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(54) Title: AQUEOUS SEPARATION OF SYNGAS COMPONENTS

(57) Abstract: Unreacted syngas containing CO_2 from Fisher-Tropsch synthesis reactor, a methanol synthesis reactor or a dual functional syngas conversion is scrubbed with an aqueous medium to absorb at least some of the CO_2. At least a portion of the unreacted CO_2-depleted syngas is then recycled to the reactor. The aqueous medium containing absorbed CO_2 is treated to desorb CO_2. A CO_2-enriched stream and CO_2-depleted stream are recovered. A portion of the CO_2-enriched stream may be recycled to a syngas generator while another portion is dissolved in an aqueous phase and disposed in a marine environment and/or a terrestrial formation. The CO_2-depleted stream preferably is used in the scrubber to absorb CO_2 from the unreacted syngas. The process reduces the amount of CO_2 released into the atmosphere while improving the over-all efficiency of the syngas conversion process.

AQUEOUS SEPARATION OF SYNGAS COMPONENTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application is related to application Serial Nos. 09/951,551, 09/951,552 and 9/951,553, filed September 14, 2001, the entire contents of which are expressly incorporated herein.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] This invention relates to a treatment of unreacted synthesis gas (syngas) produced in a gas-to-liquid synthesis and more particularly to a process of contacting unreacted syngas with water to remove CO_2.

Description of Related Art

[0003] There is a considerable economic incentive to exploit the production of natural gas which is an abundant resource normally available only at remote sites. Frequently, it is not economically viable to transport natural gas from such remote sites to commercial markets or off-site processing facilities. One approach has been to convert the natural gas into liquified natural gas (LNG) for transport to markets or processing facilities. Another approach has involved converting natural gas into methanol at the remote site without further processing of methanol into gasoline.

[0004] Natural gas is a primary source of methane which is used to manufacture synthesis gas. Synthesis gas (syngas) is primarily a mixture composed of CO and H_2. Techniques are known to convert syngas into useful products such as methanol or into synthetic fuels, lubricants and other hydrocarbonaceous products *via* Fischer-Tropsch synthesis. One method for the preparation of syngas involves catalytically reacting methane and carbon dioxide. While natural gas is a primary source of methane, coal and petroleum have also been utilized to provide hydrocarbon feeds to generate syngas.

[0005] Carbon dioxide is considered by some to be a major factor in global warming. Accordingly, there is an incentive to find means for reducing the production of carbon dioxide and limiting its release into the environment. One advantage of the aforementioned process for preparing syngas is that it utilizes carbon dioxide as a reactant.

[0006] At present, there are two gas-to-liquid (GTL) technologies which convert remote natural gas assets or coal into transportation fuels and lubricants. Both use syngas as an intermediate. The first involves the conversion of natural gas or coal into syngas by partial oxidation followed by reaction in a Fischer-Tropsch synthesis with further refining of the Fischer-Tropsch products. The second technology involves conversion of natural gas or coal into syngas by partial oxidation followed by methanol synthesis, the methanol being subsequently converted into highly aromatic gasoline by the Methanol-To-Gasoline (MTG) process.

[0007] The Fischer-Tropsch and MTG processes both have relative merits and disadvantages. One advantage of the Fischer-Tropsch process is that the products formed are highly paraffinic. These products have excellent combustion and lubricating properties. A disadvantage of the Fischer-Tropsch process is the relatively large amounts of carbon dioxide that are emitted in the facility during the conversion of natural gas into Fischer-Tropsch products. The MTG process produces a highly aromatic gasoline and LPG fraction. While the gasoline generally is suitable for use in gasoline engines, durene and other polymethyl aromatics may be present. These materials have high crystallization temperatures and can solidify upon standing. The MTG process also suffers from higher capital costs in comparison to the Fischer-Tropsch process and the product cannot be used for lubricants, diesel fuel or jet turbine fuel.

[0008] A typical Fischer-Tropsch process is illustrated in Figure 1. A feed of CH_4, O_2 and H_2O is forwarded via conduit (10) to a syngas generator (15). Effluent from the generator containing CO, H_2 and CO_2 is forwarded via conduit (20) to a Fischer-Tropsch reactor (25). The products of the reaction are forwarded via conduit (35) to a separation zone (40). Hydrocarbonaceous products including C_5+ liquids are recovered and forwarded via conduit (45) to other areas of the facility for further processing into fuels, lubes, etc. Gaseous products recovered from the separation zone (e.g. tail gas) include CO, H_2 and CO_2. A portion of the tail gas is forwarded via conduit (60) for use as a fuel in the facility. Another portion of the tail gas is recycled via conduit (50) to be mixed with the feed to the syngas generator (15).

[0009] The origin of the CO_2 emissions from the Fischer-Tropsch synthesis can best be understood by examining the stoichiometry of the reaction. The major products of a Fischer-Tropsch reaction are paraffins and olefins, and these can be represented by the formula nCH_2 which represents a paraffinic polymer of n CH2 units This formula is exact for mono-olefins and a close approximation for C_5+ paraffins. The value of n (the average carbon number of the product) is determined by the reaction conditions, e.g., temperature, pressure, space rate, catalyst type, and syngas composition. The desired net syngas stoichiometry for a Fischer-Tropsch reaction is independent of n, and is approximately 2.0 as determined by the following equation:

$$nCO + 2nH_2 \varsigma nH_2O + nCH_2$$

[0010] where nCH_2 represent the major products of a Fischer-Tropsch reaction (olefins and paraffins).

[0011] There are three general reactions that produce syngas from CH_4. These are:

[0012] Steam reforming of CH_4:

$$CH_4 + H_2O \varsigma CO + 3H_2$$

[0013] However, the ratio of H_2 to CO is 3:1 which is higher than the 2:1 ratio desired for the Fischer-Tropsch conversion.

[0014] Dry reforming, or reaction between CO_2 and CH_4:

$$CH_4 + CO_2 \varsigma 2CO + 2H_2$$

[0015] However, the ratio of H_2 to CO is 1:1, which is lower than that desired for the Fischer-Tropsch conversion. Also, dry reforming may result in rapid carbon deposition.

[0016] Partial oxidation using O_2:

$$CH_4 + \tfrac{1}{2}O_2 \varsigma CO + 2H_2.$$

[0017] This provides the desired 2:1 ratio of CO and H_2 and is the reaction that is to be emphasized.

[0018] In commercial practice, an amount of steam is added to a partial oxidation reformer in order to control carbon formation. Likewise, some CO_2 can be tolerated in the feed. So while partial oxidation is the emphasized reaction, all reactions occur to some extent in the reformer.

[0019] CO_2 is formed in partial oxidation because the reaction is not perfectly selective. Some CH_4 reacts with O_2 to form CO_2 by complete combustion according to the following:

$$CH_4 + O_2 \varsigma CO_2 + 2\,H_2$$

and

$$CH_4 + 2O_2 \varsigma CO_2 + 2\,H_2O$$

[0020] Furthermore, steam added to the reformer to control coking, or produced in the Fischer-Tropsch reaction, can react with CO to form CO_2 by the water gas shift reaction as follows:

$$CO + H_2O \varsigma CO_2 + H_2$$

[0021] This reaction reaches equilibrium, and the reverse of it is known as the reverse water gas shift reaction:

$$CO_2 + H_2 \varsigma CO + H_2O$$

[0022] Furthermore, light by-product gases, which include C_1-C_4 hydrocarbons, are frequently used as fuel in furnaces. This fuel often includes the CO_2 from the GTL facility along with some unreacted CO. The furnaces provide the heat to the process, and contribute significant amounts of CO_2. With Fischer-Tropsch catalysts that do not promote the water gas shift reaction (Co-based catalyst rather than Fe-based catalysts), and with proper operation of the reformer and other units, the major source of CO_2 is combustion of hydrocarbons in the furnaces.

[0023] Thus, a significant amount of CO_2 is formed during the conversion of CH_4 into transportation fuels and lubricants by the Fischer-Tropsch process. This CO_2 exits the GTL-Fischer-Tropsch process in the tail gas from the Fischer-Tropsch unit, i.e., in the gases that are not consumed in the Fischer-Tropsch reactor.

[0024] The overall proportion of carbon in the CH_4 that is converted to heavier hydrocarbon products is estimated to be about 68%. The remainder, about 32%, forms significant amounts of CO_2. These estimates of carbon efficiency were provided by Bechtel Corporation for a GTL complex that uses cryogenic air separation, an autothermal reformer, a slurry bed Fischer-Tropsch unit and a hydrocracker for conversion of the heavy wax into products. Details are described in "CO_2 Abatement in GTL Plant: Fischer-Tropsch Synthesis," Report # PH3/15, November 2000, published by the IEA Greenhouse Gas R&D Programme. GTL complexes using alternative technologies would have similar carbon efficiencies and CO_2 emissions.

[0025] To control the reaction, syngas conversion processes operate at less than 100% conversion of the CO in the syngas. Typical values are between 40 and 70% per-pass conversion. In Fischer-Tropsch processes which use O_2 rather than air, the unreacted syngas is recycled to the Fischer-Tropsch reactor. From the standpoint of economics and operational efficiency, the preferred Fischer-Tropsch process is a slurry bed process. Also, the most common catalyst for use in slurry bed units contains cobalt. Cobalt does not promote the water gas shift reaction to a significant extent (or the reverse of this reaction). In these units, CO_2 for the most part, is an inert gas. As CO_2 is recycled to the syngas conversion reactor, its concentration builds up. This effectively lowers the concentration of the reactive syngas components ($CO + H_2$), and reduces the rate of reaction. To compensate for the lower partial pressures of the reactive components, the pressure of the Fischer-Tropsch reactor is increased. During this recycle operation, a small amount of CO_2 in the initial syngas (typically 5 vol % but always 2% or more) increases to much larger values (typically 40 vol %). In commercial practice, typically a portion of the CO_2-enriched recycle gas is recycled to the syngas formation reactor where it promotes the dry reforming reaction and reduces the ratio of H_2 to CO in the syngas to the desired level. The recycle of CO_2 to the syngas generator reduces the selectivity for CO_2 formation and improves the selectivity for formation of the desirable syngas components CO and H_2. This is because CO_2 is produced in equilibrium with CO, H_2 and H_2O due to the water gas shift reaction. However, much more CO_2 is produced than can be consumed in the syngas generator, and the excess CO_2-enriched recycle gas is purged from the process and used as a low energy content fuel. The use of this low energy content fuel is a significant source of the CO_2 emissions from the GTL facility.

[0026] A process scheme which reduces the CO_2 emissions from a Fischer-Tropsch-GTL process while still making the desired product slate would be highly desirable. Reducing the CO_2 emissions also acts to improve the carbon efficiency of the process.

[0027] EP0 516 441A1 discusses several aspects of handling CO_2 in a Fischer-Tropsch-GTL process including: separating CO_2 from the syngas generated in the reformer, and recycling the unreacted tail gas from Fischer-Tropsch to the reformer. As discussed previously, the recycling of CO_2 is to achieve proper H_2/CO ratio of syngas. This publication notes that: "Separation of carbon dioxide is expensive. It is often carried out by amine stripping. This involves reaction with an amine, followed by boiling, and compression to reach the necessary pressure for recycle back to the reformer." (page 3, lines 4-6). Likewise: "The cost of removing and recycling the CO_2 is expensive and typically would represent around 30% of the costs associated with producing the syngas within the process." (page 4, lines 45-46).

[0028] EP 142 887 B1 discusses the benefits of having CO_2 in the feed to the reformer. It also mentions the high costs associated with the separation of the CO_2 from the syngas by amine scrubbing and subsequent compression.

[0029] Neither of these publications disclose the use of an aqueous medium to remove CO_2 from syngas. The use of an aqueous medium to remove CO_2 significantly reduces costs associated with typical amine scrubbing, and also provides a source of water for use in the reforming reaction.

[0030] It is an object of the invention to provide an efficient process which reduces the cost of separating CO_2 in recycled synthesis gas.

[0031] It is another object of the invention to develop a technique which lowers the CO_2 emissions from a GTL facility.

[0032] These and other objects and advantages of the present invention will become apparent to the skilled artisan upon a review of the following description, the claims appended thereto, and the figures of the drawings.

SUMMARY OF THE INVENTION

[0033] These and other objectives of the invention are attained by a process which includes the steps of:

A process comprising the following steps:

(a) forming a syngas which contains CO_2 in a syngas generator;

(b) reacting the syngas in a syngas conversion process to form a product stream comprising hydrocarbonaceous products and a tail gas containing unreacted syngas and CO_2;

(c) separating the hydrocarbonaceous products from the unreacted syngas and CO_2;

(d) contacting at least a portion of the unreacted syngas and CO_2 with an aqueous medium having a pH above about 6.0 in a scrubbing zone to adsorb at least a portion of the CO_2, and recovering a CO_2-enriched aqueous stream and a syngas with reduced CO_2 concentration;

(e) forwarding at least part of the recovered syngas from step (d) to the syngas conversion reactor; and

(f) desorbing at least part of the CO_2 from the CO_2-enriched aqueous stream obtained in step (d) and recovering a CO_2-rich gas and CO_2-depleted aqueous stream.

[0034] Desorption can be accomplished, for example, by contacting the CO_2-enriched aqueous stream with CH_4 in a desorption vessel. Recovered CH_4 can be recycled to the syngas generator. Portions of the recovered CO_2 can be disposed in a marine environment, a terrestrial formation or both.

[0035] The recycling of CO_2 and CH_4 to the syngas formation reactor increases the carbon efficiency of the process. The separation of CO and H_2 and the processing of these gases in the syngas conversion unit thereby avoids forwarding them to the syngas formation reactor. This reduces the total amount of gases processed in the syngas formation reactor while shifting the equilibrium towards the desired CO and H_2.

BRIEF DESCRIPTION OF THE FIGURE OF THE DRAWING

[0036] Figure 1 is a schematic flow diagram of a conventional Fischer-Tropsch synthesis.

[0037] Figure 2 is a schematic flow diagram of one embodiment of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0038] The syngas generator can be a light hydrocarbon reformer or a heavy hydrocarbon reformer. Reforming includes a variety of technologies such as steam reforming, partial oxidation, dry reforming, series reforming, convective reforming, and autothermal reforming. All have in common the production of syngas from methane and an oxidant (steam, oxygen, carbon dioxide, air, enriched air or combinations). The gas product typically contains some carbon dioxide and steam in addition to syngas. Series reforming, convective reforming and autothermal reforming incorporate more than one syngas-forming reaction in order to better utilize the heat of reaction. The processes for producing synthesis gas from C_1-C_3 alkanes are well known to the art. Steam reformation is typically effected by contacting C_1-C_3 alkanes with steam, preferably in the presence of a reforming catalyst, at a temperature of about 1300° F (705° C) to about 1675°F (913°C) and pressures from about 10 psia (0.7 bars) to about 500 psia (34 bars). Suitable reforming catalysts which can be used include, for example, nickel, palladium, nickel-palladium alloys, and the like. Regardless of the system used to produce syngas it is desirable to remove any sulfur compounds, e.g., hydrogen sulfide and mercaptans, contained in the C_1-C_3 alkane feed. This can be effected by passing the C_1-C_3 alkane gas through a packed bed sulfur scrubber containing zinc oxide bed or another slightly basic packing material. If the amount of C_1-C_3 alkanes exceeds the capacity of the synthesis gas unit, the surplus C_1-C_3 alkanes can be used to provide energy throughout the facility. For example, excess C_1-C_3 alkanes may be burned in a steam boiler to provide the steam used in a thermal cracking step.

[0039] In a heavy hydrocarbon reformer, the process involves converting coal, heavy petroleum stocks such as resid, or combinations thereof, into syngas. The temperature in the reaction zone of the syngas generator is about 1800° F-3000° F and the pressure is about 1 to 250 atmospheres. The atomic ratio of free oxygen in the oxidant to carbon in the feedstock (O/C, atom/atom) is about 0.6 to 1.5, preferably about 0.80 to 1.3. The free oxygen-containing gas or oxidant may be air, oxygen-enriched air, i.e., greater than 21 up to 95 mole % O_2 or substantially pure oxygen, i.e., greater than 95 mole % O_2. The effluent gas stream leaving the partial oxidation gas generator generally has the following composition in mole % depending on the amount and composition of the feed streams: H_2:8.0 to 60.0; CO:8.0 to 70.0; CO_2:1.0 to 50.0, H_2O:2.0 to 75.0, CH_4:0.0 to 30.0, H_2S:0.1 to 2.0, COS:0.05 to 1.0, N_2:0.0 to 80.0, Ar:0.0 to 2.0. Particulate matter entrained in the effluent gas stream may comprise generally about 0.5 to 30 wt. % more, particularly about 1 to 10 wt. % of particulate carbon (basis weight of carbon in the feed to the gas generator). Fly ash particulate matter may be present along with the particulate carbon and molten slag. Conventional gas cleaning and/or purification steps may be employed such as that described in U.S. Patent No. 5,423,894.

[0040] The mixture generated in the syngas reactor is then cycled to a syngas converter, preferably a Fischer-Tropsch reactor. As indicated earlier, the Fischer-Tropsch synthesis is well-known and widely documented in patent and technical literature. The synthesis converts syngas into a wide variety of hydrocarbonaceous products by contact with a Fischer-Tropsch catalyst under suitable temperatures and pressures. The reaction is typically conducted at temperatures ranging from about

300° -700° F, preferably about 400° -550° F, pressures ranging from about 10 to 500 psia, preferably about 30 to 300 psia, and a catalyst space velocities ranging from about 100 to 10,000 cc/g/hr., preferably about 300 to 3,000 cc/g/hr. The reaction can be conducted in a variety of reactors such as fixed bed reactors containing one or more catalyst beds, slurry reactors, fluidized bed reactors, or a combination of different types reactors. The products may range from C_1 to C_{200} + hydrocarbons with a majority in the range of C_5-C_{100}+. The syngas feed to a Fischer Tropsch reactor contains - l ess than 1 ppm, preferably less than 100 ppb, most preferably less than 10 ppb sulfur.

[0041] Products from the Fischer-Tropsch reactor are cycled to a separation zone. Hydrocarbons including C_5+ liquids are separated and forwarded to processing areas for conversion into fuels, lubricants, etc. Tail gas recovered from the separation zone contains CO, H_2, CO_2, CH_4 and other light hydrocarbons. A portion of the tail gas is drawn off and used as fuel. An important feature of the present invention involves contacting at least a portion of the tail gas with an aqueous medium in a scrubber preferably at above atmospheric pressure to remove CO_2 and optionally CH_4 by absorption and admixing the resultant CO_2-depleted tail gas with the syngas feed to the syngas converter. The CO_2-rich aqueous stream recovered from the scrubber preferably is processed to desorb at least some CO_2 and optionally CH_4. A CO_2-enriched gas is recovered and at least a portion thereof is recycled to the syngas generator. A CO_2-depleted aqueous stream is recovered from the desorbing zone and at least a portion is recycled to the scrubber. At least a portion of the CO_2-enriched gas recovered from the desorbing zone may be dissolved in an aqueous phase and disposed in a marine environment, and/or a terrestrial formation.

[0042] In the present invention, at least a portion of CO_2 generated in Fischer-Tropsch GTL process is isolated from the tail gas by scrubbing with an aqueous stream, preferably at a pressure greater than about atmospheric pressure to assist in the removal of CO_2. Although scrubbing in accordance with the present invention can be performed in any number of locations in a GTL process, preferably, scrubbing is not conducted upon streams that contain significant amounts of liquid hydrocarbons. In particular, scrubbing to remove CO_2 from streams that also contain significant amounts of liquid hydrocarbons is avoided because the presence of significant amount of liquid hydrocarbons can make separation more difficult.

[0043] Since the amount of CO_2 that can be dissolved in an aqueous stream is dependent on pressure, it is desirable to conduct scrubbing at pressures greater than atmospheric. In addition, because many CO_2-containing streams in a GTL process are at pressures greater than atmospheric, scrubbing can be conducted in a number of possible locations.

[0044] There are several sources of aqueous streams for scrubbing that are suitable for the present invention. Suitable sources include, but are not limited to, sea water, reaction water formed in a Fischer-Tropsch GTL process, spent cooling water from a FischerTropsch GTL facility, river water or other non-potable water sources, and water recovered from crude or gas production.

[0045] The pH of the aqueous stream used in scrubbing is important. Preferably, the aqueous streams exhibit a pH greater than about 6.0, preferably above 7.0 and most preferably, from about 7.5 to about 11.0. A high pH aqueous stream facilitates scrubbing of CO_2. The pH of the aqueous stream used for scrubbing CO_2 can be increased using any number of suitable techniques. These include, but are not limited to, adding an alkali such as NaOH or KOH and/or other basic materials, such as ammonia. Use of amines in the aqueous stream should be avoided - l ess than 1 wt% is preferred. However, because these materials must be disposed of, they should be inexpensive and benign to the environment in which they will be disposed. Accordingly, in view of the need to minimize cost and environment impact, preferred aqueous sources include, but are not limited to, sea water, river water, or other non-potable water sources from the environment

[0046] GTL process water may be a particularly suitable aqueous source because it is abundantly produced during Fischer-Tropsch GTL processing. For instance, when referring to the stoichiometric equation governing the conversion of synthesis gas to Fischer-Tropsch products:

$$nCO + 2nH_2 \rightarrow nH_2O + nCH_2,$$

[0047] It can be seen that the weight ratio of water to hydrocarbon produced by the reaction is about 1.25. Thus, a typical Fischer-Tropsch GTL process produces about 25% more water than hydrocarbon, on a weight basis. Although GTL process water is abundantly produced, a disadvantage of using GTL process water as an aqueous stream, is that GTL process water may contain acidic contaminants, such as, for example, acetic acid and/or other organic acids. Acidic contaminants present in GTL process water can lower the pH, thereby reducing the solubility of CO_2 therein. As a result, if GTL process water is used for scrubbing CO_2, it is preferable to remove acidic contaminants from the GTL process water before using it as a scrubbing stream. The acidic contaminants in GTL process water can be removed using various known methods. Suitable methods for removing acidic component from GTL process water include, but are not limited to, distillation, adsorption onto alumina or a basic material, oxidation, combinations thereof and the like.

[0048] In addition to pH and acidic contaminant composition, it may also be important to limit the oxygen content of the aqueous stream. Preferably, an aqueous stream is de-aerated before being used for scrubbing to increase the aqueous stream's capacity to adsorb CO_2 and to minimize the amount of air introduced into the gas stream. Suitable processes for de-aeration of aqueous streams are well known in the art and are used, for example, in desalination plants and for preparation of boiler feed water. Such processes are described in detail, for example, in John H. Perry's Chemical Engineering Handbook, 4th Edition, pages 9-51, McGraw Hill Book Company, 1963.

[0049] If the CO_2-containing tail gas stream contains relatively low amounts of CO_2 in comparison to other gases, the aqueous stream may not be as highly selective to scrubbing of CO_2. In this case, it may be preferable to conduct scrubbing in stages. For instance, a first selective CO_2 scrubbing operation may be conducted, followed by desorption to generate a concentrated CO_2 gas stream. Finally, scrubbing may be conducted with the aqueous stream. In preferred embodiments, conditions during disposal of the CO_2-enriched aqueous phase are such that a high percentage of the CO_2 removed from the CO_2-containing gas during scrubbing remains dissolved in the aqueous phase.

[0050] Scrubbing of CO_2 from gases using aqueous liquids should be performed at non-extreme pressures to avoid formation of methane, CO_2 and other hydrates. The dissolution of CO_2 in water is favored at high pressures. Thus, it is preferable to operate at as high a pressure as possible, and within economic limits. Accordingly, gas compression may be desirable, although the typical elevated pressures of a GTL facility will often suffice.

[0051] In addition to the importance of monitoring pressure during scrubbing, it may also be important to monitor temperature. For instance, at high temperatures and elevated pressures, hydrate formation can occur. In addition, at lower temperatures, gases may become more soluble in water, resulting in higher selectivity for the removal of CO_2 over methane and other valuable hydrocarbons.

[0052] In addition to pressure and temperature, salinity can also affect the solubility of hydrocarbons in water. For example, a larger "salting-out" effect can occur when using non-ionic hydrocarbons such as, for example, methane. Accordingly, variations in temperature and salinity of an aqueous solution can be used to maximize selectivity for CO_2 removal. In addition, the presence of salt in sea water can create a slight tendency to reduce the temperature at which hydrates will form. Yet another advantage of sea water as an adsorbent is its pH, which is often above 7.0, and thus facilitates the adsorption of CO2.

[0053] In recycle gas operation, the composition of a blended syngas to a Fischer-Tropsch unit will change as CO_2 is recycled to the syngas formation reactor. Other inert gas components will increase in concentration, while the reactive syngas components will remain essentially constant. The blended syngas is the mixture of the fresh syngas from the syngas generator and the syngas that is recycled. The following table provides typical ranges of blended syngas compositions for a process that generates syngas from an O_2 source of about 99.5 percent purity.

Component, mol %	Typical Fischer-	With low level of	With moderate	With high level of CO_2

	Tropsch Unit without CO_2 conversion	CO_2 removal	level of CO_2 removal	removal
H_2	30	30	30	30
CO	40	40	40	40
CO_2	20	15	10	8
N_2 + Ar	2	3	4	7
C_1 + Hydrocarbons	8	12	16	21

[0054] It should be recognized that not all the unreacted syngas from the syngas conversion reactor needs to be processed in the scrubber. Since CO_2 builds up slowly, and reasonable concentrations of CO_2 can be tolerated (< 60 mol %), only a portion of the syngas needs to be processed to achieve the desired CO_2 conversion. This can keep the size of the scrubber and CO_2 recycle stream relatively small.

[0055] Under some circumstances, it may not be desirable to process unreacted syngas from the syngas conversion reactor and recycle the CO_2-depleted syngas back to the syngas conversion reactor. It may be preferable to process the portion of the unreacted syngas from the syngas conversion reactor that is intended for use as a fuel. This option also achieves the goal of the invention to reduce CO_2 emissions.

[0056] It may be desirable to scrub the syngas from the syngas generator. In particular, the formation of syngas in the generator is known to create traces of organic nitrogen impurities (including HCN and NH_3). These organic nitrogen impurities, unlike N_2, are poisonous to the Fischer-Tropsch catalyst. The formation of these catalytically poisonous nitrogen impurities during syngas generation is described in United States patents 6,063,349 and 5,929,126. The nitrogen compounds deactivate the Fischer-Tropsch catalyst and thus require more catalyst and larger reactor volumes for this expensive process than would otherwise be needed if these nitrogen compounds were not present. In addition to deactivating the Fischer-Tropsch catalyst, the nitrogen impurities will be incorporated into the Fischer-Tropsch products. When incorporated in the Fischer-Tropsch products, they can make upgrading of these products into salable products more difficult. Under these circumstances, aqueous scrubbing of the syngas from the syngas generator to remove CO_2 also offers the advantage of simultaneously reducing the concentration of the catalytically poisonous nitrogen compounds. The level of reduction of HCN should be at least 30%, preferably at least 50%, and most preferably, at least 80%. The reduction in the NH3 level should be equivalent to the reduction of HCN. Some Fischer Tropsch catalysts will also catalyze the formation of NH3 from N2 and H2 in the feed. This can result in small quantities of catalytically poisonous NH3 in syngas streams exiting the Fischer Tropsch reactor. Aqueous scrubbing can remove this NH3.

[0057] It may not be practical to process all the recovered CO_2 in the syngas generator. Excess CO_2 can be disposed of by injecting it into a marine environment, a terrestrial formation, or both.

[0058] Water is a natural product of the syngas generation and syngas conversion reactions. Preferably, the water from both syngas generation and syngas conversion reactors is separated prior to further processing. If not removed, the water can promote the undesirable reverse water gas shift reaction which converts CO into additional CO_2. The removal of reaction water formed by the syngas generation and syngas conversion reactions will also remove some dissolved CO_2. Additional water can be added to remove more CO_2 by use of the same separation vessels which remove the reaction waters.

[0059] The desorption of CO_2 from the CO_2-rich aqueous stream obtained from the scrubber can be achieved either by lowering the pressure (commonly known as pressure swing) or increasing the temperature (commonly known as temperature swing). Since the objective is to use the CO_2 in the syngas formation reactor, which operates at pressures close to the syngas conversion unit, it is preferred not to significantly reduce the pressure to desorb the CO_2. Rather, it is preferable to desorb the CO_2 by increasing the temperature. The most common adsorbents for removal of CO_2 from gas streams are amines. These compounds will decompose if heated to excessive temperatures, and thus they are almost always used in pressure swing adsorption units. The use of an aqueous medium, without significant amounts of amines, in this invention to adsorb CO_2 eliminates the potential problems of decomposition in a temperature swing operation. Thus, the use of an aqueous medium to selectively remove the CO_2 and optionally part of the CH_4 in a temperature swing operation permits the recovery of CO_2 without significant pressure loss. In comparison, the conventional technology of using amines in a pressure swing adsorption system is quite costly. As noted previously, in EP 0 516 441 A1 it is estimated that the costs associated with removing and recycling CO_2 represents around 30% of the costs associated with producing the syngas itself. In practice, there may be some pressure drop between the adsorption and desorption steps. However, the pressure of the desorption step should be above atmospheric pressure to minimize CO_2 compression costs. Preferably, the pressure in the desorption stage should not be less than about 100 psi below the outlet pressure of the syngas conversion step. Likewise, the pressure in the adsorption scrubber preferably should not be less than about 50 psi below the outlet pressure of the syngas conversion step. In keeping with the concepts of temperature swing adsorption, the temperature of the desorption step preferably is in excess of the temperature of the adsorption step. The heat needed to desorb the CO2 from the CO2-rich stream can be provided from other streams in the GTL process including but not limited to streams associated with the syngas formation reactor, syngas conversion reactor, and reactors used to upgrade the product from the syngas conversion reactor. The CO2-depleted stream needs to be cooled prior to adsorption of the CO2. This cooling can also come from a variety of sources including but not limited to: river water, air cooling, and gas streams from the air separation unit (N2, O2, etc.), and combinations.

[0060] When excess CO_2 is to be disposed in a marine environment, a terrestrial formation or both, the aqueous scrubbing concept of this invention has an advantage over the current commercial technology of amine scrubbing because the recovered CO_2 is produced at pressures close to that of the syngas conversion unit. This minimizes the amount of expensive compression needed to dispose of the CO_2. The CO_2 leaving the desorber is not likely to be at sufficient pressure to be directly injected into a marine environment or a terrestrial formation. Most likely it would need additional compression and cooling. The energy and cooling for this step can be obtained from other sources in the process including: cooling water, the syngas generator, or gas streams associated with an O_2 purification plant (such as the cold N_2 waste gas) and the like.

[0061] There is another option for disposal of CO_2. After desorption from the aqueous solution and recovery of CO_2 gas at above atmospheric pressure, the CO_2 can be adsorbed into a second aqueous stream, such as sea water, brine, river water, or other non-potable water. This second aqueous stream containing dissolved CO_2 can then be disposed in a marine environment or terrestrial formation. Using such a two-water system permits the more valuable fresh water used in the initial recovery to be recycled, while the less valuable second aqueous stream is used as a disposal vehicle. Disposing of the CO_2 as a dissolved aqueous phase reduces the costs associated with compressing and possibly liquefying the CO_2 so that it can be disposed. Compression and liquefaction of a gas use expensive compressors, while compression of a liquid (the CO_2-containing second water stream) uses inexpensive pumps. The choice between the two options (disposal of relatively pure gaseous or liquid CO_2, or disposal of an aqueous CO_2 mixture) depends on the details of the disposal location.

[0062] The feasibility of disposing of extra water associated with the aqueous CO_2 mixture depends upon whether the marine or terrestrial formation is located at the plant site; the pressure needed for disposal in these locations, and other factors. The use of two aqueous streams has another advantage. Regulations regarding the disposal of wastes in marine environments may require very low levels of liquid hydrocarbons to avoid formation of an oil sheen or pollution. The two-water system isolates CO_2 as a CO_2-rich gas and reduces the chance that hydrocarbons will be included in the CO_2 when it is disposed in a marine environment.

[0063] An additional advantage of the process of the invention resides in the supply of water to the syngas formation reactor. Typically, some water is added to a syngas formation reactor in order to control coking, and promote steam reforming. Typical values of H_2O/carbon molar ratios are about 0.1 to 5.0/1.0, preferably 0.2 to

0.8. As the CO_2 is desorbed from the CO_2-rich aqueous stream, water will also be present in the vapor phase. This water can supplement or supply all of the water needed for the syngas formation reactor. Use of water in a temperature swing adsorption system will provide a water-rich CO_2 stream and higher temperatures can be selected in the desorption step to provide the needed amount of water. This will deplete the water in the scrubbing system, but makeup water to the scrubbing system can be obtained from boiler feed water, and the ultimate source of the water for the process can be water derived from the syngas conversion process, river water, water from an aquifer, or desalinated sea water.

[0064] Eventually, the scrubbing aqueous medium may accumulate contaminants from the syngas conversion process. These include hydrocarbonaceous species such as light paraffins, alcohols, and acids such as acetic and formic. For the most part, these contaminants are not a problem, with the exception of the acids. The acids will lower the pH of the scrubbing aqueous medium which will decrease the capacity of the system to adsorb CO_2. To prevent this decline in capacity, the aqueous scrubbing medium should be maintained in a relatively pure state with a pH value above 5, preferably above 6, and most preferably above 6.5. This can be done by a number of methods which include taking a purge stream of the scrubbing medium and replacing it with fresh water; treating the scrubbing medium with an adsorbent to remove the acids; distilling the water; and neutralization with a basic compound (caustic, sodium salt, nitrogen compound, and the like).

[0065] These processing steps can be part of the water recovery systems employed to treat the water produced in the syngas generator or the syngas converter. The pH of the aqueous stream needs to be measured on a CO_2-free sample. This can be done by bubbling N_2 through the sample at atmospheric pressure for 24 hours at 25° C at 10 cm^3 of N_2 per ml of water per minute.

[0066] It is well known in the industry that water-rich CO_2 gas streams and CO_2-rich aqueous streams are moderately corrosive. This will likely necessitate the use of a stainless steel or a corrosion inhibitor to avoid excessive corrosion. Selection of appropriate materials of construction can be done by typical methods such as coupon tests and the like. A review of the corrosion properties of CO_2 is provided in Metals Handbook, 9th Edition, Volume 13 Corrosion, ASM International, 1987, especially pages 896-897, 1233, and 1247.

[0067] The scrubbing of CO_2 from gases by an aqueous medium must operate at non-extreme pressures to avoid formation of hydrates of CH_4, CO_2, and other hydrates. The dissolution of CO_2 in water is favored at higher pressures. It is preferred to operate at as high a pressure as possible (and within economic limits; compression of the gas is not favored). There is also a tradeoff with respect to temperature. At higher temperatures, hydrate formation occurs at higher pressures. Lower temperature, on the other hand, results in higher solubility of gases into water (all else being the same), and results in higher selectivity for the removal of CO_2 over CH_4 and other valuable hydrocarbons.

[0068] From literature references, the maximum pressure that can be tolerated to avoid hydrate formation at various temperatures for CH_4 and CO_2 are:

	Pure CH_4		Pure CO_2	
	2° C	8° C	0° C	10° C
Maximum Pressure, Psia	2.9 MPa (430 psi)	6.1 MPa (900 psi)	1.3 MPa (192 psi)	14 MPa (2000 psi)
Equivalent hydrostatic water depth, feed (62.4 lb/ft^3 water density)	1000 ft	2,100 ft	450 ft	4,800 ft

(1 Pa = 1.02 X10-5 atm) (for water: 2.31 ft/psi at specific gravity)

[0069] The source of this data is E. Dendy Sloan Jr., Clathrate Hydrates of Natural Gases, Marcel Dekker, Inc. 1990. Sloan also gives numerous examples of gas mixtures and the resulting temperatures / pressures at which hydrates form. The allowable operating pressure /temperature combination is determined on a case-by-case basis for each gas composition. Methods for estimating these operating conditions are described in Sloan. For the typical case of a light gas, an operating pressure of 300 psig and 10°C will not form hydrates.

[0070] To avoid formation of hydrates, pressures less than maximum normally should be used. However, hydrate formation is also controlled by kinetics and heat transfer; thus, pressures near or above this limit can be used as long as the residence time is short.

[0071] The Henry's Law constants for CO_2 and CH_4 in pure water and sea water are:

	CH_4		CO_2	
	0° C	30° C	0° C	30° C
Henry's Law Constant in Water (atm/mole fraction)	22,000	42,000	740	1,850
Henry's Law Constant in Sea Water (estimated)	40,000		740	

Sources of Solubility Data include:

[0072] (Clifford N. Click, "Applications of Henry's Law to Waste and Process Water VOC Emissions", 85th annual meeting Air and Waste Management Association. (Gives Henry's Law coefficients for several light hydrocarbon gases in water as a function of temperature and also gives an equation for the brine effect.)

[0073] Gianni Astartita, David Savage, and Attilio Bisio, Gas Treating with Chemical Solvents, Wiley, pp 208. (Contains a plot of the Henry's Law coefficient physical solubility of CO_2 into water as a function of temperature.)

[0074] John Nighswander, Nicholas Kalogerakis, Anil Mehrotra, "Solubilities of Carbon Dioxide in Water and 1 wt% NaCl Solution at Pressures up to 10 MPa and temperatures from 80 to 200 Degrees C", J. Chem. Eng. Data 1989, 34, 355-360. (Observes that the effect of salt on CO_2 solubility in water over the ranges of 80 to 200° C and at pressures of up to 10 MPa is very small.)

[0075] While this invention reduces the amount of CO_2 released into the environment by processing more of it in the syngas formation reactor, there are other inert components in the syngas that will eventually build up to high enough levels such that some syngas will have to be ejected from the process. These components include CH_4, N_2, Ar, and other inert gas elements. The CH_4 originates from CH_4 slip in the syngas generator and CH_4 formation in the Fischer-Tropsch unit. The N_2, Ar, and other inert gas elements come from the air separation unit, and possibly from the original natural gas feedstock. Normally, CO_2 is the most abundant inert gas component, but when it is removed by the technology of this invention, the other inert gas components will increase in concentration. Thus, some purging of syngas will be necessary and a suitable use for this diluted syngas is as a fuel.

[0076] CO_2 in the recycle gas to the Fischer-Tropsch reactor provides several advantages. It acts as a diluent for the reactive syngas components. It acts to dissipate some of the heat and improves process control. As CO and H2 are consumed in the Fischer-Tropsch reactor, other inert gas components (CH_4, N_2 and Ar) build up in the recycle gas. They substitute for the extracted CO_2 by improving the management of heat release in the Fischer-Tropsch unit. This means that more of the carbon in the recycle gas can be processed. Eventually, the N_2 and Ar will have to be purged from the system.

[0077] The invention will now be illustrated by the following Example which is intended to be merely exemplary and in no manner limiting. The reference numerals in Figure 2 are the same as those used in Figure 1 and refer to identical locations.

Example 1:

[0078] With reference to Figure 2, a mixture of CH_4, O_2 and H_2O is introduced via conduit (10) to a syngas generator (15). Product from reactor (15) is conducted via conduit (20) to a syngas converter (25), specifically a Fischer-Tropsch reactor. Optionally, a scrubber (30a) can be located downstream of the syngas generator or upstream of the syngas converter (25) to remove materials such as nitrogen contaminants, particulates, excess CO_2, unreacted CH_4, etc. from the products of the syngas generator before circulation to reactor (25). The syngas in the Fischer-

Tropsch reactor is reacted in the presence of a non-shifting catalyst at a pressure of 300 psig to produce a variety of hydrocarbonaceous productors. Effluent from the reactor (25) is circulated via conduit (35) to a separation zone (40). Hydrocarbon products including C_5+ liquids are removed from the separation zone via conduct (45) to be further processed into salable products. A tail gas is collected from the separation zone. The tail gas has the following composition on a water-free basis:

CH_4	13%
CO_2	35%
CO	25%
H_2	25%
Inerts (N_2)	2%

[0079] The gas is used in two operations, recycle to the Fischer-Tropsch unit and for fuel gas. One portion is circulated via conduit (50) to a scrubbing zone (55) and scrubbed with de-aerated water to avoid introduction of contaminants into the Fischer-Tropsch unit. The fuel gas is circulated via conduit (60) to a scrubbing zone (65) and scrubbed with water. Both scrubbing operations are done at 20°C. The tail gas is scrubbed to remove 50% of the CO_2 and the fuel gas is scrubbed to remove 75%. Contact is counter-current. The pressure in the scrubbing zone (55) is generally within 100 psig and preferably within 50 psi of the pressure of the outlet of the separation zone (40).

[0080] A CO_2-depleted syngas is recovered from scrubbing zone (55). It is recycled via conduit (70) to conduit (20) where it is admixed with fresh syngas and forwarded to reactor (25).

[0081] A CO_2-enriched aqueous stream (80) is forwarded to desorption zone (75) where CO_2 and optionally CH_4 are removed and recycled (85) to reactor (15). A CO_2-depleted aqueous stream (90) is recovered from desorption zone (75) and circulated to scrubbing zone (55). A makeup water is added through conduit (100). The recovery of Co_2 from desorption zone (75) may be facilitated by injecting a gaseous stream (95), such as methane, into desorption zone (75).

[0082] Water is formed in both the syngas generator and the syngas conversion reactors. It is separated and removed from the other products of these reactions.

[0083] Henry's Law constants are given in Kohl (Arthur Kohl and Richard Nielsen, Gas Purification, Gulf Publishing Company, 1997, pp 417-465). This source also provides the temperature dependence of the constants.

CH_4	13%	37,800
CO_2	35%	1,460
CO	25%	53,600
H_2	25%	68,300
Inerts (N_2)	2%	80,400

[0084] HCN is extremely soluble in water. The Merck Index says it is water-miscible. From the International Critical Tables, Vol. 3, page 365: Henry's Constant at 25 C for HCN in Water = 4810 mm Hg / mol fraction Converting it to atm gives: H = 6.32 atm / mol fraction. One other data set on the solubility of HCN in water is at 18° C, in the form of a "Partial Pressure vs. Mole Fraction" Table. Using the most dilute point, and linear extrapolation from zero, gives H = 4.39 atm / mol fraction. Thus HCN is more solubile in water than CO_2, and systems designed to remove CO_2 should simultaneously remove an even greater amount of HCN. NH_3 is likewise easily removed by water along with CO_2.

[0085] Four cases were studied by the well-known Kremser-Brown Method. This method provides an analytical estimate of the staging, scrubbing, and stripping requirements. It is also designed to handle multi-component systems.

[0086] Case 1 - Scrubbing the tail gas. 50% of the CO_2 was absorbed from the unreacted syngas using water at 20°C and 315 psia. Then, 99.5% of the CO_2 was recovered in a water-rich CO_2 stream and recycled back to the syngas generator. No CH_4 purge is used, so all of the stripping comes from steam generation at 315 psia (217° C).

[0087] Case 2 - Scrubbing the tail gas. 50% of the CO_2 was absorbed from the unreacted syngas using water at 20 C and 315 psia. Then, 99.5% of the CO_2 was recovered using CH_4 stripping at 100° C. No reboiler is used, so there should be very little water in the desorbed gas.

[0088] Case 3 - Scrubbing the tail gas. Same flowsheet, except that CH_4 stripping is done at 50°C.

[0089] Case 4 - Scrubbing the fuel gas. 75% of the CO_2 was absorbed from the unreacted syngas using sea water at 20° C and 315 psia. The scrubbed gases are used as fuel. Then, 99.5% of the CO_2 was recovered in a water-rich CO_2 stream. The CO_2-rich, desorbed gases are sequestered. No external purge is used, so all of the stripping comes from steam generation at 315 psia (217° C).

[0090] The composition of the scrubbed gas and the desorbed gases for the four cases were calculated by the Kremser-Brown Method with a 100 mol basis of gas to the adsorber.

	Case 1			Case 2			Case 3			Case 4		
Scrubbed Gas Stream												
Total Flow, kmol	81.59			81.59			81.59			72.34		
Composition: Mol/100 mol feed to adsorber (H_2 free) mole %												
CO_2	17.5	21.4	50	17.5	21.4	50	17.5	21.4	50	8.8	12.1	75
CH_4	12.7	15.6	2	12.7	15.6	2	12.7	15.6	2	12.6	17.4	3
CO	24.6	30.2	1	24.6	30.2	1	24.6	30.2	1	24.4	33.8	2
H_2	24.7	30.3	1	24.7	30.3	1	24.7	30.3	1	24.6	34.0	2
N_2	2.0	2.4	1	2.0	2.4	1	2.0	2.4	1	2.0	2.7	1

Desorbed Gas Stream								
Total Flow, kmol/hr	23		69		139		36	
Composition: Mol/100 mol feed to adsorber (H_2 free) mole %								
CO_2	17.4	99.5	17.4	25.3	17.4	12.5	26.1	72.9
CH_4	0.26	1.1	0.26	0.4	0.26	0.2	0.40	1.1
CO	0.35	1.5	0.35	0.5	0.35	0.3	0.55	1.5
H_2	0.28	1.2	0.28	0.4	0.28	0.2	0.43	1.2
N_2	0.018	0.08	0.018	0.03	0.019	0.011	0.03	0.08
H_2O	4.56	-					8.49	-
CH_4 as Purge Gas			50.7	73.4	120.7	86.9		

[0091] The sizes of the equipment and water rates required for a commercial-scale unit are shown next.

Absorber	Case 1	Case 2	Case 3	Case 4
Feed Gas Flowrate (kmol/hr)	2000	2000	2000	5000
Operating Temperature (° C)	20	20	20	20
Operating Pressure (psia)	315	315	315	315
Theoretical Stages	4	4	4	6
Theoretical Water Requirement (mol liq/mol gas)	35.35	35.35	35.35	54.83
Practical Water Requirement (mol liq/mol gas)	52.5	52.5	52.5	82.25
Height (ft)	16	16	16	24
Diameter (ft)	12.4	12.4	12.4	24.97
Stripper				
Desorbed Gas Flowrate (kmol/hr)	460	1380	2780	1800
Operating Temperature (° C)	217	100	50	217
Operating Pressure (psia)	315	315	315	315
Theoretical Stages	3	3	3	3
Theoretical Stripping Requirement (mol liq/mol gas)	153	51.5	25.38	153
Practical Stripping Requirement (mol liq/mol gas)	76.5	25.75	12.69	76.5
Height (ft)	12	12	12	12
Diameter (ft)	8.04	7.53	7.64	15.89

[0092] These results show that reasonable designs for adsorption and desorption columns can be used to provide high levels of CO_2 removal. Removal of CO_2 does not remove significant quantities of valuable components (H_2, CH_4 and CO). The product gas streams are high purity CO_2 (when a reboiler is used) or CO_2/CH_4 mixtures when CH_4 is used as a stripping gas. The recovered CO_2, either as a neat stream or as a CO_2/CH_4 mixture, can be fed to the syngas generator.

[0093] The CO_2-water stream could be fed directly to the syngas generator. This would eliminate the need to have a separate CO_2 gas compressor for the recycle to the reformer. The portion of the CO_2-water stream not used in the syngas generator could be sent to the desorber, where the CO_2 is recovered and disposed.

[0094] When the lower CO_2-content syngas is fed back to the syngas converter, the CO_2 content in the blended synthesis drops from about 20% to lower values. Using typical flow rates, the CO_2 content will decline to about 15% if a low level of CO_2 is removed in the scrubber (about 25%), to about 10% if a moderate amount of CO_2 is removed (about 50%), and about 8% if a high level of CO_2 is removed (about 75%).

[0095] It should be recognized that while the above Example utilized a Fischer-Tropsch reactor as the preferred syngas converter, one could readily use a methanol synthesis in the scheme of the present invention. Details of the MTG process are well documented in the literature. Likewise, the benefits of the invention can be attained in a dual functional syngas conversion facility. A suitable system which integrates a Fischer-Tropsch synthesis and a methanol synthesis using syngas is described in U.S. Patent 6,248,794.

[0096] While the invention has been described with preferred embodiments, it is to be understood that variations and modification may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and the scope of the claims appended hereto.

WHAT IS CLAIMED IS:

1. A process comprising the following steps:

   (a) forming a syngas which contains CO_2 in a syngas generator;

   (b) reacting the syngas in a syngas conversion process to form a product stream comprising hydrocarbonaceous products and a tail gas containing unreacted syngas and CO_2;

   (c) separating the hydrocarbonaceous products from the unreacted syngas and CO_2 in a separation zone;

   (d) contacting at least a portion of the unreacted syngas and CO_2 with an aqueous medium having a pH above about 6.0 in a scrubbing zone to adsorb at least a portion of the CO_2, and recovering a CO_2-enriched aqueous stream and a syngas with reduced CO_2 concentration;

   (e) forwarding at least part of the recovered syngas from step (d) to the syngas conversion reactor; and

   (f) desorbing at least part of the CO_2 from the CO_2-enriched aqueous stream obtained in step (d) and recovering a CO_2-rich gas and CO_2-depleted aqueous stream.

2. A process according to claim 1 further comprising recycling at least part of said CO_2-depleted aqueous stream to said scrubbing zone.

3. A process according to claim 1, further comprising recycling at least part of said CO_2-rich gas to the syngas generator.

4. A process according to claim 1 wherein the syngas is manufactured from natural gas, coal, petroleum products or combinations thereof.

5. A process according to claim 1, wherein the amount of CO_2 removed in step (d) is between about 10 and 90 wt% of the amount present in said tail gas.

6. A process according to claim 5, wherein the amount of CO_2 removed is between about 25 and 60%.

7. A process according to claim 1, wherein the syngas conversion process is a Fischer-Tropsch synthesis.

8. A process according to claim 1, further comprising removal of at least about 5% of any CH_4 present in the unreacted syngas in step (d).

9. A process according to claim 8, wherein the amount of CH_4 removed is between about 10 and 50%.

10. A process according to claim 1, wherein pressure in the scrubbing zone is within 100 psi of the pressure of an outlet of the separator.

11. A process according to claim 1, wherein the pressure is within 50 psi of the outlet of the separation zone.

12. A process according to claim 1, wherein the pressure is within 100 psi of the outlet of the separation zone.

13. A process according to claim 1, wherein the syngas formed in step (a) is blended with the syngas recovered in step (d) and forwarded to the conversion reactor.

14. A process according to claim 13, wherein the CO_2 content of the blended syngas is about 15 wt. % or less.

15. A process according to claim 1, further including the step of disposing at least a portion of the CO_2-enriched aqueous stream from step (d) in a marine environment, a terrestrial formation, or both.

16. A process according to claim 1, further including the step of dissolving at least a portion of the CO_2 in the CO_2-rich gas from step (f) in an aqueous phase and disposing the aqueous phase in a marine environment, a terrestrial formation, or both.

17. A process according to claim 16, wherein the source of the aqueous medium is sea water, river water, brine, non-potable water, or combinations thereof.

18. A process according to claim 1, wherein the scrubbing and desorbing steps are conducted at a pressure above atmospheric.

19. A process according to claim 1, wherein the aqueous medium used in step (d) has a pH of about 7.5 to 11.0 when measured on a CO_2-free sample.

20. A process comprising the following steps:

(a) forming a syngas which contains at least about 2 vol % CO_2 in a syngas generator;

(b) reacting at least a portion of the syngas in a Fischer-Tropsch process to form a product stream comprising hydrocarbonaceous products and a tail gas containing unreacted syngas and CO_2;

(c) contacting at least a portion of the unreacted syngas and CO_2 with an aqueous medium having a pH above about 7.0 in a scrubbing zone at above atmospheric pressure to preferentially absorb at least part of the CO_2 and recovering a CO_2-enriched aqueous stream, and a syngas with a reduced CO_2 concentration;

(d) recycling at least part of the syngas from step (c) to the Fischer-Tropsch process;

(e) desorbing the CO_2-enriched aqueous stream from step (c) to obtain a CO_2-rich gas and a CO_2-depleted aqueous stream; and

(f) circulating the CO_2-depleted aqueous stream to the scrubber in step (c).

21. A process according to claim 20, wherein at least part of said CO_2- rich gas is recycled to the syngas generator.

22. A process according to claim 20, wherein a portion of the syngas and CO_2 from step (c) is used as a fuel.

23. A process according to claim 20, wherein the pH of the aqueous medium is about 7.5 to 11.0.

24. A process for manufacture of products from syngas comprising:

(a) forming a syngas which contains CO_2 in a syngas generator;

(b) contacting at least a portion of the syngas with an aqueous medium having a pH above about 7.0 in a scrubbing zone at above atmospheric pressure to remove at least a portion of the CO_2 and recovering a CO_2-enriched aqueous stream and syngas with a lower CO_2 concentration than the syngas obtained in step (a);

(c) reacting at least a portion of the syngas obtained in step (b) in a syngas conversion reaction to form a product stream comprising hydrocarbonaceous products and a tail gas containing CO_2 and unreacted syngas;

(d) desorbing at above atmospheric pressure at least part of the CO_2 in the CO_2-enriched aqueous stream from step (b) to obtain a CO_2-rich gas and CO_2-depleted aqueous stream;

(e) forwarding at least part of the CO_2-rich gas to the syngas generator;

(f) recycling at least part of the tail gas from step (c) to the syngas conversion reactor; and

(g) dissolving at least part of the CO_2-rich gas in an aqueous medium.

25. A process according to claim 24, further comprising using at least part of the tail gas as a fuel.

26. A process according to claim 24, wherein the hydrocarbonaceous products from step (c) are further processed into salable products.

27. A process according to claim 24, further comprising the step of removing at least 30% of any NH_3 or HCN present in the syngas during the scrubbing operation in step (b).

28. A process according to claim 24, wherein the syngas conversion reaction in step (c) comprises a Fischer-Tropsch synthesis.

29. A process according to claim 24, where the aqueous medium in step (b) has a pH of about 7.5 to 11.0 when when measured on a CO_2-free sample.

FIGURE 1

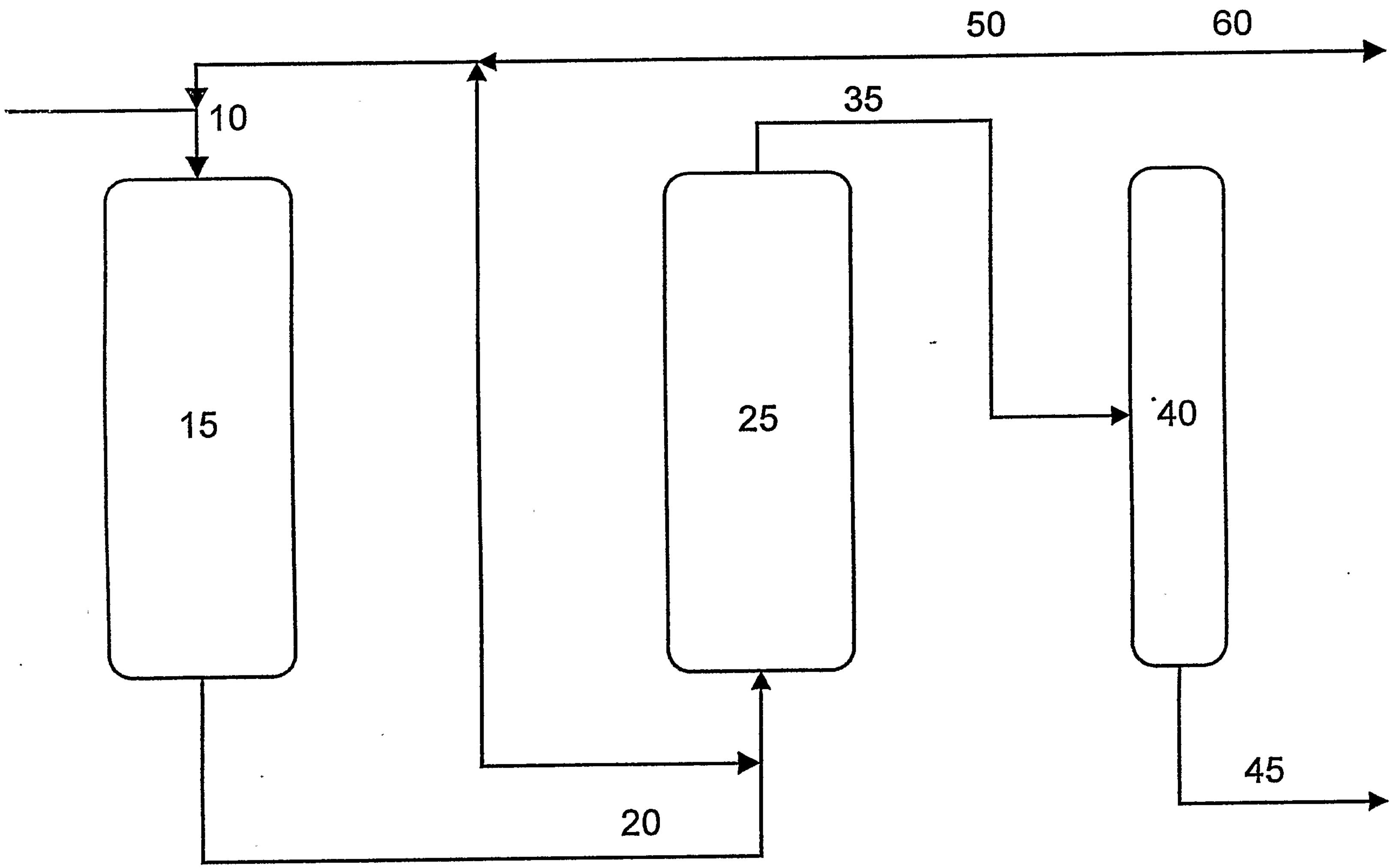
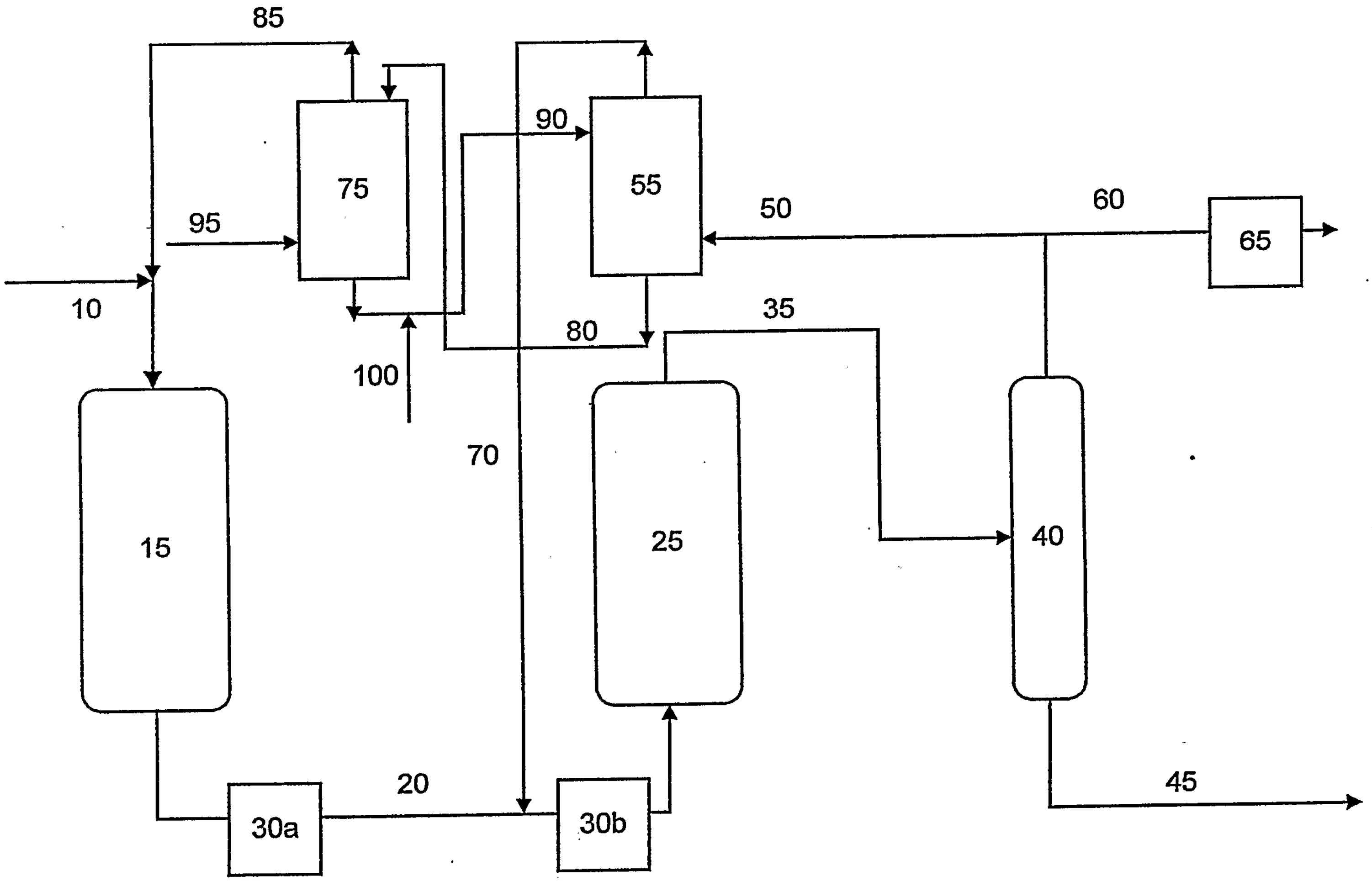


FIGURE 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US03/10248

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C07C 27/00
US CL : 518/700, 702, 705
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)
U.S. : 518/700, 702, 705

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 practicable, search terms used)
EAST, WEST AND CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,763,716 A (BENHAM et al.) 09 June 1998, see entire document.	1-29
Y	US 6,248,794 B1 (GIESKES) 19 June 2001, see entire document.	1-29
Y	US 4,322,227 A (COOK ET AL) 30 March 1982, see entire document.	1-29

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

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search 29 June 2003 (29.06.2003)	Date of mailing of the international search report 12 SEP 2003
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Dorothea Lawrence For Jafar Parsa Telephone No. (703) 308-1235

Form PCT/ISA/210 (second sheet) (July 1998)