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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [6] **:**
C10G 2/00, C07C 1/04, C01B 3/36

A1

(11) International Publication Number: **WO 98/01514**

(43) International Publication Date: 15 January 1998 (15.01.98)

(21) International Application Number: PCT/US97/12242

(22) International Filing Date: 9 July 1997 (09.07.97)

(30) Priority Data:
08/679,402 9 July 1996 (09.07.96) US

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
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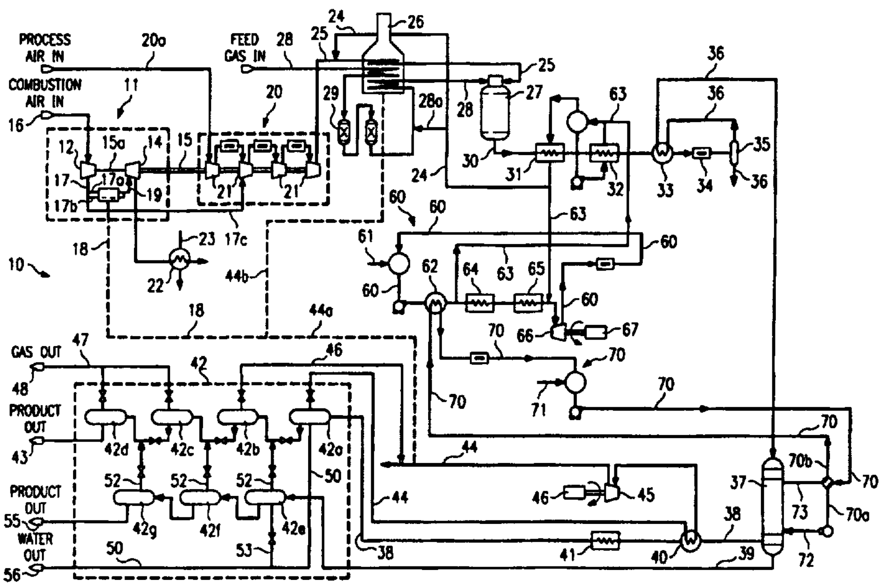
(54) Title: PROCESS FOR CONVERTING GAS TO LIQUIDS



(57) Abstract

A process for converting a hydrocarbon gas (e.g. natural gas) to syngas which, in turn, is converted into a liquid hydrocarbon product wherein a substantial amount of the heat generated in the process is recovered for use in generating steam needed in the process or for conversion into mechanical energy. Further, tail gas produced by the process is used to fuel the gas turbine which, in turn, is used to power the compressor needed for compressing the air used in the process. By using tail gas to fuel the gas turbine, less of the compressed combustion-air is needed to cool the combustion gases in the turbine and, instead, can be used to provide a portion of the process-air required in the process; thereby possibly saving up to 20 to 30 percent of the horsepower otherwise needed to compress the required volume of the process-air.

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PROCESS FOR CONVERTING GAS TO LIQUIDS

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a process for converting gases to liquids and in one of its aspects relates to a highly-efficient process for converting hydrocarbon gas (e.g. methane) to a hydrocarbon liquid (e.g. gasoline, distillates, etc.) which includes the improved operation for providing the required process-air and wherein waste heat and tail gas is efficiently recovered to be used within the process and/or to generate auxiliary power.

BACKGROUND OF THE INVENTION

The desirability to convert light, hydrocarbon gases (e.g. natural gas) to liquids (e.g. methanol, gasolines, distillates, etc.) has long been recognized. Probably the most commonly-proposed process for carrying out this type of conversion is one wherein natural gas is first flowed through an Autothermal Reformer, e.g. a partial oxidation reformer, to convert the natural gas to a synthesis gas ("syngas", i.e. a gas comprised of carbon monoxide (CO) and hydrogen (H_2)). The syngas is then fed to a Fischer-Tropsch type of reactor which is loaded with an appropriate catalyst which, in turn, converts the syngas to a desired product (e.g. methanol, gasolines, distillates, etc.) depending on the catalyst and the operating conditions within the reactor. Such processes are well-known in the industry; for example of Fischer-Tropsch ("F-T") processes of this type, see U.S. Patents 1,798,288; 2,500,533; 2,552,308; 4,579,985; and 4,973,453.

While the type of basic process has been known for some time, efforts are continuously being made to improve its efficiency in order to make it more commercially attractable. For example, where possible, air instead of oxygen is used as a reactant in the ATR stage since air is obviously cheaper and more readily available than pure oxygen; e.g. see U.S. Patents 2,500,533; 2,552,308, et sec.. Further, a continuing search is on-going to find the ultimate catalyst for use in the F-T reactor; e.g. see U.S. Patents 4,522,939; 4,755,536; et sec.. Also, improvements in the various elements (e.g. partial oxidation reformer) used in the process are important considerations in attempting to optimize the process (e.g. see U.S. 3,549,335; 4,778,826) for commercial use.

Another very important consideration in the commercialization of such a process is maximizing the recovery of otherwise wasted heat and gases from the process for use in the process, itself, or for generating excess energy (i.e. heat and/or mechanical power) which, in turn, can be sold or used in other applications. For example, (a) energy may be generated by reacting off-gas from the process in a fuel cell, see U.S. Patent 4,048,250; (b) dry or tail gas may be used for generating heat used in the process, see U.S. 4,048,250; (c) heat recovered from a gas turbine, which is used in the process to both compress the process-air and drive an electrical generator, may be used in the ATR, see U.S. Patent 4,315,983; and (d) heat, recovered from the product after it passes through the reformer, may be used to generate a separate stream of superheated steam while the syngas may be expanded through a turbine to recover mechanical energy, see U.S. Patent 4,074,991. While each of these approaches add to the operating efficiency of the overall conversion process, there is still much which can be done in the optimizing the process to make it more commercially acceptable.

SUMMARY OF THE INVENTION

The present invention provides a process for converting a hydrocarbon gas (e.g. natural gas) to syngas which, in turn, is converted into a liquid hydrocarbon product wherein a substantial amount of the heat generated in the process is recovered for use in the process or to be converted to mechanical energy. Further, the tail gas generated in the process is used to fuel the gas turbine which is used to power the compressors which, in turn, are used to compress the process-air. By using tail gas to fuel the gas turbine, less of the compressed combustion-air has to be used to cool the combustion gases from the combustor of the turbine and, instead, can be used to provide a portion of the process-air required in the process. This can save up to 20 to 30 percent of the horsepower which otherwise would be needed to compress the volume of process-air needed for the process.

More specifically, the present invention provides a process for converting a hydrocarbon feed gas to a hydrocarbon liquid wherein the process-air needed for carrying out the process is compressed by a compression unit which is powered by a gas turbine wherein the gas turbine has a compressor section, a combustor, and a turbine section. The compressor section compresses combustion-air, a first portion of which is supplied to the combustor where it is mixed with tail gas which, in turn, is recovered from the process, itself.

A typical tail gas recovered from the present process is comprised of methane, carbon monoxide, carbon dioxide, hydrogen, nitrogen, and other light hydrocarbons (e.g. C_2-C_4) which burns substantially cooler than do higher-BTU fuels such as natural gas thereby producing combustion gases at lower temperatures. This allows a substantially smaller second portion of the compressed combustion-air to be used to cool the same volume of combustion gases to the temperature required for safe operation of the turbine section of the gas turbine. By using less of the compressed air for cooling, a substantial remaining portion (e.g. about 30 to 40% of the original volume) of the compressed combustion-air from said compressor section can be supplied directly to said process to form a portion of the process-air required to carry out the present process.

Once the process air has been compressed, it is mixed with steam and is heated in a heater before the mixture is passed to an Autothermal Reforming Unit (ATR). A hydrocarbon feed gas (e.g. methane) is also mixed with steam and is heated in the heater (the heater possibly being fueled with tail gas from the process) before this mixture is also passed into the ATR where it is mixed with the mixture of process-air and steam mixture in the presence of a catalyst to form a syngas which, in turn, is comprised of nitrogen, carbon monoxide and hydrogen. Heat is recovered from the syngas and is used to generate steam, some of which is mixed with both the process-air and the feed gas.

The syngas is then passed over a catalyst in a Fischer-Tropsch reactor to thereby convert at least a portion of said syngas to liquid hydrocarbons. Heat is also recovered from the reactor as said syngas being converted to a liquid hydrocarbon and can be used in generating the steam needed in the present process. The products from the reactor are passed to a separation section where the unconverted syngas is separated from the liquid hydrocarbon. It is this unconverted syngas and by-products (methane, C_2-C_4m carbon dioxide, and nitrogen) which forms the "tail gas" which is used for fuel in the process. Also, at least a portion of the tail gas may be expanded through a turbine to recover mechanical energy therefrom.

BRIEF DESCRIPTION OF THE DRAWINGS

The actual construction, operation, and apparent advantages of the present invention will be better understood by referring to the drawings which are not necessarily to scale and in which like numerals refers to like parts and in which:

FIGURE 1 is a schematic representation of an integrated gas conversion system for carrying out a process in accordance with the present invention;

FIGURE 2 is a schematic representation of a gas turbine as it is operated in the prior art;

FIGURE 3 is a schematic representation of the gas turbine of FIGURE 2 as operated in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring more particularly to the drawings, FIGURE 1 discloses a schematical diagram of the system 10 which can be used in carrying out a conversion process in accordance with the present invention. Throughout the following description, examples of temperatures and pressures are given at respective stages of a process carried in accordance with the present invention. However, it should be recognized that these temperatures and pressures are only illustrative of the anticipated conditions within the system 10 and actual values may vary for any particular process without departing from the present invention. The recited conditions are based on a typical process in accordance with the present invention wherein 52.1 million standard cubic feet of feed gas (e.g. natural gas) is processed per day.

System 10 is comprised of a standard gas turbine 11 (e.g. 32,500 horsepower) which furnishes power for compressing the air needed in the present process. As will be understood in the art, gas turbine 11 is comprised of a compressor section 12, a combustor section 13, and a power turbine section 14 which, in turn, has a primary power output shaft 15 for driving the process-air compressors and a secondary shaft 15a which drives compressor section 12.

As best seen in FIGURE 2, in prior-art turbines of this type, air is supplied to the compressor section 12 of gas turbine 11 through inlet 16 at approximately atmospheric conditions (e.g. 14.7 psi and 80° F.) and is compressed before it is supplied to combustor 13 through line 17. A portion of the air is fed to combustor 13 through line 17a where it is mixed with a high BTU fuel from line 18a and burned to produce a hot gas.

As will be understood in the art, when a high-BTU fuel such as natural gas (e.g. methane) is burned stoichiometrically in a typical combustor in a gas turbine of this type, the resulting gases have a very high temperature (e.g. 2800° F.) which is too hot to be expanded through turbine section 14 without causing serious damage thereto. Accordingly, remaining air in line 17 from compressor section 12 (i.e. cooling air) is flowed through line 17b in heat exchange with combustor 13 to keep the combustion gases from combustor 13 at a temperature (e.g. 1800° F.) which can be safely handled by turbine section 14. The cooling air in line 17b is mixed with the combustion gases in line 19 before the mixture, is expanded through turbine section 14 to rotate shafts 15, 15a.

In accordance with one aspect of the present invention, the amount of air needed for cooling the combustion gases to roughly the same temperatures as before (e.g. 1800° F.) is substantially reduced so that only a portion (e.g. about 60-70%) of the compressed "combustion-cooling" air will be used for mixing with the fuel and cooling of the combustion gases. This is accomplished by using the tail gas which is produced in the present process as fuel in place of a higher-BTU fuel such as methane. The tail gas which is comprised of methane, other light hydrocarbons, carbon monoxide, carbon dioxide, hydrogen, and substantial amounts of nitrogen produces the same quantity of combustion gases but at a significant lower temperature (e.g. 2100° F.); hence, less cooling is required to lower the gas temperature to that required (e.g. 1800°) for safe operation of turbine section 14.

Referring to FIGURE 3, the compressed air from section 12 is fed to the combustor 13 through line 17a where it is mixed with fuel from line 18 and through line 17b to cool the combustion gases from combustor 13 similarly as described above. Again, the fuel in line 18 is tail gas which is recovered within system 10 as be further discussed below. The remainder of the compressed combustion-cooling air (e.g. about 30-40% of total flow) which is not needed for combustion-cooling is supplied through line 17c directly to process-air compression unit 20 which, in turn, is comprised of one or more compression stages 21 (four shown).

The primary "process-air" is supplied to compression unit 20 at ambient conditions through inlet 20a. By using the portion of the compressed, combustion-cooling air from compressor section 12 which is not needed for combustion/cooling in turbine 11 to make up part of the process-air needed to carry out the present process, the horsepower required for compressor unit 20 may be reduced as much as 20-30% from that which otherwise would be needed.

As before, the combustion gases from combustor 13 are expanded through power turbine section 14 to drive the turbine which, in turn, drives both the compressor section 12 of turbine 11 through shaft 15a and all of the compression stages 21 of unit 20 through output shaft 15, as will be understood in the art. The exhaust from turbine 14, in turn, is passed through exchanger 22 wherein bustantially amounts of heat (e.g. as much as 93 MMBTUs per hour) can be transferred into feed water in line 23 to thereby generate steam for use within the process or for use in auxiliary applications (not shown).

Compressed process-air (e.g. about 600 psia and 328° F.) exists compression unit 20 through line 25 and is mixed with superheated steam (e.g. about 1200 psia and 900° F.) from line 24. The air/steam mixture is further heated in furnace 26 (which can also be fired by the tail gas from the process) to about 1000° F. and reaches a pressure of about 595 psia before the process-air/steam steam is delivered to Autothermal Reforming Unit ("ATR") 27. Feed gas (e.g. natural gas at about 610 psi and 100° F.) flows through the inlet of line 28 and is (a) heated in furnace 26, (b) passed through hydrogen sulfide removers 29 (two shown), and (3) re-heated in furnace 26 to reach a temperature about 1000° and a pressure of about 595 psia before it is delivered to ATR 27 through line 28.

As will be understood in the art, ATR 27 may take different forms but generally is comprised of a vessel having a reforming catalyst (e.g. nickel-containing catalyst) therein which converts the air/steam/natural gas to a synthesis gas "syngas" (i.e. CO and H_2); e.g. see U.S. Patent 4,973,453. The syngas along with nitrogen and unreacted light hydrocarbons leave ATR 27 through outlet 30 at about 590 psi and 1806° F. and is cooled in a (a) exchangers 31 and 32 to about 600° F., (b) exchanger 33 to about 336° F, and (c) cooler 34 to about 100° F. (optional) before being delivered to separator 35 where any condensed water is removed through outlet 36.

The syngas then flows from separator 35 through exchanger 33 in line 36 where it is heated to about 415° F. (565 psia) before it is delivered to the Fischer-Tropsch ("F-T") reactor 37. Again, as will be understood in the art, F-T reactors of this type are well known in the art and basically comprised of a vessel containing an appropriate catalyst (e.g. cobalt-containing catalyst) therein. There are several known catalyst which are used in converting a synthesis gas depending on the product desired; e.g., see U.S. Patents 4,579,985 and 4,579,986.

The product (about 415° F., 535 psia) flows from F-T reactor 37 at about 535 psia and 415° F. through two separate outlets 38, 39. The product in outlet 38 is first cooled in exchange 40 to about 309° F. and then in cooler 41 to about 100° F. before it is delivered to the first separator 42a in a first row of separators 42a-d in separator section 42. The series of separators reduce the pressure of the product in increments from about 525 psia to about 15 psia before the product is sent through outlet line 43 to storage or for further processing (e.g.

hydorcracking) or for other use. Tail gas (uncondensed light hydrocarbons, nitrogen, etc.) is taken off the first separator 42a at about 520 psia through line 44 and is passed through exchanger 40 to cool the product in line 38 and to raise the temperature of the tail gas to about 350° F.. In some applications, the tail gas may be expanded through power turbine 44 to reduce its pressure and recover mechanical power, e.g. drive an electrical generator 45 or the like. Any condensed water is removed from separator 42a through line 50.

Tail gas also flows from the second separator 42b through line 46 and is combined with the tail gas in line 44. The tail gas still has a good BTU value and can be used as fuel within the process; e.g. fuel for the combustor 13 in turbine 11 (dotted line 44a, line 18); furnace 26 (dotted line 44b), etc.. Any remaining tail gas as in line 44 can be used or sold as a particular situation dictates. Any gas remaining in the product once it has reached separators 42c, 42d is likely to be at too low of pressure to be used as fuel within the process so it is carried through line 47 to a flare 48 or for similar disposal.

The product in the other outlet line 39 is delivered to a first separator 42e in a second row of separators 42e-g in separator section 42 and undergoes stepped-pressure reduction before it is delivered to storage through line 55. Any gas which separates from the product in separators 42e-g is conveyed to respective separators in the first row through lines 52 and is accordingly processed. Water which separates from the product in separator 42e is removed through line 53 and is combined with the water in line 50 for disposal at outlet 56.

In accordance with the present invention, heat is recovered and utilized at almost every station within the system. That is, two utilities loops are provided which generate steam and recover excess energy from the system as the process is being carried out. Referring again to the FIGURE 1, boiler feed water is delivered under high pressure (e.g. about 1200 psia) into the first utilities loop 60 through "make-up" inlet 61 and is raised to about 350° F. as it passes through exchanger 62.

A split stream of heated water is taken from line 60 through line 63 and is passed through heat exchangers 31 and 32 to recover heat from the product leaving ATR 27 thereby raising the temperature of the water (now superheated steam) to about 900° before it is returned to line 60. A portion of the superheated steam can be directed (a) through line 24 into the compressed, process-air in line 25 and (b) through line 28a to heat the feed gas in line 28.

The remainder of the heated water is passed through boiler 64 and superheater 65 in line 60 (both of which can be fueled by tail gas) to raise its temperature to about 900° before being recombined with the steam from line 63 which is also at the same temperature and pressure. The steam is then expanded through turbine 66 to covert the recovered heat to usable mechanical power (e.g. drive electrical generator 67 or the like).

The second utilities loop 70 is comprised of line 70 wherein make-up water is delivered to loop 70 through inlet 71. The water flows into F-T reactor 37 through line 72 at a temperature of about 390° and out line 73 at a temperature of about 415° F.. The water is then flowed through exchanger 62 where the heat recovered from reactor 27 is transferred to the boiler feed water in loop 60 thereby adding to the overall efficiency of the process.

The above describes a system and a process for converting natural gas or the like to syngas which, in turn, is then converted into a liquid hydrocarbon product wherein most of the heat generated in the process is recovered for use in the process or is converted to mechanical energy. Also, the tail gas generated in the process is used as the primary fuel required in the process. Further, the turbine used to compress the process-air is operated to provide a portion of the required process-air itself.

WHAT IS CLAIMED IS:

1. In a process for converting a gas to a liquid having a gas turbine for driving at least one compressor which, in turn, compress process-air for use in said process wherein said gas turbine has a compressor section, a combustor, and a turbine section, the method for operating said gas turbine comprising:

compressing combustion-air in said compressor section;

supplying a first portion of said compressed combustion-air to said combustor;

supplying a tail gas which is recovered from said process to said combustor to mix with said first portion of said compressed air before burning said mixture in said combustor to produce combustion gases;

mixing a second portion of said compressed combustion-air with said combustion gases to cool same before said compressed air before burning said mixture in said combustor to produce combustion gases;

supplying the remaining portion of said compressed combustion-air from said compressor section directly to said process for use therein.

2. The method of claim 1 wherein said remaining portion of said compressed combustion-air comprises about 30% to about 40% of the total volume of compressed combustion-air.

3. The method of claim 1 wherein said tail gas is comprised of methane, carbon monoxide, carbon dioxide, hydrogen, and nitrogen.

4. The method of claim 1 including:

recovering heat from said combustion gases after said gases have passed through said turbine section.

5. A process for converting a hydrocarbon feed gas to a hydrocarbon liquid comprising:

compressing process-air for use in said process;

mixing said compressed process-air with steam;

mixing said compressed process-air and steam mixture with said hydrocarbon feed gas in the presence of a catalyst to form a syngas comprised of carbon monoxide and hydrogen;

recovering heat from said syngas for use in said process;

passing said syngas after said heat has been recovered over a catalyst in a reactor to convert at least a portion of said syngas to a liquid hydrocarbon;

recovering heat from said reactor as said syngas is converted to said liquid hydrocarbon for use in said process; and

separating unconverted syngas from said liquid hydrocarbon to provide a tail as for use in said process.

6. The process of claim 5 including:

mixing steam with said feed hydrocarbon gas before said feed gas is mixed with said mixture of said compressed air and steam wherein said steam which is mixed with both said compressed process-air and said feed gas is generated by using said heat recovered from said syngas.

7. The process of claim 6 wherein said process-air is compressed using a compression unit which is fueled by said tail gas.

8. The process of claim 6 wherein said process-air is compressed using a compression unit powered by a gas turbine wherein said gas turbine has a compressor section, a combustor, and a turbine section and method for operating said gas turbine comprising:

compressing combustion-air in said compressor section;

supplying a first portion of said compressed combustion-air to said combustor;

supplying said tail gas to said combustor to mix with said first portion of said compressed air before burning said mixture in said combustor to produce combustion gases;

mixing a second portion of said compressed combustion-air with said combustion gases to cool same before said gases are expanded through said turbine section; and

supplying the remaining portion of said compressed combustion-air from said compressor section directly to said process to form a portion of said process-air.

9. The process of claim 6 including:

heating both said mixture of said process-air and steam mixture and said mixture of said feed gas and said steam before they are mixed to form said syngas by passing both through a heater which is fueled by said tail gas.

10. The process of claim 9 including:

expanding at least a portion of said tail gas through a turbine to recover mechanical energy therefrom.

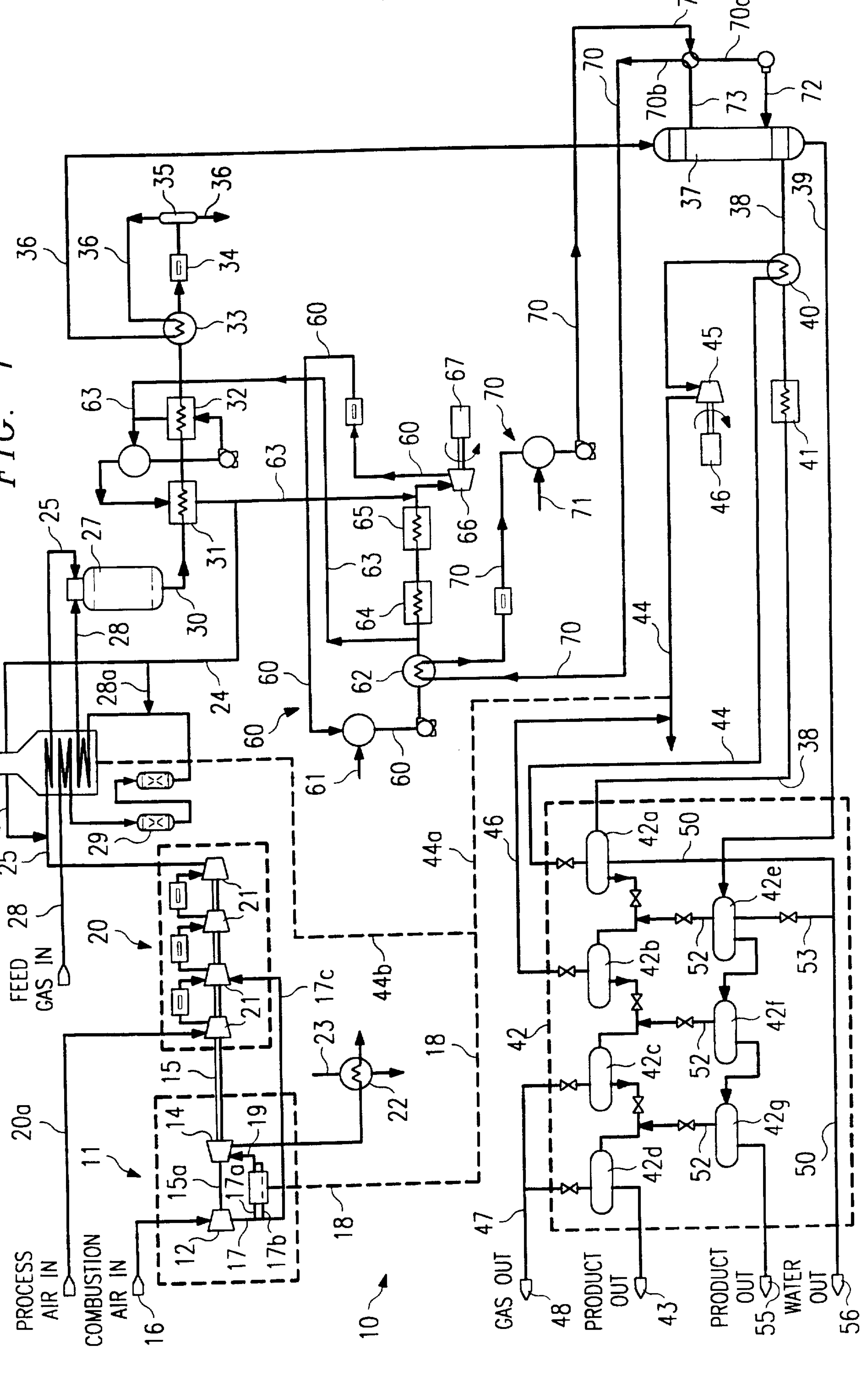
PROCESS AIR IN
COMBUSTION AIR IN
FEED GAS IN
GAS OUT
PRODUCT OUT
PRODUCT OUT
WATER OUT

FIG. 1

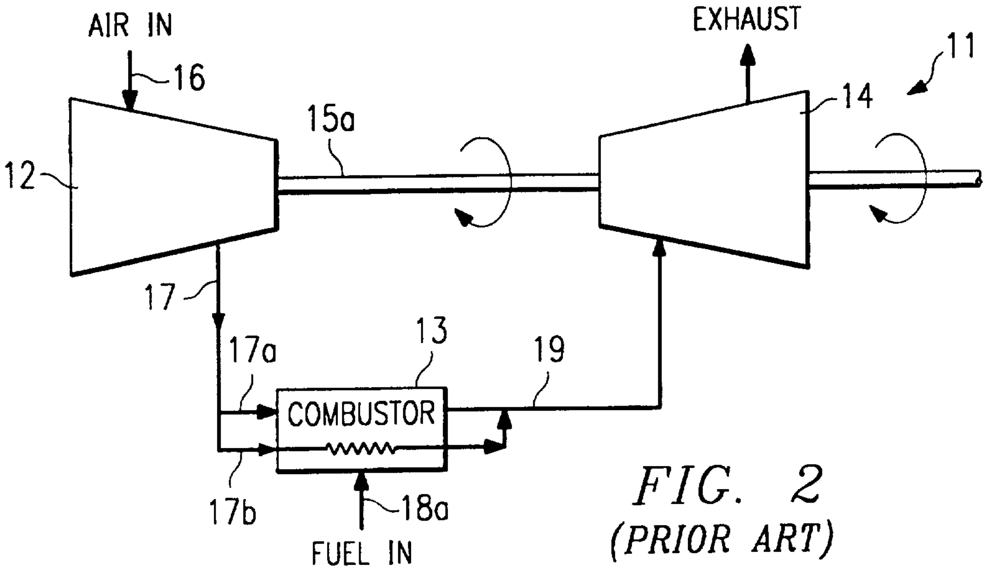

FIG. 2
(PRIOR ART)

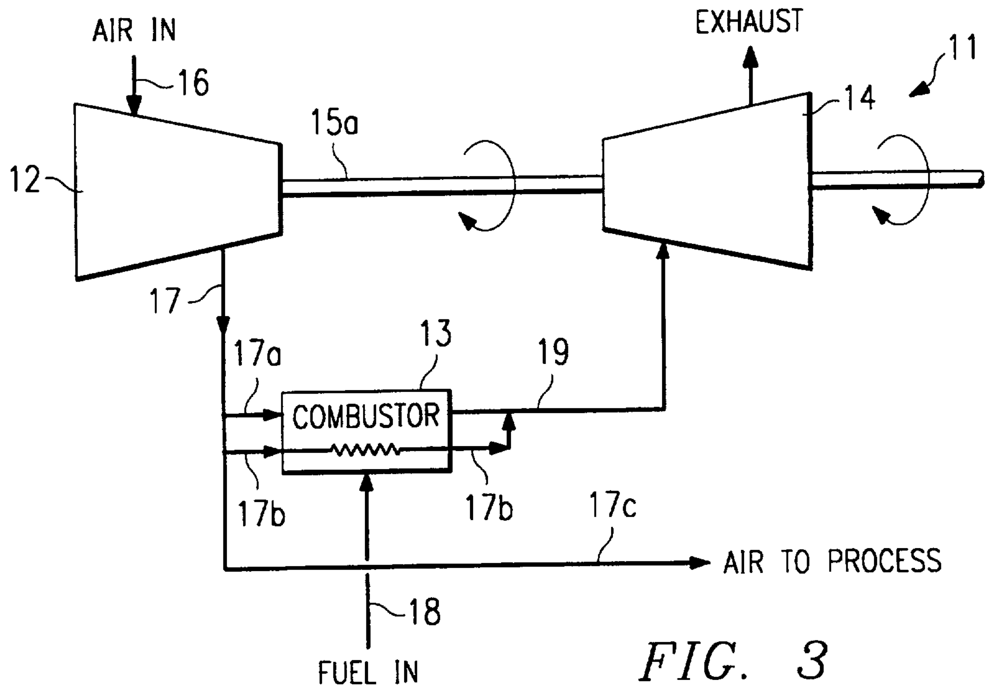

FIG. 3

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 97/12242

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G2/00 C07C1/04 C01B3/36

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)
IPC 6 C10G C07C C01B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 32 10 411 A (SHELL INT RESEARCH) 7 October 1982 see claims 1,3 see page 22, line 30 - page 5, line 20 see figure 1 ---	1,3,5,7, 8
A	US 4 132 065 A (TEXACO) 2 January 1979 see claims 1,24 see column 10, line 53 - line 58 see column 11, line 27 - line 37 see figure 1 -----	1,4

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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1

Date of the actual completion of the international search	Date of mailing of the international search report
22 October 1997	31.10.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	De Herdt, O

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 97/12242

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3210411 A	07-10-82	NL 8101447 A	18-10-82
		AU 544933 B	20-06-85
		AU 8175982 A	30-09-82
		CA 1195632 A	22-10-85
		US 4433065 A	21-02-84
US 4132065 A	02-01-79	DE 2845498 A	24-04-80
		BE 872436 A	30-05-79