(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 July 2007 (12.07.2007)

PCT

(10) International Publication Number
WO 2007/077137 A1

(51) International Patent Classification:
E21B 43/16 (2006.01) ***B01D 53/14*** (2006.01)
C10G 2/00 (2006.01) ***C01B 31/20*** (2006.01)

(21) International Application Number: PCT/EP2006/070052

(22) International Filing Date: 21 December 2006 (21.12.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
05113095.3 30 December 2005 (30.12.2005) EP

(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel Van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **BRAS, Eduard Coenraad** [NL/NL]; Carel Van Bylandtlaan 30, NL-2596 HR The Hague (NL). **GEUZEBROEK, Frank Haiko** [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). **KNAAP, Mariette Catharina** [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).

(74) Agent: SHELL INTERNATIONAL B.V.; Intellectual Property services, PO Box 384, NL-2501 CJ The Hague (NL).

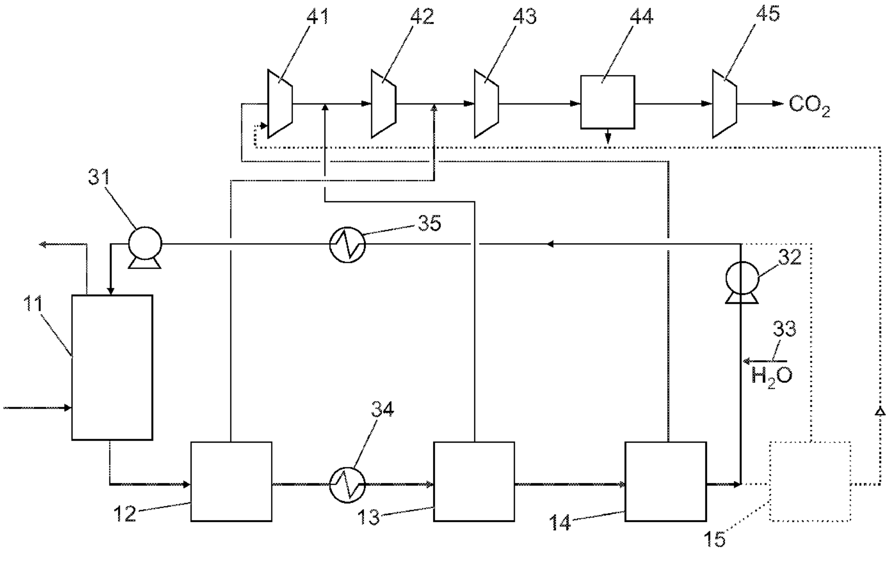
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

[Continued on next page]

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



(57) Abstract: The process comprises the step of injecting a gaseous mixture comprising carbon dioxide into a subsurface reservoir to enhance the recovery of hydrocarbons from the reservoir, wherein the carbon dioxide content in the gaseous mixture has been enriched by a process of solvent absorption. A carbon dioxide depleted stream is also produced and used as a fuel gas for a gas to liquids plant. In preferred embodiments the solvent absorption process comprises a series of flash columns which progressively release carbon dioxide . Much of the carbon dioxide can therefore be recovered at increased pressures thus reducing the amount of compression required before the carbon dioxide is injected into the subsurface reservoir.

WO 2007/077137 A1

Published:

— *with international search report*

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

This invention relates to a process for the enhanced recovery of hydrocarbons, especially oil, from a subsurface reservoir by injecting a carbon dioxide containing gas into the reservoir, in combination with the production of hydrocarbons and carbon dioxide from a hydrocarbonaceous source, especially a natural gas stream. This 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).

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, 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, 6th edition, Elsevier, Amsterdam/New York, 1983, p. 91-97. See also the 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 it 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 their viscosity, which enhances the recovery of hydrocarbons from the reservoir.

Carbon dioxide can be recovered from a number of sources but the sources are typically impure, containing other gases such as hydrogen, nitrogen, hydrocarbons, especially C_1-C_4 hydrocarbon, and/or carbon monoxide.

One known technique for extracting carbon dioxide from impure mixtures is solvent absorption, using organic solvents or aqueous solutions of organic solvents. 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).

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

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. Such systems show good absorption capacity and good selectivity against moderate investment costs and operational costs. They perform very well at high pressures, especially between 20 and 90 bara.

A combination of chemical and physical solvents may be used.

In the known systems to remove carbon dioxide from a mixture of gases, the regenerated solvent absorbs carbon dioxide and some hydrocarbons, leaving the mixture with varying amounts of carbon dioxide (0.005-2.0%), depending on the downstream requirements. The remaining (carbon dioxide depleted) mixture can then proceed to further processing, for example to an LNG process or, preferably, to a hydrocarbon synthesis plant.

The hydrocarbons absorbed by the solvent are then flashed off in a flash column, leaving most of carbon dioxide in the solvent, which is removed in a low pressure regenerator. In the regenerator, steam stripping cleans the solvent of carbon dioxide so that it is sufficiently lean before it returns to the absorber. The carbon dioxide produced is at a pressure typically between 1.2 and 1.8 bar.

This separation technique is generally satisfactory. However when the carbon dioxide extracted is to be used at higher pressures, it is preferable to extract the carbon dioxide at elevated pressures to reduce the amount of compression required. However, the pressure within the regenerator cannot be increased to produce such higher pressure carbon dioxide since this would result in the formation of steam at temperatures which might degrade the solvent.

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

The invention provides a process for enhanced oil recovery in combination with the production of liquid hydrocarbons from synthesis gas, the process comprising:

(a) converting synthesis gas into normally gaseous hydrocarbons and normally liquid hydrocarbons and optionally normally solid hydrocarbons, at elevated temperatures and pressures;

(b) recovering off-gas at a pressure between 10-150 bar, preferably 20-100 bar, more preferably 40-80 bar, from said conversion of synthesis gas into liquid hydrocarbons in step (a);

(c) treating the off-gas using the process of solvent absorption, in order to produce a first stream enriched in carbon dioxide and a second stream depleted in carbon dioxide;

(d) recovering hydrocarbons from a subsurface reservoir using at least a portion of the first stream enriched in carbon dioxide produced in step (c), wherein the process of solvent absorption comprises:

(i) allowing the off-gas to come into contact with a solvent in a first vessel and for a portion of the carbon dioxide within the off-gas to be absorbed therein;

(ii) directing the solvent and absorbed carbon dioxide to a second vessel where a portion of the carbon dioxide absorbed in the solvent are released and recovered therefrom, the carbon dioxide having a pressure of at least 5 bar, preferably 10 bar. The term "normally" refers to STP-conditions, i.e. 0 °C and 1 bar.

The synthesis gas may be produced by a partial oxidation process and/or an autothermal reforming process of a hydrocarbonaceous stream. Preferably a portion of the synthesis gas is also produced by steam methane reforming. The hydrocarbonaceous stream to be used in the present invention is suitably natural gas, associated gas, coal bed methane or mixtures thereof. These gas streams usually contain at least 60 vol% methane based on the total stream, preferably at least

70%, more preferably at least 80%. The remaining compound usually will be ethane, propane, butane and minor amounts of higher alkanes. Some inerts 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 hydrocarbonaceous stream may also be coal, biomass, residual oil fractions (including tar sand oils), peat, municipal waste etc.

The second stream may be used as fuel gas for a gas to liquids plant, in particular the second stream could be used for gas turbines or as a fuel gas in an SMR furnace. The second stream may also be used a feed for the syngas preparation and/or the preparation of hydrogen.

Typically the first vessel is an absorber. Typically a portion of gases are not absorbed by the solvent in the absorber. Typically the gases not absorbed by the solvent in the absorber form the carbon dioxide depleted stream. Optionally the carbon dioxide depleted stream may be used as a fuel gas for a gas to liquids plant, in particular the carbon dioxide depleted stream could be used for turbine, or as feed or fuel for a steam methane reforming unit.

The inventors of the present invention have found that the carbon dioxide depleted stream may be used as fuel gas. Although it is preferred to minimise the carbon dioxide content in the carbon dioxide depleted stream, the carbon dioxide depleted stream can in fact contain more carbon dioxide than that conventionally permitted for a carbon dioxide depleted stream which was processed further. Thus the process to remove the carbon dioxide can be less severe.

Preferably the pressure in the first vessel is suitably 20 - 100 bar, especially 40 - 80 bar, more especially approximately 60 bar, preferably at least 50 bar, preferably no more than 70 bar.

Preferably the temperature in the first vessel is approximately 45°C - 60°C, preferably at least 30°C, more preferably no more than 70°C.

Typically the second vessel is a first flash column.

Typically the gases released from the solvent in the second vessel comprise carbon dioxide and said released gases are injected after repressurization into a subsurface reservoir to enhance the recovery of oil from the reservoir.

Preferably at least one of the temperature and pressure in the second vessel is different compared to the temperature and pressure of the first vessel.

Preferably the pressure in the second vessel is between 20 and 70% of the off-gas pressure, preferably 30 and 60%, especially between 5 and 40 bar, more especially between 10-30 bar.

Preferably the temperature in the second vessel is approximately 45°C-60°C, preferably at least 30°C, more preferably no more than 70°C.

In another embodiment, the gases may be heated by 20-50°C before they enter the second vessel, which can cause an increased amount of carbon dioxide to be released from the solvent in the second vessel. This is especially useful when the amount of other gases that are released from the solvent in the second vessel is low.

Preferably the solvent absorption process includes a step (iii), step (iii) comprising: directing the solvent and absorbed gases to a third vessel where a portion of the gases absorbed in the solvent are released and recovered therefrom. Typically the third vessel is a second flash column.

Typically the gases released from the solvent in the third vessel comprise carbon dioxide and said released gases are injected into a subsurface reservoir to enhance the recovery of hydrocarbons from the reservoir.

Preferably at least one of the temperature and pressure in the third vessel is different compared to the temperature and pressure of the second vessel.

Preferably the pressure in the third vessel is between 10 and 45% of the off-gas pressure, preferably 15 and 50%, especially between 3-20 bar, more especially between 4 and 15 bar.

Preferably the temperature in the third vessel is approximately 90°C, preferably at least 60°C, more preferably at least 70°C. Preferably the temperature in the third vessel is no more than 110°C.

Preferably the solvent absorption process includes a step (iv), step (iv) comprising: directing the solvent and absorbed gases to a fourth vessel where a portion of the gases absorbed in the solvent are released and recovered therefrom. Typically the fourth vessel is a third flash column.

Typically the gases released from the solvent in the fourth vessel comprise carbon dioxide and said released gases are injected into a subsurface reservoir to enhance the recovery of hydrocarbons from the reservoir.

Preferably at least one of the temperature and pressure in the fourth vessel is different compared to the temperature and pressure of the third vessel.

Preferably the pressure in the fourth vessel is between 3 and 35% of the off-gas pressure, preferably between 4 and 20%, especially, between 2-7 bar, more especially between 3 and 5 bar, wherein the temperature in the fourth vessel is between 60 °C and 110 °C.

Preferably the temperature in the fourth vessel is approximately 90°C, preferably at least 60°C, more preferably at least 70°C. Preferably the temperature in the fourth vessel is no more than 110°C.

Preferably make up water is added to the process, preferably downstream of the fourth vessel.

Typically the gases released from each vessel are recovered at a pressure equivalent to the pressure in the respective vessel.

Optionally the solvent and absorbed gases may be directed to further vessels where further gases may be released.

Typically at least one of the temperature and pressure in the further vessels is different compared to the temperature and pressure of the preceding vessel.

Preferably each successive vessel operates at a reduced pressure compared to the previous vessel.

Optionally the solvent and absorbed gases may be directed to a regenerator, typically using steam stripping to enhance the removal of CO_2 from the solvent. Typically the gases released from the solvent in the regenerator can comprise carbon dioxide and said gases are injected into a subsurface reservoir to enhance the recovery of hydrocarbons from the reservoir.

Preferably the pressure in the regenerator is approximately 1.5 bar, preferably at least 1 bar, preferably no more than 2 bar.

Preferably the temperature in the regenerator is approximately 120°C, preferably at least 100°C, more preferably at least 110°C. Preferably the temperature in the regenerator is no more than 140°C, more preferably no more than 130°C.

Preferably the solvent comprises an amine, preferably a tertiary amine such as methyldiethanolamine (MDEA).

Preferably the solvent is regenerated. Preferably therefore the solvent is returned from a last vessel, which may be the fourth vessel, to the first vessel.

The invention also provides a process for the production of carbon dioxide, the process comprising obtaining a gaseous mixture comprising heavy paraffin synthesis (HPS) off-gas and recovering carbon dioxide from the heavy paraffin synthesis (HPS) off-gas by the process of solvent absorption, the process of solvent absorption comprising:

(i) allowing the off-gas to come into contact with a solvent in a first vessel and for a portion of the gases within the off-gas to be absorbed therein;

(ii) directing the solvent and absorbed gases to a second vessel where a portion of the gases absorbed in the solvent are released and recovered therefrom.

The gaseous mixture may comprise heavy paraffin synthesis (HPS) off-gas. The HPS off-gas will contain a certain amount of unconverted synthesis gas (i.e. carbon monoxide and hydrogen), carbon dioxide, C_1-C_4 hydrocarbons (formed in the hydrocarbon synthesis reaction) and, optionally, inerts (mainly nitrogen and some argon).

In most cases the HPS off-gas will contain 10-40 wt% hydrogen, especially 15-35 vol%, 20-65 vol% Co, especially 30-55 vol%, 10-50 vol% CO_2, especially 15-45 vol% and 10-55 vol% N2, especially 15-50 vol%.

Preferably the process of solvent absorption is the process of solvent absorption as described herein.

According to a further aspect of the present invention there is provided a process for the sequestration of carbon dioxide, the process comprising injecting a carbon dioxide containing stream into a subsurface formation, wherein the carbon dioxide containing stream has been obtained from a gaseous mixture by the process of solvent absorption.

The process of solvent absorption according to said further aspect of the invention may include any feature or any combination of features described for the process of solvent absorption according to earlier aspects of the invention.

The gaseous mixture may comprise heavy paraffin synthesis (HPS) off-gas.

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.

Preferably the synthesis gas is converted into liquid hydrocarbons 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 C5+ 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 68th 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, VIIB and/or VIIIB 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, manganese, iron, 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 0.001 to 100, preferably 0.05 to 20, preferably 0.1 to 15 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 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.

Thus the invention also provides a hydrocarbon synthesised by a Fischer-Tropsch process, wherein off gas from the Fischer-Tropsch process has been used by a process described herein.

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.

An embodiment of the present invention will now be described, by way of example only, with reference to the accompanying figure which is a flow diagram showing a carbon dioxide recovery process.

The gist of the present invention is the use of carbon dioxide present in the off-gas of a hydrocarbon synthesis process, especially a Fischer-Tropsch process, in an enhanced oil recovery process in such a way that repressuration is kept to a minimum. Thus, the carbon dioxide is extracted from the off-gas by means of a solvent extraction process, especially an aqueous amine extraction process not using an additional physical solvent. The carbon dioxide is removed from the loaded solvent by flashing, preferably at two or more stages, especially three stages, at decreasing pressures. Thus, a part of the carbon dioxide becomes available at a relatively high pressure, a part becomes available at an intermediate pressure and a part becomes available at a relatively low pressure, which low pressure is still above the pressure that is used in a conventional stripping unit (e.g. 1.5 bar). Thus, the energy needed to re-pressurize the carbon dioxide is kept to a minimum.

The carbon dioxide containing stream to be used in the enhanced oil recovery process of the present invention suitably contains at least 80 vol% of carbon dioxide, preferably 90 vol%, more preferably 96 vol%. The amount of nitrogen is suitably less than 10 vol%, more preferably less than 4%, more preferably less than 2%. The miscibility of nitrogen in the oil fraction in the EOR process is considerably less than the miscibility of carbon dioxide. Nitrogen is especially suitable for pressure increase of the reservoir, for instance by injection into the gas cap. Carbon dioxide is suitably injected via injection wells at high pressure at 200-1200 meters from the production well directly into the oil containing layer. The carbon dioxide will assist transport of the oil to the production well. Lower hydrocarbons may be present in relatively large amounts, as these compounds will also increase the transport of the oil via a miscible process mechanism C_1-C_4 hydrocarbon may suitable be present up till 20 vol%, especially 10 vol%. It is observed that from a technical point (high H/C ratio) as from an economical point, it is preferred to use the lower hydrocarbons (C_1-C_4 hydrocarbons) in the hydrocarbon synthesis process, for instance as feed to the syngas manufacturing unit, or, preferably, as feed for the manufacture of hydrogen.

The carbon dioxide containing stream to be used in the present invention may be combined with other carbon dioxide streams. For instance carbon dioxide made in the SMR-process, optionally in combination with a hot and/or cold shift process to convert carbon monoxide and water into hydrogen and carbon dioxide, or carbon dioxide extracted from flue gases, e.g. gas turbine flue gases, boiler furnaces flue gas, and/or (especially) SMR-furnace flue gas, may be used.

Fig. 1 shows a flash recovery process 10 which receives off-gas from a heavy paraffin synthesis unit (not shown), the off gas typically referred to as HOG.

The HOG received from heavy paraffin synthesis contains approximately 10-50% preferably 30% carbon dioxide along with C1-C4 hydrocarbons, carbon monoxide and hydrogen and optionally inerts such as nitrogen. It is an object of the present invention to enrich the carbon dioxide content preferably so that it may be injected into a reservoir to enhance the recovery of hydrocarbons.

A series of compressors 41, 42, 43, 45 are provided to gradually increase the pressure of the recovered carbon dioxide along with a dehydration unit 44 to remove water. The final pressure required of the carbon dioxide depends on the particular reservoir into which it will be injected, but in this example a pressure of around one hundred and fifty bara is required. The number of compressors and the pressure increase provided by each compressor can be varied but in this example the first compressor 41 boosts the pressure up to around five bara, the second compressor 42 boosts the pressure up to around fifteen bara, the third compressor 43 boosts the pressure up to around fifty bara and the fourth compressor 45 boosts the pressure up to around one hundred and fifty bara.

Depending on the pressure of the carbon dioxide when it is separated from the HOG, it may be injected immediately upstream of the first 41, second 42 or third 43 compressor, thus reducing the amount of compression required compared to carbon dioxide recovered at ambient pressures.

The HOG received from the heavy paraffin synthesis unit is at a pressure of around 55-60 bar and a temperature of around 55 - 60°C. At the start of the process, it is injected into an absorber 11.

In the absorber 11, the HOG is mixed with regenerated solvent at a temperature of around 40-70°C and a pressure of around 60 bar. The solvent is typically an amine-based solvent such as, monoethanol amine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA) or preferably methyldiethanolamine (MDEA). Unless otherwise stated, the temperatures stated below are especially suited to chemical solvents.

In alternative embodiments physical solvents may be used. Suitable physical solvents include cyclo-tetramethylenesulfone and its derivatives, aliphatic acid amides, N-methylpyrrolidone, N-alkylated pyrrolidones and the corresponding piperidones, methanol, ethanol, propylenecarbonate, N-formyl-morpholine, N-acetyl-morpholine and mixtures of dialkylethers of polyethylene glycols.

A combination of chemical and physical solvents may also be used.

When using physical solvents the temperature of the absorber 11 can be different. For example, if using methanol, the temperature may be around -40 °C to -60 °C For other physical solvents the temperature may be around 40-50 °C.

Most of the carbon dioxide and a proportion of the carbon monoxide and hydrocarbons are absorbed into the solvent whilst nitrogen, hydrogen, carbon monoxide along with some C1-C6 hydrocarbons are retained in the treated gas. Some water may evaporate from the solvent. The treated gas is sent back and used as fuel gas especially for a gas to liquids plant, particularly for example gas turbines or as a fuel gas in an SMR furnace.

Optionally these latter gases may be fed into an expander before they are used as fuel gas in order to make use of their increased pressure (around 55-60 bar) which is not required when the mixture is used as a fuel gas.

The gases absorbed into the solvent proceed to a first flash column 12 at a temperature of around 45-5 °C.

The first flash column 12 operates at a relatively high pressure, that is around 15 bar and a temperature of approximately 45 - 50 °C. In the first flash column 12, the reduction in pressure compared with the absorber 11 causes a mixture of carbon dioxide, carbon monoxide and C1-C6 hydrocarbons to be evaporated. Some carbon dioxide, and small amounts of other gases are left in the solvent. The gas recovered, which contains approximately 84% carbon dioxide at a relatively high pressure, can then be recovered for injection into a subsurface reservoir. The high pressure carbon dioxide recovered here is at a pressure of around 15 bar and so is injected upstream of the third compressor 43 but downstream of the first and second compressors 41, 42.

An advantage of recovering gas containing carbon dioxide at this early stage in the solvent absorption process is that it is produced at a higher pressure than convention carbon dioxide removal techniques. Since the carbon dioxide is preferably injected into the subsurface reservoir at high pressure, this eliminates the need to compress the carbon dioxide to the same extent, although typically some compression will still be required, such as that provided by the third 43 and fourth 45 compressors.

In alternative embodiments, the gas recovered from the flash column 12 may be used as a fuel gas since it typically contains light end hydrocarbons in addition to the carbon dioxide.

When using physical solvents the temperature of the flash column 12 can be different. For example, if using methanol, the temperature may be around 20 °C to 40 °C. For other physical solvents the temperature may be around 15 - 35 °C.

The solvent and the dissolved gases from the first column 12 proceed to a heater 34. The heater 34, which operates on low pressure steam, heats the fluids to a temperature of around 90 °C. These fluids proceed to the second flash column 13.

The second flash column 13 operates at a temperature of around 90°C and a pressure of approximately 5 - 7 bar. In this column, the increased temperature and reduced pressure compared with the first flash column 12 causes carbon dioxide within the solvent to be evaporated, leaving the solvent and some remaining carbon dioxide behind. The carbon dioxide recovered from the second flash column 13 is at a medium pressure, for example approximately 5 bar and is over 97% carbon dioxide (with the main impurity being water) and so proceeds to the second compressor 42, downstream of the first compressor 41. Thus the recovery of carbon dioxide gas here also benefits from requiring less pressure boosting than convention carbon dioxide removal techniques before it is injected into the subsurface reservoir.

A condenser (not shown) may be used to cool the flashed gas to approximately 40 °C, to reduce the water content of the carbon dioxide stream. This reduces the amount of make-up water required downstream.

Before proceeding to the last flash column, which in this embodiment is a third flash column 14, the solvent and dissolved gases may proceed to any number of further flash columns where more carbon dioxide may be removed therefrom at medium pressure.

When using physical solvents, the stream may bypass the heater 34 and proceed to the second flash column 13. The temperature of the second flash column 13 can be different, for example, if using methanol, the temperature may be around 20 °C to 40 °C. For other physical solvents the temperature may be around 10 - 30°C.

In this embodiment, the solvent and remaining carbon dioxide proceed to the third flash column 14. The third flash column 14 operates at a temperature of 90 °C and a pressure of approximately 1.5 bars. Here, the further decrease in pressure causes most of the remaining carbon dioxide in the solvent to be evaporated. More carbon dioxide is recovered, this time at a low pressure such as approximately 1.5 bar, for injection into a reservoir. The low pressure carbon dioxide recovered here is over 90% carbon dioxide with water being the main impurity and is fed into the first compressor 41.

A further condenser (not shown) may also be used to cool the flashed gas to approximately 40 °C, to reduce the water content of the carbon dioxide stream and reduce the amount of make-up water required.

When using physical solvents, the temperature of the third flash column 14 will typically be different. For example for certain physical solvents the temperature of the third flash column 14 may be around 0 - 20°C.

The solvent can be regenerated and returned to the absorber 11. It first proceeds from the third column 14, through a pressuriser 32, a cooler 35, a further pressuriser 31 and then into the absorber 11 where it starts the cycle again.

Make up water 33 is added to the solvent upstream of the pressuriser 32 to make up for the water which is evaporated during the process.

An advantage of certain embodiments of the invention is that the solvent need not be completely pure when it is returned to the absorber 11 since there is not a strict specification on the returned HOG as a fuel gas. Thus most of the carbon dioxide can be recovered from the solvent at lower temperatures compared to known techniques, thus saving on energy consumption.

Nevertheless, in an alternative embodiment, a conventional regenerator 15 may also be included or may replace the third flash column 14. The regenerator 15 can strip solvent of dissolved gases by heating the solvent to around 120 °C, for example in a reboiler, causing the water within the solvent to evaporate. The carbon dioxide can then be efficiently removed from the solvent and injected upstream of the first compressor 41 and a lean solvent returned to the absorber 11.

An advantage of such alternative embodiments includes the recovery of more carbon dioxide and the lower loading of the solvent allows less solvent to be used.

A benefit of certain embodiments of the present invention is that around 60-80% of the carbon dioxide in the HOG may be recovered at elevated pressures, thus reducing the amount of compression required before it is injected into the reservoir.

In a preferred embodiment the process of the present invention comprises a process in which the carbon dioxide from the second, the third and optionally fourth vessel are pressurized to the same pressure, preferably in one compressor.

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

CLAIMS

1. A process for enhanced oil recovery in combination with the production of liquid hydrocarbons from synthesis gas, the process comprising:

(a) converting synthesis gas into normally gaseous hydrocarbons and normally liquid hydrocarbons and optionally normally solid hydrocarbons, at elevated temperatures and pressures;

(b) recovering off-gas at a pressure between 10-150 bar, preferably 20-100 bar, more preferably 40-80 bar, from said conversion of synthesis gas into liquid hydrocarbons in step (a);

(c) treating the off-gas using the process of solvent absorption, in order to produce a first stream enriched in carbon dioxide and a second stream depleted in carbon dioxide;

(d) recovering hydrocarbons from a subsurface reservoir using at least a portion of the first stream enriched in carbon dioxide produced in step (c), wherein the process of solvent absorption comprises:

(i) allowing the off-gas to come into contact with a solvent in a first vessel and for a portion of the carbon dioxide within the off-gas to be absorbed therein;

(ii) directing the solvent and absorbed carbon dioxide to a second vessel where a portion of the carbon dioxide absorbed in the solvent are released and recovered therefrom, the carbon dioxide having a pressure of at least 5 bar, preferably 10 bar.

2. A process as claimed in claim 1, wherein the pressure in the second vessel is between 20 and 70% of

the off-gas pressure, preferably 30 and 60%, especially between 5 and 40 bar, more especially between 10-30 bar.

3. A process as claimed in claim 1 or 2, wherein the solvent absorption process includes a step (iii), step (iii) comprising: directing the solvent and absorbed carbon dioxide from step (ii) to a third vessel where a further portion of the gases absorbed in the solvent are released and recovered therefrom.

4. A process as claimed in claim 3, wherein the carbon dioxide released from the solvent in the third vessel is injected into a subsurface reservoir to enhance the recovery of hydrocarbons from the reservoir.

5. A process as claimed in claim 4, wherein the pressure in the third vessel is between 10 and 45% of the off-gas pressure, preferably 15 and 50%, especially between 3-20 bar, more especially between 4 and 15 bar.

6. A process as claimed in claim 4 or 5, wherein the temperature in the second and the third vessel is between 45 and 60 °C, respectively between 60 °C and 110 °C.

7. A process as claimed in any one of claims 3 to 6, wherein the solvent absorption process includes a step (iv), step (iv) comprising: directing the solvent and absorbed carbon dioxide to a fourth vessel where a portion of the carbon dioxide absorbed in the solvent is released and recovered therefrom, preferably said released carbon dioxide being injected into a subsurface reservoir to enhance the recovery of hydrocarbons from the reservoir.

8. A process as claimed in claim 7, wherein the pressure in the fourth vessel is between 3 and 35% of the off-gas pressure, preferably between 4 and 20%, especially, between 2-7 bar, more especially between 3

and 5 bar, wherein the temperature in the fourth vessel is between 60 °C and 110 °C.

9. A process as claimed in any one of claims 1 to 8, wherein the solvent and absorbed carbon dioxide are directed to a regenerator, preferably using steam stripping.

10. A process as claimed in any one of claim 1 to 9, wherein the second stream is used as fuel gas, especially for a gas to liquids plant or as a feed gas for the preparation of synthesis gas and/or hydrogen.

11. A process for the treatment of off gas from a heavy paraffin synthesis unit, the process comprising: treating off gas from a heavy paraffin synthesis unit by the process of solvent absorption in order to produce a first stream enriched in carbon dioxide and a second stream depleted in carbon dioxide in the way as described in any one of claim 1-10, wherein the first stream enriched in carbon dioxide is sequestrated into a subsurface formation.

12. A process as claimed in any one of claims 1 to 11, wherein the synthesis gas is converted into liquid hydrocarbons by the Fischer-Tropsch process.

13. A hydrocarbon synthesised by a Fischer-Tropsch process, wherein off gas from the Fischer-Tropsch process has been used by a process as claimed in claim 1-12, preferably a hydrocarbon which has undergone the steps of hydroprocessing, preferably hydrogenation, hydroisomerisation and/or hydrocracking.

14. A process according to any one of claims 1 to 12, in which the carbon dioxide streams from the second, the third and optionally fourth vessel are pressurized to the same pressure, preferably in one compressor.

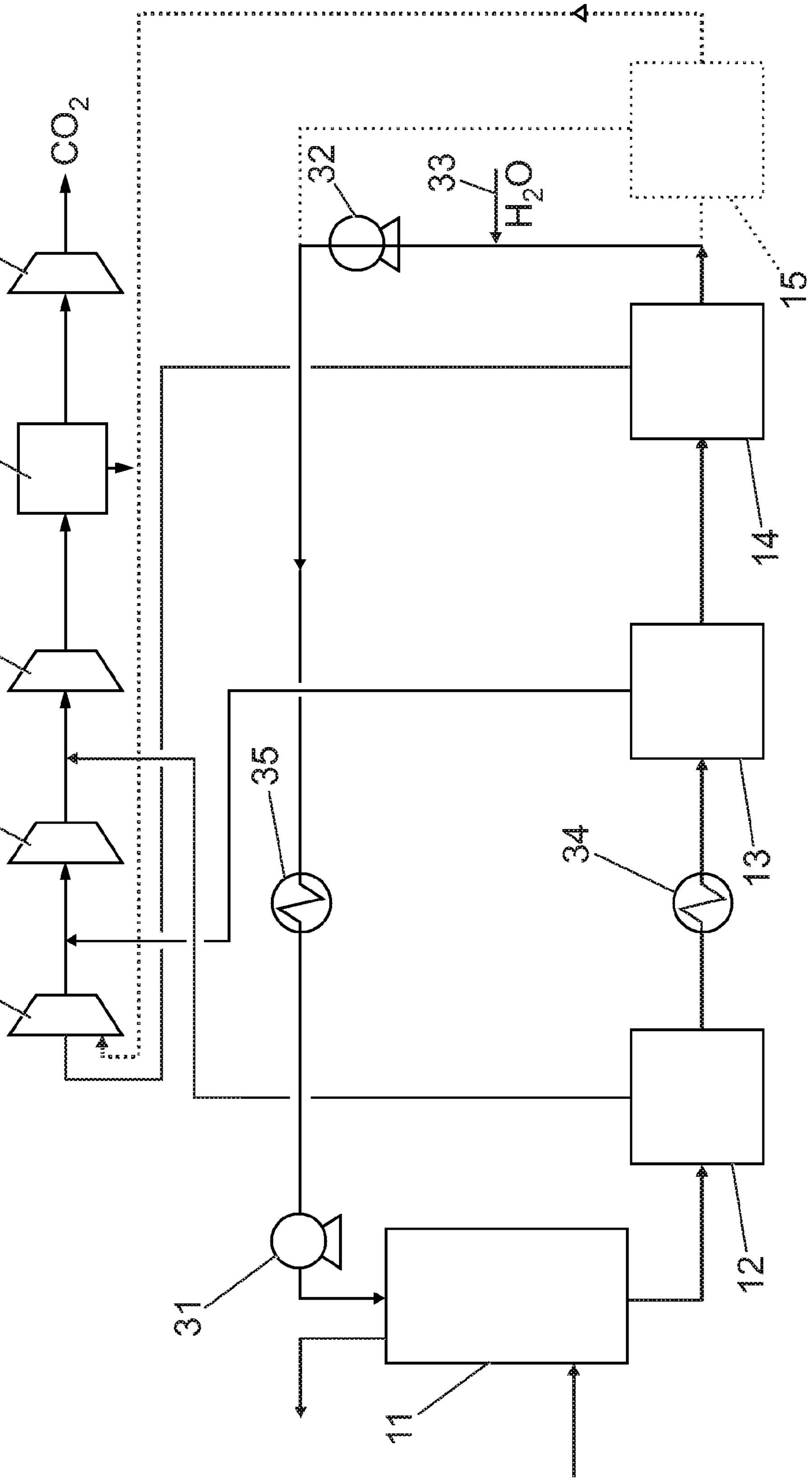


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/070052

A. CLASSIFICATION OF SUBJECT MATTER
INV. E21B43/16 C10G2/00 B01D53/14 C01B31/20

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 C10G B01D C01B

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/120017 A1 (BOHN MARK S [US] ET AL) 29 August 2002 (2002-08-29)	13
Y	paragraphs [0008], [0047], [0054], [0083], [0088], [0091], [0092]	1-12,14
Y	US 5 061 465 A (CARTER CECIL O [US]) 29 October 1991 (1991-10-29) column 1, lines 20,21 column 1, lines 44-47 column 2, lines 35-44 column 3, line 50 - column 4, line 17; figure 1	1-12,14
X	US 5 506 272 A (BENHAM CHARLES B [US] ET AL) 9 April 1996 (1996-04-09)	13
A	column 14, lines 26-34	1-12,14
	-/--	

☒ 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

"E" earlier document but published on or after the international filing date

"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)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search
5 April 2007

Date of mailing of the international search report
18/04/2007

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
BELLINGACCI, F

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/070052

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 957 715 A (GROVER BHADRA S [US] ET AL) 18 September 1990 (1990-09-18) column 7, lines 24-33	1-14
X	WO 2004/055322 A (STATOIL ASA; PETROSA LTD; SHAW, GARETH, DAVID, HUNTLEY; OLSVIK, OLA;) 1 July 2004 (2004-07-01)	13
A	page 1, lines 11-14 page 3, lines 15-19 page 10, lines 16-20 page 15, lines 32-34	1-12,14
X	US 2004/244973 A1 (PARSLEY ALAN JOHN ET AL) 9 December 2004 (2004-12-09)	13
A	paragraphs [0001], [0003], [0021], [0022], [0030], [0035], [0044]	1-12,14
A	US 4 218 326 A (CROUCH, WILLIAM B ET AL) 19 August 1980 (1980-08-19) column 4, lines 35-42	1-14
A	US 4 093 029 A (WEISZ ET AL) 6 June 1978 (1978-06-06) column 1, lines 12-22 column 2, lines 35-45 column 4, lines 24-50	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2006/070052

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002120017 A1	29-08-2002	NONE	
US 5061465 A	29-10-1991	NONE	
US 5506272 A	09-04-1996	US 5500449 A	19-03-1996
US 4957715 A	18-09-1990	NONE	
WO 2004055322 A	01-07-2004	AU 2002351515 A1	09-07-2004
		BR 0215983 A	01-11-2005
		CA 2509944 A1	01-07-2004
		MX PA05006314 A	08-02-2006
		US 2006231252 A1	19-10-2006
US 2004244973 A1	09-12-2004	CA 2457075 A1	27-02-2003
		EA 5346 B1	24-02-2005
		WO 03016676 A1	27-02-2003
		GC 0000244 A	29-03-2006
		MX PA04001341 A	05-05-2004
		NO 20041056 A	12-03-2004
US 4218326 A	19-08-1980	NONE	
US 4093029 A	06-06-1978	US 4098339 A	04-07-1978