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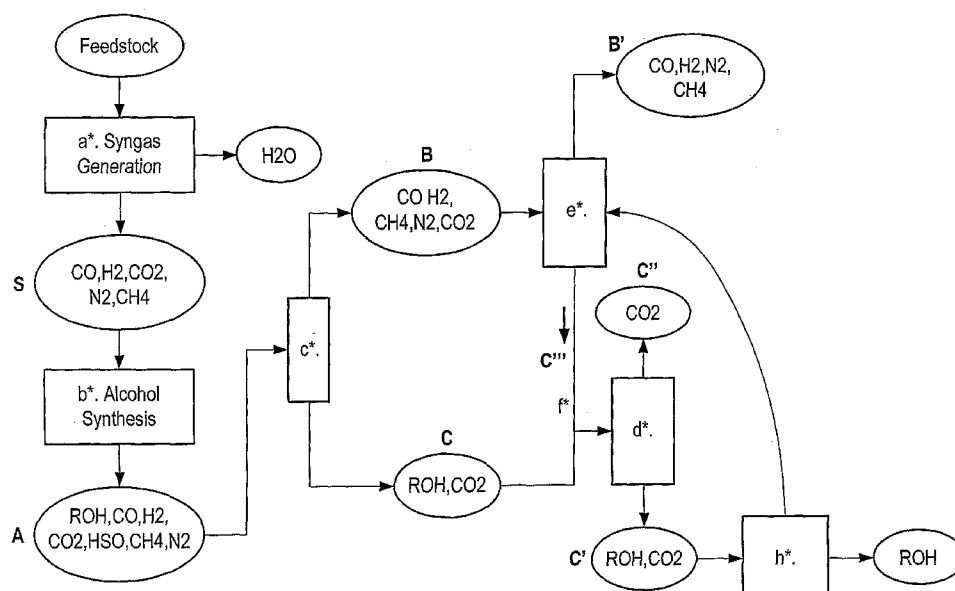
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(54) Title: PROCESS FOR HYDROGEN, CO₂ AND ALCOHOL PRODUCTION



(57) Abstract: This invention relates to the production of alcohol, CO₂ and hydrogen from a hydrogen and carbon-containing compound, such as a hydrocarbon. More specifically, this invention relates to the production from a hydrogen and carbon containing compound of - mixed alcohol's for hydrogen and CO₂ improved separation and recovery, - CO₂ for hydrocarbon improved recovery from wells with optional CO₂ sequestration in the wells, - Alcohol's and CO₂ for enhanced hydrocarbon recovery from wells through the introduction of a stream containing the said alcohol's and CO₂ into the wells with optional sequestration of CO₂, and - hydrogen for power generation.



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PROCESS FOR HYDROGEN, CO₂ AND ALCOHOL PRODUCTION

This invention relates to the production of alcohol, CO₂ and hydrogen from a hydrogen and carbon containing compound, such as a hydrocarbon. More specifically, this invention relates to the production from a hydrogen and carbon containing compound of

- mixed alcohols for hydrogen and CO₂ improved separation and recovery,
- CO₂ for hydrocarbon improved recovery from wells with optional CO₂ sequestration in the wells,
- Alcohols and CO₂ for enhanced hydrocarbon recovery from wells through the introduction of a stream containing the said alcohols and CO₂ into the wells with optional sequestration of CO₂, and
- hydrogen for energy generation (e.g. power and heat generation and fuel cells) and/or chemical use.

US 4,122,110 relates to a process for manufacturing alcohols, particularly linear saturated primary alcohols, by reacting carbon monoxide with hydrogen at a pressure between 20 and 250 bars and a temperature between 150 °C and 400 °C., in the presence of a catalyst, characterized in that the catalyst contains at least 4 essential components: (a) copper (b) cobalt (c) at least one element M selected from chromium, iron, vanadium and manganese, and (d) at least one alkali metal.

US 4,831,060 relates to the production of mixed alcohols from carbon monoxide and hydrogen gases using a catalyst, with optionally a co-catalyst, wherein the catalyst metals are molybdenum, tungsten or rhenium, and the co-catalyst metals are cobalt, nickel or iron. The catalyst is promoted with a Fischer-Tropsch promoter like an alkali or alkaline earth series metal or a smaller amount of thorium and is further treated by sulfiding. The composition of the mixed alcohols fraction can be selected by selecting the extent of intimate contact among the catalytic components.

Journal of Catalysis 114, 90-99 (1988) discloses a mechanism of ethanol formation from synthesis gas over CuO/ZnO/Al₂O₃. The formation of ethanol from CO and H₂ over a CuO/ZnO methanol catalyst is studied in a fixed-bed microreactor by measuring the isotopic distribution of the carbon in the product ethanol when C(13) methanol was added to the feed.

The combustion of fossil fuels to generate electrical power and/or pressurised

steam results in the formation of carbon dioxide, which is a so-called "greenhouse gas". The level of carbon dioxide present in today's atmosphere is a well documented environmental concern, as carbon dioxide is considered to be the most prominent of all the "greenhouse gases", and therefore one of the main pollutants in the present atmosphere. It is becoming increasingly desirable to minimise atmospheric emissions of such greenhouse gases to the atmosphere in order to reduce the potential harm that such greenhouse gases have on the global climate.

Increasing attention is being focused on hydrogen as a fuel, as the energy produced per unit mass is high, and the only combustion product is water. However, most hydrogen currently produced is derived from fossil fuels, for example from refining processes such as catalytic reforming, through processes such as steam reforming or autothermal reforming of hydrocarbons or oxygenated hydrocarbons, or through partial oxidation of hydrocarbons.

Processes describing the production of hydrogen from carbon-based fuels include, for example, that described in WO 02/45838, which relates to an apparatus having a plurality of modules for the production of substantially pure hydrogen from a hydrocarbon fuel, in which the apparatus comprises a module with a steam reforming and partial oxidation catalyst to produce hydrogen, carbon dioxide and carbon monoxide, and additional modules for high temperature and low temperature water gas shift reactions for converting carbon monoxide to carbon dioxide. Also provided is a module for sulphur removal, and a module for low temperature oxidation to remove residual traces of carbon monoxide. The resulting hydrogen-rich gas can be fed to a fuel cell for power and/or electricity generation, either with or without prior purification to remove other components such as carbon dioxide, water and residual hydrocarbon.

The separation of hydrogen from other gases can be achieved using a selectively permeable membrane. For example, US 4,810,485 describes a reactor for a hydrogen-forming reaction, for example a steam reforming or water-gas-shift reaction, which comprises a hydrogen-ion porous foil, such as a palladium foil. This is capable of selectively removing hydrogen produced in the hydrogen-forming reaction, which shifts the equilibrium and enables higher conversions of hydrogen-containing reactant and higher hydrogen yields to be achieved.

WO02/70402 describes a further reactor for the reforming of a vapourisable hydrocarbon to produce hydrogen and carbon dioxide using a reactor with a hydrogen-permeable membrane, and which is heated by flameless distributed combustion in a region of the reactor separate to that in which the steam-reforming and hydrogen separation processes occur. US 5,741,474 also describes the production of high-purity hydrogen by feeding hydrocarbon, water and oxygen to a reactor comprising a catalyst for steam reforming and partial oxidation, in which hydrogen is separated within the reactor by use of selective hydrogen-permeable membrane tubes, wherein the permeated hydrogen is combined with a low pressure inert gas to remove or flush it from the tubes.

Itoh et al in *Catalysis Today*, 2003, vol 82, pp119-125 describe that, in a process for dehydrogenation of cyclohexane using a palladium-membrane reactor for selectively removing hydrogen, the rate of dehydrogenation and the rate of hydrogen recovery is enhanced when the pressure difference across the membrane is increased, and states that it is advantageous to maintain the pressure on the permeate-side of the membrane as low as possible in order to improve the rate of hydrogen production. This is corroborated by the teaching of US 4,810,485, which describes how increasing hydrogen permeation rate is achievable with increased pressure-drop across the hydrogen separation membrane.

Figure 1 represents one embodiment of a process scheme according to the present invention. This said embodiment comprises optional, and/or preferred, process steps according to the present invention. The letter references in Figure 1 correspond to those used in the present description and appending claims.

Thus, the present invention provides a process for the production of alcohol, CO₂ and hydrogen from a hydrogen and carbon containing compound, which comprises the steps of;

- a) converting in a syngas reactor hydrogen and carbon containing compound(s) into a stream S, consisting of a mixture of carbon oxide(s) and hydrogen, CH₄ and optionally N₂,
- b) converting in a alcohol synthesis reactor a carbon oxide(s) and hydrogen feed from stream S into a alcohol stream A, comprising alcohols, H₂ and CO, CO₂, H₂O, CH₄ and optionally N₂,

- c) separating the alcohol stream A into a stream B, comprising essentially H₂, CO, most of the CO₂, CH₄ and optionally N₂, and a stream C comprising the alcohols and the remaining CO₂,
- d) separating stream C into a purified alcohol feedstock C' and a CO₂ feedstock C'',
- e) backwashing stream B, with alcohol taken from feedstock C', and recovering a stream C''', comprising essentially alcohol and CO₂ and a hydrogen stream B', comprising essentially H₂, CO, CH₄ and optionally N₂, and
- f) introducing the recovered stream C''' into step d).

It is thus now possible according to the integrated process of the present invention to co-produce, in an efficient process, an alcohol (C'), CO₂ (C'') and H₂ (B') feedstock from a hydrogen and carbon containing compound. Part of the alcohol is advantageously used in the integrated process in order to isolate the CO₂ (C''') from the H₂ rich feedstock (B).

According to an embodiment of the present invention, at least part, preferably all of the remaining alcohol can be sold or further dehydrated into olefins.

As indicated, step (f) consists of introducing the recovered stream C''' into step d). This can be achieved by introducing C''' separately from the stream C into the separator step (d) or, preferably, by adding stream C''' to stream C and introducing the combined stream into the separation step (d).

The isolated CO₂ can advantageously be used for hydrocarbon (oil and/or gas) improved recovery from wells. This recovery of hydrocarbon, e.g. oil, can even be further enhanced by introducing a stream containing the said CO₂ together with some of the produced alcohols into the wells.

Optionally, the recovered CO₂ can be sequestered for long term storage into wells.

Sequestration can be defined as being the net removal of CO₂ from the atmosphere (i.e. the removal of part or all of the CO₂ that may be emitted during the present process) into long-lived pools of carbon. Where the 'long-lived pools of carbon' may be any one or more of the following: living aboveground biomass (e.g. trees); wood products with a long, useful life created from biomass (e.g. lumber); living biomass in soils (e.g. roots and microorganisms) and/or recalcitrant organic and inorganic carbon in soils; and deeper subsurface environments (e.g. such as oceans and geolocial formations).

According to an embodiment of the present invention, the preferred “long-lived carbon pools” are those that are a product of geologic formations, as these provide a necessary longer term storage when compared to the other pools proposed.

The geological formations that are most suitable for CO₂ sequestration are: (1) deep brine formations, (2) oil and gas formations, and (3) coal formations.

Whilst not wishing to be bound by theory, it is believed by the applicants, that there are three principal methods by which the CO₂ may be sequestered into these said geologic formations:

1. CO₂ may be trapped as a gas, or as a supercritical fluid, under a low permeability caprock, e.g. by using a similar method to that used when natural gas is trapped in gas reservoirs, or the method used when gas is stored in aquifer gas storage. This method of sequestration is commonly referred to as hydrodynamic trapping and, in the short term, is likely to be the most important mechanism for CO₂ sequestration.
2. CO₂ may be dissolved into the fluid phase. This method is referred to as “solubility trapping”. In oil reservoirs, this lowers the viscosity and swells the oil, which provides the basis for one of the more common enhanced oil recovery (EOR) techniques. The relative importance of “solubility trapping” depends on a large number of factors, such as the sweep efficiency of CO₂ injection, formation of fingers, and the effects of formation heterogeneity.
3. CO₂ can be reacted, either directly or indirectly, with the minerals and organic matter in the geologic formations to become part of the solid mineral matrix. Formation of carbonate minerals such as calcite or siderite and adsorption onto coal are examples of “mineral trapping”.

In practice, the mechanism of choice is heavily dependent on the type of geological formation used for sequestration.

Finally, the H₂ feedstock can be advantageously used for energy generation (e.g. power and heat generation and fuel cells) and/or for chemical use.

Figure 2 represents another embodiment of a process scheme according to the present invention. This said embodiment comprises optional and/or preferred process steps according to the present invention. The letter references in Figure 2 correspond to those used in the present description and appending claims. In the said Figure 2 it can be seen

that the hydrogen stream B' which also comprises CO, CH₄ and optionally N₂, is subjected to an additional separation step g) wherein a purified H₂ feedstock and a CO, CH₄ and optionally N₂ stream are separately recovered.

Thus, according to a preferred embodiment of the present invention, there is provided a process for the production of alcohol, CO₂ and hydrogen from a hydrogen and carbon containing compound, which comprises the steps of;

- a) converting in a syngas reactor hydrogen and carbon containing compound(s) into a stream S, consisting of a mixture of carbon oxide(s) and hydrogen, CH₄ and optionally N₂,
- b) converting in a reactor, a carbon oxide(s) and hydrogen containing feedstock from stream S, into an alcohol stream A, comprising alcohols, H₂ and CO, CO₂, H₂O, CH₄ and optionally N₂,
- c) separating the alcohol stream A, into a stream B, comprising essentially H₂, CO and most of the CO₂, CH₄ and optionally N₂; and a stream C, comprising the alcohols and the remaining CO₂,
- d) separating stream C, into a purified alcohol feedstock C', and a CO₂ feedstock C'',
- e) backwashing stream B with alcohol taken from feedstock C' and recovering a stream C''', comprising essentially alcohol and CO₂ and a hydrogen stream B' comprising essentially H₂, CO, CH₄ and optionally N₂,
- f) introducing the recovered stream C''' into step (d), and
- g) separating hydrogen stream B' into a purified hydrogen feedstock and a separated CO, CH₄ and optionally N₂ stream.

Any hydrogen and carbon containing compound that can be converted into a feedstock comprising carbon oxide(s) and hydrogen, most preferably into a synthesis gas (or "syngas"), is useful as primary feedstock in the processes of the invention.

The hydrogen and carbon containing compound (hydrocarbon feedstock) used according to the present invention is preferably a carbonaceous material, for example biomass, plastic, naphtha, refinery bottoms, smelter off gas, crude syngas (from underground coal gasification or biomass gasification), LPG, gas oil, vacuum residuals, shale oils, asphalts, various types of fuel oils, municipal waste, hydrocarbon containing process recycle streams and coal and/or natural gas; with coal and natural gas being the preferred sources and natural gas being the most preferable source.

Natural gas, the most preferred hydrocarbon feedstock used according to the process of the present invention, usually contains varying amounts of N₂ and other inert gases (e.g. He) that make some well fields economically unattractive. This, combined with the potential incomplete conversion of the hydrocarbon(s) to syngas can necessitate a higher purge from the syngas process e.g. a methanol process. Similarly, natural gas can also contain CO₂ which again make some well fields economically unattractive. An advantage according to the process of the present invention is that the present process can cope with the said N₂ and/or CO₂ presences by advantageously recovering the said N₂ and/or the said CO₂ and, for example, re-injecting the said N₂ and/or the said CO₂ into the well field in order to improve the natural gas recovery; this makes more fields economically attractive and also increases the lifetime thereof. For example, from the H₂ recovery step (g), the N₂ stream can also be used to enhance hydrocarbon recovery from the well.

While natural gas is the most preferred feedstock used according to the present invention, coke, coal biomass and refinery bottoms can also advantageously be used according to an embodiment of the present invention. Indeed, while the use of the said coke, coal biomass and refinery bottoms feedstocks generates sub stoichiometry syngas, the corresponding CO₂ sequestration allows economic use thereof with lowered environmental impact.

Processes for producing mixtures of carbon oxide(s) and hydrogen (commonly known as synthesis gas) are well known. Each method has its advantages and disadvantages, and the choice of using a particular reforming process over another is governed by economic and available feed stream considerations, as well as by the desire to obtain the optimum (H₂-CO₂):CO+CO₂) molar ratio in the resulting synthesis gas, that is suitable for further chemical processing. The synthesis gas may be prepared using any of the processes known in the art including partial oxidation of hydrocarbons (POX), steam reforming (SR), advanced gas heated reforming (AGHR), microchannel reforming (as described in, for example, US 6,284,217), plasma reforming, autothermal reforming (ATR) and any combination thereof.

A discussion of these synthesis gas production technologies is provided for in "Hydrocarbon Processing" V78, N.4, 87-90, 92-93 (April 1999) and/or "Petrole et

Techniques", N. 415, 86-93 (July-August 1998), which are both hereby incorporated by reference.

It is also known that the synthesis gas may be obtained by catalytic partial oxidation of hydrocarbons in a microstructured reactor as exemplified in "IMRET 3: Proceedings of the Third International Conference on Microreaction Technology", Editor W Ehrfeld, Springer Verlag, 1999, pages 187-196. Alternatively, the synthesis gas may be obtained by short contact time catalytic partial oxidation of hydrocarbonaceous feedstocks as described in EP 0303438.

Preferably, the synthesis gas is obtained via a "Compact Reformer" process as described in "Hydrocarbon Engineering", 2000, 5, (5), 67-69; "Hydrocarbon Processing", 79/9, 34 (September 2000); "Today's Refinery", 15/8, 9 (August 2000); WO 99/02254; and WO 200023689.

Feedstocks comprising carbon monoxide and hydrogen, e.g., synthesis gas may undergo purification prior to being fed to any of the above reaction zones. Synthesis gas purification may be carried out by processes known in the art. See, for example, Weissermel, K. and Arpe H.-J., Industrial Organic Chemistry, Second, Revised and Extended Edition, 1993, pp. 19-21.

According to an embodiment of the present invention, the syngas used in the present invention is obtained via a methane steam reforming (MSR) or via the combination of methane steam reforming with a partial oxidation of hydrocarbons.

According to another embodiment of the present invention, the syngas used in the present invention is obtained via a autothermal reforming (ATR) process; indeed, the use of a large scale ATR technology makes the overall economics of the process according to the present invention even more attractive.

Optionally the overall carbon footprint, that is the level of emissions to the environment, can be further reduced by sequestering the CO₂ generated by the use of fuel for the SMR and/or ATR/SMR syngas generation units.

Typically, for commercial syngas production the pressure at which the synthesis gas is produced ranges from approximately 1 to 100 bar, preferably 20 to 50 bar and the temperature at which the synthesis gas exits the reformer ranges from approximately 700 °C to 1300 °C. The synthesis gas contains a molar ratio of hydrogen to carbon oxide [i.e.

(H₂-CO₂):(CO+CO₂)] ranging from 0.8 to 3.0, which is dependent on the hydrocarbon feedstock(s) and the method of reforming used.

According to an embodiment of the present invention, the (H₂-CO₂):(CO+CO₂) molar ratio of stream S obtained from the syngas reactor when natural gas is used is of at least 0.8, preferably between 1.0 and 3.0 and most preferably between 2.4 and 2.8.

According to an embodiment of the present invention, the (H₂-CO₂):(CO+CO₂) molar ratio of the carbon oxide(s) and hydrogen feed from stream S introduced into the alcohol synthesis reactor is comprised between 0.5 and 2.0, preferably comprised between 0.8 and 1.3. The potential excess of hydrogen can usefully be used for energy generation (e.g. power and heat generation and fuel cells) and/or for further chemical processing. For example, this excess hydrogen can easily be separated from stream S by using a membrane or a cryogenic separation if high purity hydrogen is required.

According to an embodiment of the present invention, the alcohols produced in step (b) are mainly methanol, ethanol, propanol(s) (predominately n-propanol with low amounts of iso-propanol) and butanol(s) (predominately n- butanol and isobutanol); said methanol, ethanol, propanol(s) and butanol(s) preferably represent together at least 50% by weight of the liquid products (under STP conditions) obtained from the alcohol synthesis reactor, more preferably at least 75% by weight and most preferably at least 90% by weight.

According to another embodiment of the present invention, water and carbon dioxide are also produced in the reactor; and the water and alcohols preferably represent together at least 80% by weight of the liquid products (under STP conditions) obtained from the reactor, preferably at least 90wt%, more preferably at least 95wt% and most preferably at least 99wt%.

The particulate catalyst according to the present invention for the conversion of carbon oxide(s) and hydrogen containing feedstocks, e.g. synthesis gas or syngas, to alcohols is preferably a particulate modified molybdenum sulphide based catalyst and/or a modified methanol based catalyst and/or a modified Fischer-Tropsch catalyst and/or a rhodium-based heterogeneous catalyst.

Molybdenum sulphide based catalysts are preferred; these can be modified by a promoter. Promoter(s) can be added as salts during the catalyst preparation, and are preferably potassium ions (e.g. derived from a salt of potassium, such as potassium

carbonate or acetate). The preferred loadings of potassium ions per molybdenum is comprised between 0.7 and 1.5, most preferably between 1.0 and 1.4.

The preferred catalyst, according to the present invention, is a molybdenum sulphide based catalysts containing cobalt, the cobalt to molybdenum molar ratio being preferably comprised between 0.5 and 3.0, more preferably between 0.5 and 1.0 and most preferably between 0.5 and 0.9. According to an embodiment of the present invention, for the Molybdenum based catalyst, the temperature in the alcohol synthesis reaction zone is selected from the range of starting from about 200°C to about 400°C.

For purposes of this invention, GHSV is gas hourly space velocity which is the rate of gas flow over the catalyst. It is determined by dividing the volume of gas (at 25°C. and 1 atmosphere) which passes over the catalyst in one hour by the volume of the catalyst.

The gas hourly space velocity (GHSV) of the feedstock (litres of feedstock/hr/litre of catalyst) passing through the reaction zone can vary significantly, depending upon a variety of factors such as, for example, reaction conditions, composition of the feedstock and quantity and type of catalyst being used. Preferably, the GHSV can be maintained at any rate in the range of from about 1 to about 30,000 hr⁻¹ or more, preferably will be maintained at a rate of between about 500 and 20,000 hr⁻¹, and most preferably will be maintained at a rate of between 1,000 and 10,000 hr⁻¹.

The pressure in the reaction zone may be selected from the range of from about 50 to 200 bar, preferably a pressure in the range of from about 80 to 150 bar. The hydrogen and carbon monoxide partial pressures should be sufficient to enable the production of the alcohols. Hydrogen and carbon monoxide may be fed separately to the conversion reactor or, preferably in combination, e.g., as synthesis gas.

The conversion to alcohols reaction can be carried out in a conversion reactor by passing the mixture of hydrogen and carbon monoxide over the conversion catalyst as a vapour phase reaction or as a liquid phase reaction, e.g., slurry reaction or trickle bed fluidized bed reactor.

The term conversion reactor as used in the present invention pertains to any appropriate reactor, e.g. a tubular reactor using a fixed bed of the catalyst. The reactants may be fed upwards or downwards to the catalyst, or a combination of both, to a fixed bed located in a tubular reactor. The reaction may be effected in a dynamic bed of the catalyst. In such a reaction, the bed of catalyst is moving such as in the case of a fluid bed of the

catalyst. The conversion reactor may preferably be chosen amongst tubular, multitubular, slurry, moving bed, fluidised bed, radial bed, multibed or reactive distillation reactor. According to an embodiment of the present invention, a fixed bed reactor is used, preferably a radial bed(s) or a multitubular vapour phase reactor or a combination thereof is used. Most preferably the conversion reactor comprises a series of adiabatic fixed bed reactors operated either in a longitudinal and/or radial flow mode.

The exit gas stream from the step (b) alcohol synthesis reactor can be modified by adding water and performing a water gas shift (WGS) reaction to generate CO₂ and H₂, both of which are the added value products obtained according to the present process. This additional WGS reaction can be conveniently conducted in the alcohol synthesis reactor by adding water to a WGS active catalyst; alternatively, this can be conducted in a separate reaction stage on process streams A and/or B and/or B', preferably on streams A and/or B.

According to an embodiment of the present invention, the hot stream A from the alcohol synthesis reactor is cooled to facilitate the separation (step c) of the alcohols (stream C) from the gas stream B by using a knockout drum or a dephlegmator. This separation is preferably conducted at the alcohol synthesis reaction pressure. The said stream B is then washed with alcohol taken from feedstock C', allowing to recover a stream C''' comprising essentially alcohol and CO₂ and a hydrogen rich stream B' comprising essentially H₂, CO, CH₄ and optionally N₂. The efficiency of the alcohol wash can be improved by pre-chilling the alcohol taken from feedstock C'. An additional optional improvement to reduce the alcohol potentially entrained with the hydrogen rich stream B' is to use a fraction of C₂+ alcohols (from ethanol to higher alcohols) instead of methanol containing alcohols; the preferred alcohol range used for performing the wash is ethanol and/or propanol. Such a stream can be conveniently obtained by conventional distillation, e.g. as shown as stage h) in figures 1 and 2.

The alcohol washing requires good gas/liquid contact. Common methods used include vessel internals which increase internal surface area of contact between liquid and gas, such as packings, structured packings, baffles, sieve plates.

Alternatively, said CO₂ rich stream B' may be recovered by any suitable method(s) known to those skilled in the art, for example, by reacting with amines; performing a methanol wash (i.e. the RECTISOL process) and/or by using hot potassium carbonate (e.g. the BENFIELD process).

According to an alternative embodiment of the present invention, steps c) and e) can advantageously be combined into a single vessel.

As shown in Figure 2, stream B' can be additionally treated to generate a purified hydrogen feedstock and a separated CO, CH₄ and optionally N₂ stream. Said treatment can be performed by using a membrane separation technique. For very high purity hydrogen generation (e.g. chemical use), a cryogenic stage may also be employed according to the present invention.

The streams B and/or B' and/or B'' can be used in their entirety as a fuel, e.g. for power generation and/or syngas. However, treatment e) and g) are advantageously used to reduce the undesirable CO₂ emissions.

The function of stage d) is to separate stream C and stream C''' into an alcohol feedstock C' and a CO₂ feedstock C''. The CO₂ feedstock C'' is preferably produced at superatmospheric pressure in order to meet the feed requirement of chemical and sequestration processes. The degassing of the mixture is conveniently conducted by heating the mixture to reduce the solubility of the CO₂ in the alcohols.

This is preferably done by degassing the mixture at intermediate pressures between the alcohol synthesis pressure and the atmospheric pressure; this can be done in several consecutive stages; the CO₂ gas obtained from the lower pressure stage may require compression.

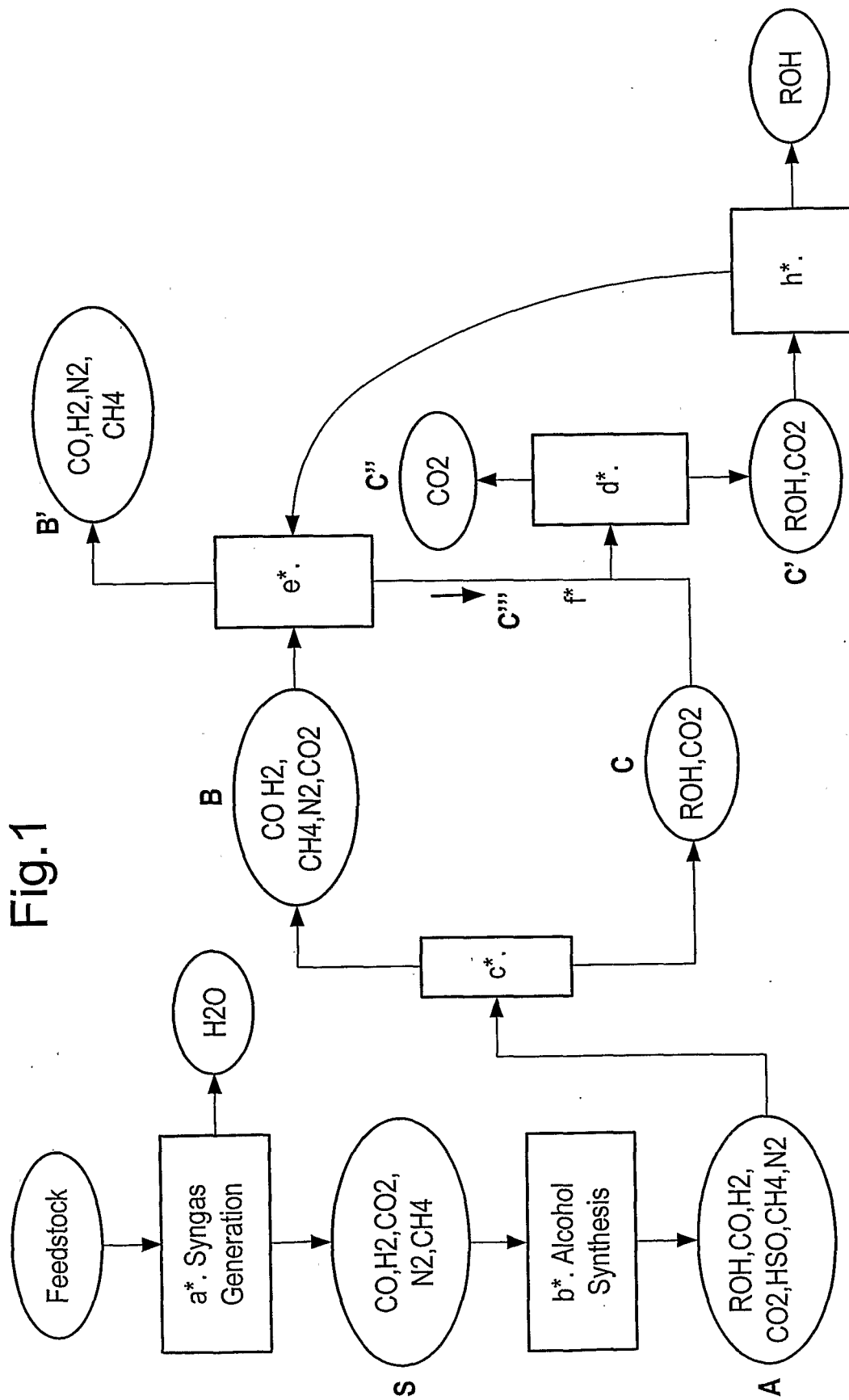
In an embodiment of the present invention, the carbon dioxide produced by the process (for example in the alcohol synthesis and/or in the fuel side of the syngas generation) is sequestered and stored so that it is not released into the atmosphere. Preferably this is achieved by feeding the carbon dioxide into an oil and/or gas well, which ensures that the carbon dioxide is unlikely to be released to the atmosphere, while simultaneously enabling improved extraction of oil and/or gas therefrom.

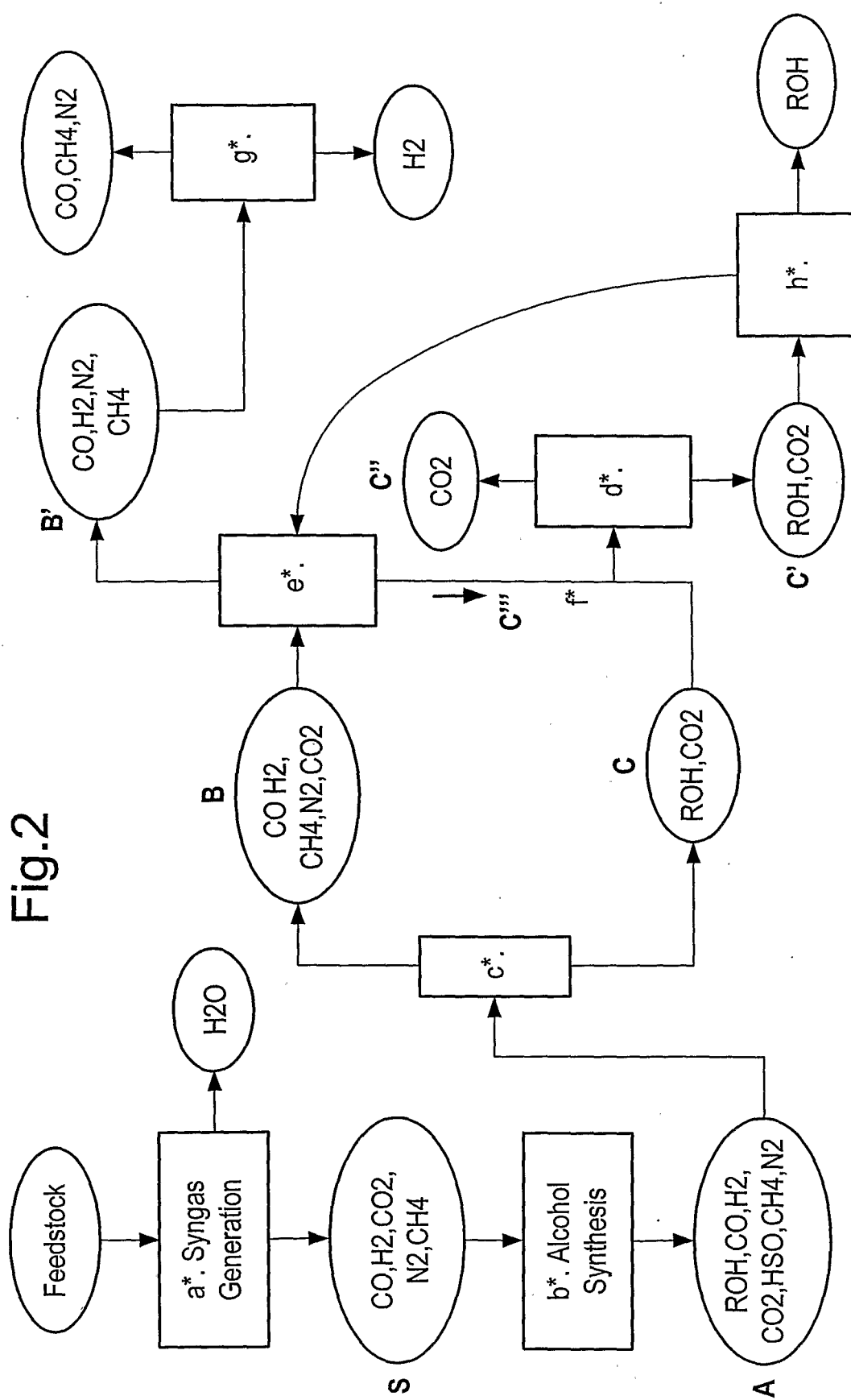
The carbon dioxide is preferably dried before sequestration to prevent potential corrosion problems. This is typically achieved by cooling the wet carbon dioxide stream to ambient temperature, typically below 50°C, preferably below 40°C, and feeding it to a water separator, in which the water condenses and a stream of dry carbon dioxide is produced. The condensed water can optionally be re-used in the process, for example as a feed to a pressurised steam supply or as a feed to one or more of the reactors.

Claims

1. Process for the production of alcohol, CO₂ and hydrogen from a hydrogen and carbon containing compound, which process comprises the steps of;
 - a) converting in a syngas reactor a hydrogen and carbon containing compound into a stream S consisting of a mixture of carbon oxide(s) and hydrogen, CH₄ and optionally N₂,
 - b) converting in a alcohol synthesis reactor a carbon oxide(s) and hydrogen feed from stream S into a alcohol stream A comprising alcohols, H₂ and CO, CO₂, H₂O, CH₄ and optionally N₂,
 - c) separating the alcohol stream A into a stream B comprising essentially H₂, CO, most of the CO₂, CH₄ and optionally N₂, and a stream C comprising the alcohols and the remaining CO₂,
 - d) separating stream C into a purified alcohol feedstock C' and a CO₂ feedstock C'',
 - e) backwashing stream B with alcohol taken from feedstock C' and recovering a stream C''' comprising essentially alcohol and CO₂ and a hydrogen stream B' comprising essentially H₂, CO, CH₄ and optionally N₂, and
 - f) introducing the recovered stream C''' into step d).
2. Process for the production of alcohol, CO₂ and hydrogen from a hydrogen and carbon containing compound, which process comprises the steps of;
 - a) converting in a syngas reactor a hydrogen and carbon containing compound into a stream S consisting of a mixture of carbon oxide(s) and hydrogen, CH₄ and optionally N₂,
 - b) converting in a reactor a carbon oxide(s) and hydrogen feed from stream S into a alcohol stream A comprising alcohols, H₂ and CO, CO₂, H₂O, CH₄ and optionally N₂,
 - c) separating the alcohol stream A into a stream B comprising essentially H₂, CO, most of the CO₂, CH₄ and optionally N₂, and a stream C comprising the alcohols and the remaining CO₂,
 - d) separating stream C into a purified alcohol feedstock C' and a CO₂ feedstock C'',
 - e) backwashing stream B with alcohol taken from feedstock C' and recovering a stream C''' comprising essentially alcohol and CO₂ and a hydrogen stream B' comprising essentially H₂, CO, CH₄ and optionally N₂,

- f) introducing the recovered stream C''' into step d), and
 - g) separating hydrogen stream B' into a purified hydrogen feedstock and a separated CO, CH₄ and optionally N₂ stream.
3. Use of the CO₂ feedstock C'' obtained according to any of the preceding claims for hydrocarbon (oil and/or gas) improved recovery from wells and/or for sequestration for long term storage into wells.





INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2007/001865

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C29/151 C07C31/02 C07C31/04 C07C31/08 C07C31/10
C07C31/12 C01B3/36 C01B3/38 E21B43/16

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)

C07C C01B E21B

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 03/029174 A2 (TECHNOLOGY CONVERGENCE INC [CA]; SHAW JOHN M [CA]) 10 April 2003 (2003-04-10) page 2, line 7 - line 31 page 4, line 13 - page 5, line 11 claims; figures	1,2
Y	EP 0 650 950 A1 (MITSUBISHI GAS CHEMICAL CO [JP]) 3 May 1995 (1995-05-03) page 11; example 4 figure 2	1,2
Y	EP 0 067 491 A2 (STAMICARBON [NL]) 22 December 1982 (1982-12-22) page 7; claims; examples	1,2
X	US 6 505 683 B2 (MINKKINEN ARI [FR] ET AL) 14 January 2003 (2003-01-14) the whole document	3

☐ 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

11 July 2007

Date of mailing of the international search report

30/07/2007

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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