal from Group VIII of the Periodic Table. (References herein to the Periodic Table relate to the previous IUPAC version of the Periodic Table of Elements such as that described in the 68<sup>th</sup> Edition of the Handbook of Chemistry and Physics (CPC Press)). Particular catalytically active metals include ruthenium, iron, cobalt and nickel. Cobalt is a preferred catalytically active metal. Typically, the catalysts comprise a catalyst carrier. The catalyst carrier is preferably porous, such as a porous inorganic refractory oxide, more preferably alumina, silica, titania, zirconia or mixtures thereof.

The optimum amount of catalytically active metal present on the carrier depends inter alia on the specific catalytically active metal. Typically, the amount of cobalt present in the catalyst may range from 1 to 100 parts by weight per 100 parts by weight of carrier material, preferably from 10 to 50 parts by weight per 100 parts by weight of carrier material.

The catalytically active metal may be present in the catalyst together with one or more metal promoters or co-catalysts. The promoters may be present as metals or as

the metal oxide, depending upon the particular promoter concerned. Suitable promoters include oxides of metals from Groups IIA, IIIB, IVB, VB, VIB and/or VIIB of the Periodic Table, oxides of the lanthanides and/or the actinides. Preferably, the catalyst comprises at least one of an element in Group IVB, VB and/or VIIB of the Periodic Table, in particular titanium, zirconium, manganese and/or vanadium. As an alternative or in addition to the metal oxide promoter, the catalyst may comprise a metal promoter selected from Groups VIIB and/or VIII of the Periodic Table. Preferred metal promoters include rhenium, platinum and palladium.

A most suitable catalyst comprises cobalt as the catalytically active metal and zirconium as a promoter. Another most suitable catalyst comprises cobalt as the catalytically active metal and manganese and/or vanadium as a promoter.

The promoter, if present in the catalyst, is typically present in an amount of from 0.1 to 60 parts by weight per 100 parts by weight of carrier material. It will however be appreciated that the optimum amount of promoter may vary for the respective elements which act as promoter.

The Fischer-Tropsch synthesis is preferably carried out at a temperature in the range from 125 to 350°C, more preferably 175 to 275 °C, most preferably 200 to 260 °C. The pressure preferably ranges from 5 to 150 bar abs., more preferably from 5 to 80 bar abs.

The Fischer-Tropsch synthesis can be carried out in a slurry phase regime or an ebullating bed regime, wherein the catalyst particles are kept in suspension by an upward superficial gas and/or liquid velocity.



Hydrogen and carbon monoxide (synthesis gas) is typically fed to the three-phase slurry reactor at a molar ratio in the range from 0.4 to 2.5. Preferably, the hydrogen to carbon monoxide molar ratio is in the range  
5 from 1.0 to 2.5.

Another regime for carrying out the Fischer-Tropsch reaction is a fixed bed regime, especially a trickle flow regime. A very suitable reactor is a multitubular fixed bed reactor.

10 Thus the invention also provides a hydrocarbon synthesised by a Fischer-Tropsch process, the Fischer-Tropsch process being supplied by syngas, at least a portion of the syngas being produced by a method as described herein.

15 The hydrocarbon may have undergone the steps of hydroprocessing, preferably hydrogenation, hydroisomerisation and/or hydrocracking.

The hydrocarbon may be a fuel, preferably naphtha, kero or gasoil, a waxy raffinate or a base oil.

20 In a preferred embodiment of the invention, a Fischer-Tropsch process is carried out in which synthesis gas from a partial oxidation process (or optionally a autothermal reforming process) is used together with the synthesis gas from a reforming process. The partial  
25 oxidation synthesis gas suitably has an H<sub>2</sub>/CO ratio of 1.6-2.0, preferably 1.7-1.9. The reforming synthesis gas suitably has an H<sub>2</sub>/CO ratio of 3-8, preferably 4-6.

Especially the Fischer-Tropsch process is carried out in a two-stage set-up in which off-gas from the first step  
30 together with reforming synthesis gas is sent to the second stage. The off gas from the second stage, containing unconverted syngas, lower (C<sub>1</sub>-C<sub>4</sub>) hydrocarbons, and inerts (nitrogen, carbon dioxide) is

used for heating the reforming furnace. An amine extraction process using commercially available oxygen-stable amines is used to extract the carbon dioxide from the flue gas. After pressurisation the pure carbon dioxide is used for enhanced oil recovery. The feed for the reforming process is preferably hydrogenated (to remove olefins) and shifted (to remove CO) off gas from the Fischer-Tropsch process, optionally in combination with natural gas associated gas and/or coal bed methane. The steam for the reforming process is preferably water made in the Fischer-Tropsch process. In addition, as hydrogen is needed for the upgrading of the Fischer-Tropsch hydrocarbons, part of the reforming syngas is to be shifted (in which process carbon monoxide is reacted with water to obtain carbon dioxide and hydrogen). The hydrogen is to be separated from the carbon dioxide. Any steams containing the carbon dioxide optionally in combination with hydrogen (e.g. regeneration gas from a PSA or pressure swing adsorption unit) may be added to the feed gas or the flue gas of the reformer, depending especially on the hydrogen content. In this way a very efficient process is obtained. All carbon dioxide made in the overall process is used for enhanced oil recovery, while all energy containing compounds are used for energy generation.

An embodiment of the present invention will now be described, by way of example only, with reference to the accompanying drawing, in which Fig. 1 is a process diagram of a Fischer-Tropsch Process.

Fig. 1 shows a flow diagram of a Fischer-Tropsch process. Methane and oxygen are introduced into a gasifier 10 which produces a mixture of carbon monoxide

and hydrogen for use in heavy paraffin synthesis in a Fischer-Tropsch unit 12.

5 Steam and methane are introduced into a steam methane reformer (SMR) 14 producing a hydrogen rich mixture of carbon monoxide and hydrogen which is also used for heavy paraffin synthesis in the Fischer-Tropsch unit 12.

10 A portion of the product in the SMR 14 is sent to a high temperature shift reactor 16 to convert the carbon monoxide therein to carbon dioxide. This carbon dioxide is then removed in a Pressure Swing Adsorption (PSA) unit 18 to leave pure hydrogen.

15 A membrane separation filter 17 may be provided between the high temperature shift reactor 16 and the pressure swing adsorption unit 18 in order to remove carbon dioxide.

The SMR 14 operates at an outlet temperature of between of 800 °C and 900 °C. To heat the SMR unit 14, an integral furnace 15 is provided.

20 The fuel gas for the furnace 15 can be supplied from a number of sources, including off gas from the Fischer-Tropsch unit 12, the PSA unit 18 or the SMR unit 14 itself. Alternatively natural gas or any other hydrocarbonaceous based gas may be used to fuel the furnace.

25 Typically the fuel gas provided comprises methane, other gaseous hydrocarbons, carbon dioxide and carbon monoxide.

30 The carbon dioxide content of the fuel gas will be increased by the combustion of the hydrocarbons in the furnace 15. Around 14% of the flue gas may be carbon dioxide. Heat is recovered by production of steam so the temperature of the flue gas is reduced to around 150oC. The flue gases produced (which include combustion

products and uncombusted gases) proceed to gas cooling and boosting fans 20 and then to an amine recovery unit 22.

5 Carbon dioxide from the membrane separation filter 17 and/or the pressure swing adsorption unit 18 may also be directed to the amine recovery unit 22.

10 In the amine recovery unit 22, solvent extraction is used to extract carbon dioxide from the flue gas mixture. The carbon dioxide extracted need not be pure - a purity of 80%, preferably 95% is sufficient for the purposes of the present invention.

15 The carbon dioxide stream from the amine recovery unit 22 then proceeds to a series of compressors 24 where the pressure of the carbon dioxide is progressively increased. Depending on the purity of the carbon dioxide removed by the membrane separation filter 17 and pressure swing adsorption unit 18, carbon dioxide recovered therefrom may be sent directly to the compressors 24.

20 Thereafter a dehydration unit 26 removes any water from the carbon dioxide stream before a final compressor 24 boosts the pressure of the carbon dioxide further.

The carbon dioxide can then be injected into a reservoir to encourage the production of hydrocarbons therefrom.

25 A benefit of the invention is that the greenhouse gas, carbon dioxide, is injected into a subsurface reservoir rather than released to the atmosphere.

30 In some embodiments of the present invention the carbon dioxide may be sequestered, that is injected into a reservoir in order to dispose of the carbon dioxide without releasing it into the atmosphere.

Typically the pressure of the carbon dioxide injected into the reservoir should be greater than the reservoir

pressure. Thus in certain embodiments, the number of compressors can be reduced or increased depending on the pressure of the subsurface reservoir.

Modifications and improvements may be made without departing from the scope of the invention.

The term "normally gaseous hydrocarbon" describes hydrocarbons which are gaseous at STP (0 °C, 1 bar). These hydrocarbons are especially methane, ethane, propane and butane and their unsaturated derivatives. The term "normally liquid hydrocarbons" describes hydrocarbons which are liquid at STP (0 °C, 1 bar). This group of compounds comprises C<sub>5</sub> up till normal -C<sub>14</sub> as well as some C<sub>15</sub>-C<sub>18</sub> isomers. The group also includes the unsaturated derivatives. The term "normally solid hydrocarbons" describes hydrocarbon that are solid at standard temperature and pressure condition (STP, 0 °C, 1 bar). This group comprise all n-C<sub>15</sub>-alkanes and most iso-C<sub>16</sub><sup>+</sup> alkanes. The group also comprise any unsaturated derivatives.

C L A I M S

1. A process for enhanced oil recovery from a subsurface reservoir in combination with the production of normally liquid hydrocarbons and optionally normally solid hydrocarbons from one or more hydrocarbonaceous streams, the process comprising:

(i) combusting a fuel gas containing a hydrocarbonaceous source to produce heat, the combustion products of said fuel gas, along with any carbon dioxide already present in the fuel gas, producing a flue gas containing carbon dioxide;

(ii) heating a first hydrocarbonaceous stream together with steam using the heat generated in step (i) and reforming the mixture of the hydrocarbonaceous stream and steam to produce a first synthesis gas stream;

(iii) recovering hydrocarbons from a subsurface reservoir using at least a portion of the flue gas produced in step (i), preferably at least a portion of the carbon dioxide in the flue gas produced in step (i);

(iv) producing a second synthesis gas stream, the second synthesis gas stream being made or obtained by partial oxidation of a second hydrocarbonaceous stream, optionally in combination with catalytic reforming; and

(v) producing normally liquid hydrocarbons, normally gaseous hydrocarbons, including liquefied petroleum gas, and optionally normally solid hydrocarbons, from the synthesis gas streams.

2. A process as claimed in claim 1, wherein the synthesis gas is converted into normally liquid hydrocarbons, optionally in combination with normally solid hydrocarbons and normally gaseous hydrocarbons

including liquefied petroleum gas, by the Fischer-Tropsch process.

3. A process as claimed in claim 1 or 2, wherein the source of the fuel gas is one, or a combination, of:

5 (1) a third hydrocarbonaceous stream;  
(2) off-gas from a heavy paraffin synthesis reactor; and,  
(3) typically under transient conditions, product from a reformer, particularly a steam methane reformer, preferably (2).

10 4. A process as claimed in any one of claims 1 to 3, wherein the source of the fuel gas further comprises a carbon dioxide containing gas from a unit adapted to remove carbon dioxide from a mixture containing hydrogen and carbon dioxide, especially a regeneration gas from a  
15 pressure swing adsorption unit.

5. A process as claimed in any preceding claim, wherein the flue gas is treated to capture its carbon dioxide content, preferably wherein solvent extraction is used to capture the carbon dioxide content in the flue gas.

20 6. A process as claimed in claim 5, wherein the captured carbon dioxide is at least 80% carbon dioxide preferably at least 90% carbon dioxide.

7. A process as claimed in any preceding claim, wherein the hydrocarbons recovered from the subsurface reservoir  
25 are substantially in the liquid phase optionally in combination with a mixture of light hydrocarbons especially methane, preferably wherein carbon dioxide is produced with the hydrocarbons from the reservoir and at least a portion of the carbon dioxide produced is  
30 reinjected into the reservoir.

8. A process as claimed in any preceding claim, wherein the carbon dioxide is sequestered in the reservoir.

9. A hydrocarbon synthesised by a Fischer-Tropsch process, the Fischer-Tropsch process being supplied by synthesis gas, at least a portion of the synthesis gas being produced by a process as claimed in any one of  
5 claims 1 to 15, preferably a hydrocarbon wherein the steps of hydroprocessing, preferably hydrogenation, hydroisomerisation and/or hydrocracking, have been applied to the hydrocarbon.

10. A process for enhanced oil recovery from a subsurface reservoir in combination with the production of normally liquid hydrocarbons and optionally normally solid hydrocarbons from one or more hydrocarbonaceous streams, the process comprising:

(i) combusting a fuel gas containing a hydrocarbonaceous source to produce heat, the combustion  
15 products of said fuel gas, along with any carbon dioxide already present in the fuel gas, producing a flue gas containing carbon dioxide;

(ii) heating a first hydrocarbonaceous stream together with steam using the heat generated in step (i) and reforming the mixture of the hydrocarbonaceous stream and steam to produce a first synthesis gas stream;

(iii) recovering hydrocarbons from a subsurface reservoir using at least a portion of the flue gas produced in step (i), preferably at least a portion of  
25 the carbon dioxide in the flue gas produced in step (i);

(iv) producing a second synthesis gas stream, the second synthesis gas stream being made or obtained by partial oxidation of a second hydrocarbonaceous stream, optionally in combination with catalytic reforming; and  
30

(v) sequestration of the carbon dioxides by mineral carbonation.



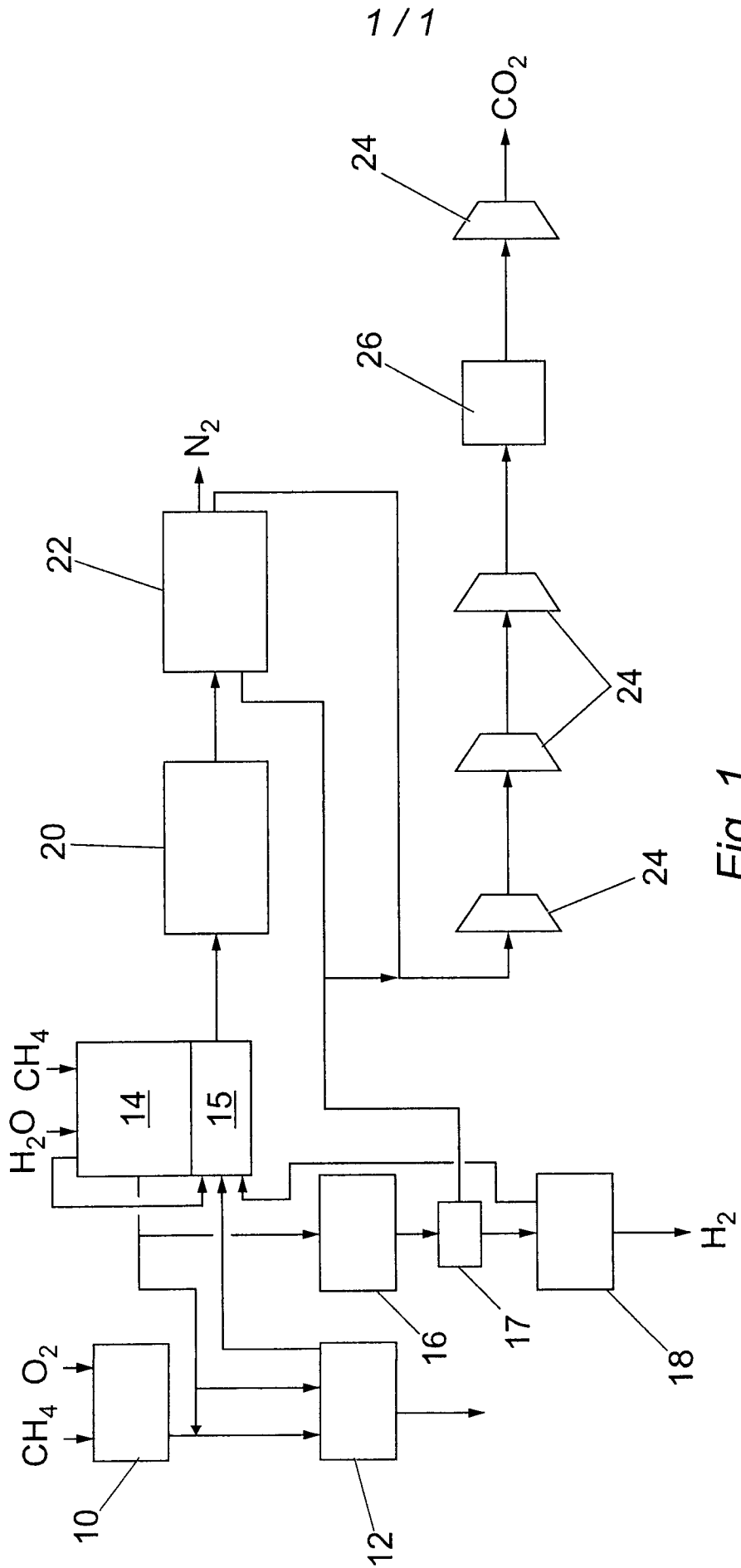


Fig. 1

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/EP2006/069571

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. E21B43/16 C01B3/38 C10G2/00

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
E21B C01B C10G

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
EPO-Internal, WPI Data, TULSA

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  <b>26 January 2007</b>	Date of mailing of the international search report  <b>01/02/2007</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  <b>Schouten, Adri</b>
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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/069571

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