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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 July 2002 (04.07.2002)

PCT

(10) International Publication Number
WO 02/051744 A1

(51) International Patent Classification[7]: **C01B 3/38**, 3/36, 3/56, 3/50, 3/48, C10G 2/00, F25J 3/04

(21) International Application Number: PCT/IB01/02615

(22) International Filing Date: 21 December 2001 (21.12.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00204757.9 27 December 2000 (27.12.2000) EP

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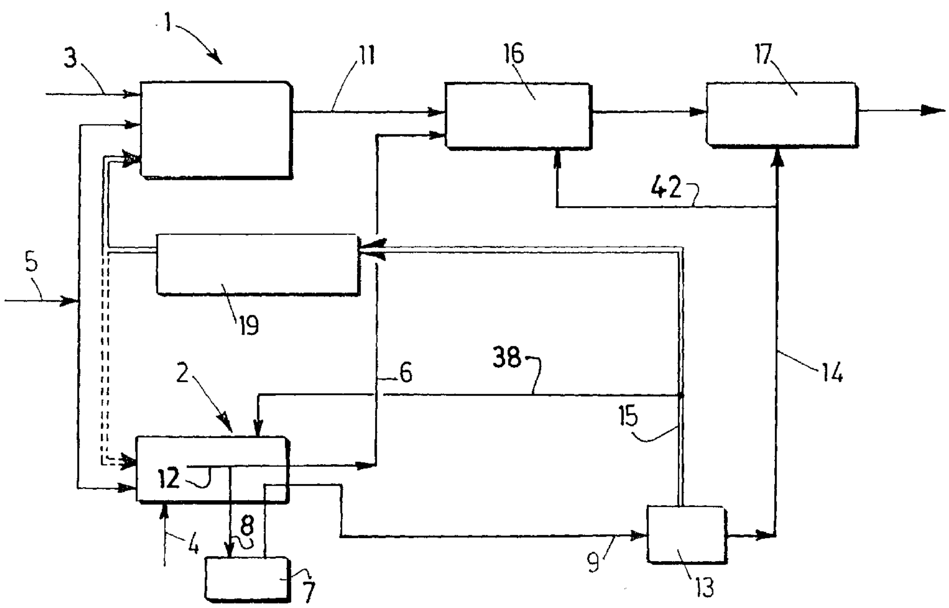
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

[Continued on next page]

(54) **Title:** INTEGRATED PROCESS AND INSTALLATION FOR THE PRODUCTION OF SYNTHESIS GAS



(57) **Abstract:** In an integrated process for the production of synthesis gas, a partial oxidation unit (1) and a stream methane reformer (2) are used to convert natural gas or another fuel to first and second mixtures (11, 12) of at least carbon monoxide and hydrogen, only the first process consuming oxygen. Carbon dioxide (15, 25) derived from the second mixture is sent to the inlet of the first to process to reduce the oxygen consumption. The first and optionally second mixtures may be used as synthesis gas for a process such as a Fischer Tropsh process (16).

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTEGRATED PROCESS AND INSTALLATION FOR THE PRODUCTION OF SYNTHESIS GAS

The present invention relates to an integrated process and installation for the production of synthesis gas. In particular it relates to a process using two reactors producing synthesis gases containing at least hydrogen and carbon monoxide with a global hydrogen/carbon monoxide ratio between 1.8:1 and 3:1.

Due to the economic benefits associated with using natural gas on certain gasfields or oilfields and recent advances in catalytic processes, a certain number of projects for converting natural gas to synthetic hydrocarbons are presently being studied. The processes used can, for example, produce synthetic fuel by the gas-to-liquid process (GTL), olefins by the gas-to-olefins process (GTO), methanol or dimethyl ether (DME). GTL processes are described in 'Shell Middle Distillates Synthesis' by P. Tijm et al., Alternate Energy '94 April 26-29 1994.

These processes generally include three steps:

1) production of synthesis gas (mixture of hydrogen and carbon monoxide)
2) synthesis of hydrocarbon chains
3) distillation and/ or finishing and/or hydrocracking

Most of these processes use large amounts of oxygen or oxygen enriched air to produce the synthesis gases in partial oxidation reactors using a non-catalytic or catalytic process. A suitable air separation unit for producing oxygen is described in EP-A-0982554.

The following explanation and description relates to GTL plants but applies also to other synthetic hydrocarbon plants, such as GTO, DME or methanol plants.

For GTL processes, the Fischer-Tropsch reaction

$nCO + 2nH_2 \rightarrow (-CH_2)n + nH_20$

requires a stoechiometric synthesis gas make-up to be produced with a molar ratio of 2:1.

Additional amounts of hydrogen are needed for the finishing and to compensate for losses in by-products and/or purge gases leading to an increased global H_2/CO ratio of between 2.1 :1 and 2.7 :1.

Typically a non-catalytic partial oxidation POX unit, when fed with natural gas, produces a synthesis gas with an H_2/CO ratio of about 1.8 :1 depending on the composition of the natural gas. This ratio can vary too when other oxidants, such as steam or carbon dioxide, are sent to the unit.

The global H_2/CO ratio can be reached

- either by partial shift conversion of the CO produced in the POX unit as described in EP-A-0484136

$$CO + H_20 \rightarrow C0_2 + H_2$$

- or by coproducing a second synthesis gas from a steam methane reformer unit (SMR), fed also by natural gas, the second synthesis gas having a H_2/CO ratio typically between 2.7/1 and 6/1.

Thus, the synthesis gas from the POX unit can be combined with synthesis gas from an SMR unit to produce the required global ratio.

When the POX unit is fed with heavier feed stock, such as coal, residues or intermediate by-products, the H_2/CO ratio is typically lower and the above techniques must be used to balance the overall H_2 requirements.

Catalytic partial oxidation processes, when fed with natural gas or other light hydrocarbon mixtures, produce synthesis gas with a higher H_2/CO ratio between 2/1 and 3/1 and can be used, as stand alone processes or not, to satisfy the global ratio.

For a given size of GTL plant, using an oxygen fed reactor such as a POX unit and a process which does not use oxygen such as an SMR unit, it is an object of the present invention to optimise the size and number of the POX modules and/or SMR modules and/or ASU modules, constituting the POX unit, SMR unit and the air separation unit, using the latest technical developments for the various modules.

Particularly, in recent years, the output of air separation units has considerably increased. Modular units presently produce 3500 tonnes of oxygen per day and the module should be able to produce 6000 tonnes of oxygen per day in the near future.

According to the invention, there is provided a process for the production of at least one synthesis gas for a synthesis unit consuming at least one mixture of at least carbon monoxide and hydrogen with a global hydrogen/carbon monoxide ratio between 1.8:1 and 3:1 comprising:

a) sending oxygen having a concentration of at least 99 mol. % and at least one of natural gas, coal and petroleum residues to a first reactor which is a partial oxidation unit to produce a first mixture containing at least carbon monoxide and hydrogen,

b) sending steam and at least one of natural gas and another mixture of light hydrocarbons to a second reactor which is a steam methane reformer to produce at least one second mixture containing at least hydrogen, carbon monoxide and carbon dioxide,

c) sending at least part of the first mixture to form a synthesis gas to be sent to the synthesis unit, and

d) deriving at least one gas containing at least 40 mol.% carbon dioxide from at least part of the second mixture and sending at least part of the at least one gas containing at least 40 mol.% carbon dioxide to inlet of the first reactor.

Optionally the process may also include the following steps :

- no air is sent to the first reactor ;
- sending oxygen to the first reactor from an air separation unit in which liquid is pumped to an operating pressure of the first reactor, vaporised and supplied as gas to the first reactor or alternatively in which gaseous oxygen is warmed and compressed to an operating pressure of the first reactor ;
- the first mixture has a hydrogen/carbon monoxide ratio of less than 1,8, ;
- sending an oxidant to the second reactor, preferably constituted at least in part by steam and possibly sending a gas containing at least 40 mol.% carbon dioxide derived from the second reactor to inlet of the second reactor ;
- treating at least part of the second mixture to form at least one stream containing at least 40 mol.% carbon dioxide and a gas enriched in hydrogen and possibly a synthesis gas with an H_2/CO ratio higher than 2/1 ;
- producing the hydrogen enriched gas from the second mixture by using shift conversion and either pressure swing adsorption and/or CO_2 removal and methanation processes ;
- producing the hydrogen enriched gas from the second mixture by using permeation and either pressure swing adsorption and/or methanation processes ;
- said synthesis gas with a H_2/CO ratio higher than 2/1 is the second mixture or a third mixture produced by the CO_2 removal process or a fourth mixture produced by the permeation process.

The CO_2 rich gas comes from the PSA unit and/ or the CO_2 removal unit, which may for example be a washing unit

- sending at least part of the stream enriched in hydrogen to the synthesis unit ;
- sending at least part of the stream enriched in hydrogen to a finishing unit ;
- sending at least part of the second mixture to the synthesis unit ;
- producing a hydrogen enriched gas and the gas containing at least 40 mol.% carbon dioxide from the second mixture using pressure swing adsorption and possibly shift conversion.

- producing a hydrogen enriched gas from the second mixture and the gas containing at least 40 mol.% carbon dioxide using CO_2 removal and possibly a methanation process ;

- sending at least part of a stream enriched in hydrogen derived from at least part of the second mixture to a finishing process downstream the synthesis unit ;

- the CO_2 removal unit is a washing unit, an adsorption unit or a permeation unit ;

- sending a gas containing at least carbon monoxide and hydrogen from the CO_2 removal unit to the synthesis unit and/or to a methanation unit and/or to a permeation unit ;

- sending a gas containing at least carbon monoxide and hydrogen from the CO_2 removal unit to a permeation unit, said gas constituting a third mixture, and sending a hydrogen enriched gas from the permeation unit to an adsorption unit and/or a hydrogen depleted gas to the synthesis unit ;

- sending part of the third mixture to the synthesis unit ;

- sending at least part of the gas containing carbon monoxide and hydrogen from the CO_2 removal unit to a permeation unit and sending a fourth mixture depleted in hydrogen from the permeation unit to the synthesis unit.

The first reactor may be a non-catalytic or a catalytic partial oxidation reactor.

Preferably the first reactor is fed by an oxygen enriched stream and the second reactor is not fed by an oxygen enriched stream.

According to a further aspect of the invention, there is provided an installation for the production of synthesis gas for a process taking place within a synthesis unit consuming a mixture of at least carbon monoxide and hydrogen with a hydrogen/carbon monoxide ratio of between 1.8:1 and 3:1 comprising: first and second reactors said first reactor being a partial oxidation unit and said second reactor being a steam methane reformer, said first and second reactors each having a respective inlet and outlet, means for sending oxygen having a concentration of at least 99 mol. % to the inlet of the first reactor, said means comprising a cryogenic air separation unit, means for removing liquid oxygen from a column of the air separation unit, means for pumping the liquid oxygen to an operating pressure of the first reactor , means for vaporising the pumped liquid and means for sending the pressurised gas thus produced to the inlet of the first reactor, there being no means for sending air to the inlet of the first reactor, means for sending at least one of natural gas, coal and petroleum residues to the inlet of the first reactor, means for sending steam and natural gas to the inlet of the second reactor; means for producing a first mixture containing at least carbon monoxide and hydrogen constituting a synthesis gas at the outlet of the first reactor, means for producing at least one second mixture containing at least hydrogen, carbon dioxide and carbon monoxide at the outlet of the second reactor, means for deriving at least one gas containing at least carbon dioxide from the outlet of the second reactor and means for sending at least part of the gas containing at least carbon dioxide to the inlet of the first reactor and possibly to the inlet of the second reactor.

Preferably the first reactor is a partial oxidation reactor, with or without a catalyst bed.

Optionally:

- the means for deriving a gas containing at least carbon dioxide from the outlet of the second reactor include a CO_2 removal unit, such as a washing unit, means for sending a gas from the outlet of the second reactor to the CO_2 removal unit and means for sending at least part of the gas containing carbon dioxide from the CO_2 removal unit to the inlet of the first reactor and optionally to the inlet of the second reactor ;

- the installation comprises means for sending a gas containing at least carbon monoxide and hydrogen from the CO_2 removal unit to the outlet of the first reactor and/or to the synthesis unit ;

- the installation comprises a permeation unit and means for sending a third mixture from the CO_2 removal unit to the permeation unit and means for sending a gas containing hydrogen and carbon monoxide from the permeation unit to the synthesis unit consuming the synthesis gas ;

- the means for deriving a gas containing at least carbon monoxide and hydrogen from the outlet of the second reactor include an adsorption unit and optionally a shift reactor upstream the adsorption unit, means for sending gas from the outlet of the second reactor to the adsorption unit, optionally via the shift reactor and/or via the CO_2 removal unit and the permeation unit, and means for sending a gas containing at least carbon dioxide from the adsorption unit to the inlet of the first reactor and/or of the second reactor ;

- the installation comprises means for sending a gas containing at least hydrogen from the adsorption unit to the outlet of the finishing unit and/or to the synthesis unit ;

- the installation comprises a synthesis unit consuming a mixture of at least carbon monoxide and hydrogen with a hydrogen/carbon monoxide ratio of between 1.8:1 and 3:1, a finishing unit, means for sending fluid from the outlet of the first reactor to the synthesis unit and means for sending fluid from the outlet of the synthesis unit to the finishing unit.

Preferably the gas containing at least hydrogen sent from the adsorption unit to the finishing unit is purer in hydrogen than the gas containing at least hydrogen sent from the adsorption unit to the outlet of the first reactor or to the synthesis unit.

Preferably the hydrogen enriched stream is sent to the finishing unit and a synthesis gas containing an H_2/CO ratio higher than 2/1 is sent to the synthesis unit.

Preferably at least a part of the CO_2 present in this synthesis gas is removed in order to minimise the CO_2 which is sent to the synthesis unit.

In some cases at least two CO_2 rich gases are sent to the first reactor, each being derived from the different means such as a CO_2 removal washing unit and an adsorption unit.

The process consuming a synthesis gas with a hydrogen/carbon monoxide ratio of between 1.8:1 and 3:1 may for example be a process for production of olefins, methanol, synthetic fuel, DME etc..

By adding carbon dioxide to the feed of the first reactor, which may be of the catalytic or non-catalytic partial oxidation type, the equilibrium of the reaction is modified so that the same quantity of carbon monoxide is produced, with less oxygen feed and the ratio of H_2CO is reduced at the outlet of the first reactor.

Thus the quantities of hydrogen and synthesis gas from the first reactor decrease and the capacity of the second reactor is increased to balance the overall hydrogen requirements.

In this way, less oxygen can be used in the first reactor since the CO_2 takes part in the partial oxidation.

The invention will now be described with reference to the accompanying drawings of which :

Figure 1 is a process flow diagram of an integrated process according to the invention using a shift conversion unit and a pressure swing adsorption unit to produce a hydrogen rich stream ;

Figure 2 is a process flow diagram of an integrated process according to the invention using a shift conversion unit, a CO_2 removal unit and a methanation unit, to produce a hydrogen rich stream ;

Figure 3 is a process flow diagram of an integrated process according to the invention using a shift conversion unit, a pressure swing adsorption unit to produce a hydrogen rich stream and a CO_2 removal system to treat part of the second mixture ;

Figure 4 is a process flow diagram of an integrated process according to the invention using a CO_2 removal system, a permeation unit, a permeate recompression unit and a pressure swing adsorption unit to treat at least part of the second mixture.

In Figure 1, natural gas 5 is sent to a first reactor 1 which is the POX type and to a second reactor 2 which is of the SMR type. A gas 3 containing at least 99 mol.% oxygen is also sent to the first reactor 1 to produce a first mixture 11 containing at least hydrogen and carbon monoxide in proportions of less than 1.8 :1 to be sent to a synthesis unit 16. Steam 4 is sent to the second reactor 2.

The second reactor 2 produces a second mixture 12 containing at least carbon monoxide, carbon dioxide and hydrogen. At least part 8 of this mixture is then sent to a shift converter 7 where at least part of the carbon monoxide is converted to hydrogen and the gas 9 produced by the shift unit 7 is sent to an adsorption unit 13 of the PSA type to produce a stream rich in hydrogen 14 and a stream rich in carbon dioxide 15 containing between 40 and 70 mol.% carbon dioxide. Part 38 of the stream rich in carbon dioxide may be sent to the second reactor 2 to serve as unpressurised fuel.

It will be appreciated that it is not absolutely necessary in all cases for the second mixture to undergo shift conversion.

The rest 6 of the second mixture 12 is sent to the synthesis unit 16. Alternatively all the second mixture may be sent to the adsorption step (possibly following shift conversion).

All or part of the hydrogen rich stream 14 is sent to the finishing unit 17.

Part 42 of the stream rich in hydrogen 14 may also be sent to the synthesis unit 16. The products of the synthesis unit 16 are treated in a finishing unit 17 before leaving the installation. All or part of the carbon dioxide rich stream 15 is sent to a compressor 19 where it is compressed to a higher pressure, before being fed to the first reactor 1 as a feed gas and, optionally, as shown in dashed lines, to the second reactor 2. Any remaining portion 38 of the carbon dioxide rich stream may be sent to the second unit 2 as fuel.

It will be appreciated that the first reactor could be of the catalytic or non-catalytic type. It will further be appreciated that streams 11,6 and/or 42 may be sent separately to synthesis unit 16 or may be mixed beforehand.

In Figure 2, natural gas 5 is sent to a first reactor 1, which is of the POX type and/or to a second reactor 2 which is of the SMR type.

A gas 3 containing at least 99 mol.% oxygen is sent to the first reactor 1 to produce a first mixture 11 containing at least hydrogen and carbon monoxide in proportions of less than 1.8 :1 to be sent to the synthesis unit 16, which may be of the Fischer Tropsch type.

Steam 4 is sent to the second reactor 2.

The second reactor 2 produces a second mixture 12 containing at least carbon monoxide, carbon dioxide and hydrogen. Part 6 of the second mixture may be sent directly to synthesis unit 16 without mixing with another gas (in this example). Another part 8 or all of this second mixture is then sent to a shift conversion unit 7, then stream 28 formed in the shift converter is sent to a CO_2 removal unit 18, such as an amine washing unit , to produce a third mixture stream 24 containing carbon monoxide and a stream rich in carbon dioxide 25, preferably containing between 90 and 100 mol.% carbon dioxide.

Other types of CO_2 removal unit 18 may also be envisaged such as a permeation unit or a washing unit employing a washing solution other than an amine solution.

Part of the stream 23 may be sent to the synthesis plan 16.

The rest 24 of the hydrogen rich stream 23 from the CO_2 removal unit 18 is sent to a methanation unit 22 in which the last traces of carbon monoxide and carbon dioxide are removed. This purified hydrogen rich gas is sent to the finishing unit 17 (streams 14) and part of it may be sent to the synthesis unit 16 (stream 42).

All or part of the carbon dioxide rich stream 25 is sent to a compressor 19 where it is compressed to a higher pressure, before being fed to the first reactor 1 and , optionally, as shown in dashed lines to the second reactor 2.

Part 43 of the stream 25 may be removed as a purge stream. The products of the synthesis unit 16 are treated in a finishing unit 17 before leaving the installation.

It will be appreciated that the first reactor 1 could be of the catalytic or non-catalytic type. It will further be appreciated that streams 11,6 and/or 24 and/or 42 may be sent separately to synthesis unit 16 or may be mixed beforehand.

In Figure 3, natural gas 5 is sent to a first reactor which is of the POX type 1 and/or to a second reactor 2 which is of the SMR type. A gas 3 containing at least 99 mol.% oxygen is also sent to the first reactor 1 to produce a first mixture 11 containing at least hydrogen and carbon monoxide in proportions of less than 1.8 :1. Steam 4 is sent to the second reactor 2.

The second reactor 2 produces a second mixture 12 containing at least carbon monoxide, carbon dioxide and hydrogen. Part 6 of this mixture may or may not then be sent to a shift conversion unit 7 integrated within the second reactor 2 where at least part of the carbon monoxide is converted to hydrogen and the gas 9 produced by the shift unit is sent to an adsorption unit 13 of the PSA type to produce a stream rich in hydrogen 14 and a stream rich in carbon dioxide 15 containing between 40 and 70 mol.% carbon dioxide. The stream rich in carbon dioxide may be sent totally or in part (41) to the second reactor 2 as fuel or may be totally or in part (25 in dashed lines) recycled to the inlet of the first reactor 1 as previously described.

At least a part 28 of the second mixture is sent to a carbon dioxide removal unit 18, such as a washing unit, which produces a further stream rich in carbon dioxide 35 and a third mixture containing hydrogen and carbon monoxide 34. The other part 36, if there is one, is directly sent to the synthesis unit 16. The stream rich in carbon dioxide 35 is partially or totally compressed in 19 and returned to the inlet of the first reactor 1 and possibly of the second reactor 2. The third mixture containing hydrogen and carbon monoxide 34 is sent to the unit 16. Part 43 of the stream 35 may be removed as a purge stream.

The stream rich in hydrogen 14 from the PSA unit 13 is fed to the finishing unit 17 and possibly sent directly to the synthesis unit 16 as stream 42.

The products of the synthesis plant 16 are treated in a finishing plant 17 before leaving the installation.

It will be appreciated that the first reactor could be of the catalytic or non-catalytic type. It will further be appreciated that streams 11 and/or 34 and/or 36 and/or and/or 42 may be sent separately to synthesis unit 16 or may be mixed beforehand.

In Figure 4, natural gas 5 is sent to a first reactor 1 which is of the POX type and/or to a second reactor 2 which is of the SMR type. A gas 3 containing at least 99 mol.% oxygen is also sent to the first reactor 1 to produce a first mixture 11 containing at least hydrogen and carbon monoxide in proportions of less than 1.8 :1. Steam 4 is sent to the second reactor 2.

The second reactor 2 produces a second mixture 12 containing at least carbon monoxide, carbon dioxide and hydrogen.

Part of the second mixture is sent to a carbon dioxide removal unit 18, such as a washing unit, which produces a stream rich in carbon dioxide 145 and a third mixture containing hydrogen and carbon monoxide. The rest 49 of the second mixture may be sent to the synthesis unit 16. Alternatively all the second mixture may be sent to the carbon dioxide removal step 18.

Part of the stream rich in carbon dioxide 145 is compressed in 19 and returned to the inlet of the first reactor 1 and possibly to the second reactor. The other part of the stream 145 may be removed as a purge stream 43.

Part of the third mixture containing hydrogen and carbon monoxide is sent to a permeation unit 43 in which a selective membrane separates the mixture to produce a fourth mixture stream 47 containing hydrogen and carbon monoxide, which is hydrogen depleted and a stream 46 containing hydrogen and carbon monoxide, which is hydrogen enriched. The other part 24 of the third mixture is sent to the synthesis unit 16.

The hydrogen depleted stream 47 is sent to the synthesis reactor 16.

The hydrogen enriched stream 46 is compressed in compressor 45 and sent to an adsorption unit 13 which produces a hydrogen rich stream 14 and a CO_2 rich stream which may be recycled (as stream 15 in dashed lines) to the carbon dioxide compressor 19 and/or as sent as fuel 41 to the second reactor.

The stream rich in hydrogen 14 is sent to the finishing unit 17 and/or to the synthesis unit 16 (as stream 42).

The products produced by the synthesis plant 16 are sent to a finishing plan 17 before leaving the installation.

It is to be noted that this embodiment does not involve a shift conversion step.

It will be appreciated that the first reactor could be of the catalytic or non-catalytic type. It will further be appreciated that streams 11 and/or 24 and/or 42 and/or 47 and/or 49 may be sent separately to synthesis unit 16 or may be mixed beforehand.

- In all the figures, the first mixture has a hydrogen/carbon monoxide ratio of less than 1,8 :1 ,preferably less than 1,7 :1. For all the figures, oxygen is supplied via an air separation unit wherein liquid oxygen is pumped to the operating pressure of the first reactor, vaporised and supplied to the first reactor as pressurised gas. No air is supplied to the first reactor in any case.

Claims

1. Process for the production of at least one synthesis gas for a synthesis unit (16) consuming a mixture of at least carbon monoxide and hydrogen with a global hydrogen/carbon monoxide ratio between 1.8:1 and 3:1 comprising :

a) sending oxygen having a concentration of at least 99 mol. % and at least one of natural gas, coal and/petroleum residues (5) to a first reactor (1) which is a partial oxidation unit to produce a first mixture (11) of at least carbon monoxide and hydrogen,

b) sending steam and at least one of natural gas and another mixture of light hydrocarbons (5) to a second reactor (2) which is a steam methane reformer to produce at least one second mixture (12) containing at least hydrogen, carbon dioxide and carbon monoxide,

c) sending at least part of the first mixture to form a synthesis gas to be sent to the synthesis unit (16) and,

d) deriving at least one gas containing at least 40 mol.% carbon dioxide (15, 25, 35, 145) from at least part (8) of the at least one second mixture (12) and sending at least part of the gas containing at least 40 mol.% carbon dioxide to an inlet of the first reactor.

2. Process according to Claim 1 comprising sending at least 99 mol.% oxygen to the inlet of the first reactor (1) from a cryogenic air separation unit in which liquid oxygen is removed from a column of the air separation unit, pumped to an operating pressure of the first reactor, vaporised and sent as pressurised gas to the inlet of the first reactor or gaseous oxygen is removed from a column of the air separation unit, compressed to an operating pressure of the first reactor and sent to the first reactor.

3. Process according to Claim 1 or 2 wherein the first mixture has a hydrogen :carbon monoxide ratio of less than 1.8:1

4. Process according to Claim 1, 2 or 3 comprising treating at least part of the second mixture (12) to form at least one stream (15, 25, 35, 145) containing at least 40 mol.% carbon dioxide and a stream (14) enriched in hydrogen and possibly a synthesis gas (6, 24, 34, 36, 47, 49) with an H_2/CO ratio higher than 2/1.

5. Process according to Claim 4 comprising sending at least part (42) of the stream enriched in hydrogen to the synthesis unit (16).

6. Process according to Claim 4 or 5 comprising sending at least part of the stream (14) enriched in hydrogen to a finishing unit (17).

7. Process according to Claim 4, 5 or 6 comprising sending at least part (6, 29, 36, 49) of second mixture (12) to the synthesis unit (16).

8. Process according to Claim 4, 5, 6 or 7 comprising producing a hydrogen enriched gas and at least part of the gas containing at least 40 mol.% carbon dioxide from the second mixture using pressure swing adsorption (13) and possibly shift conversion (7).

9. Process according to Claim 4, 5, 6, 7 or 8 comprising producing a hydrogen enriched gas from the second mixture (12) and at least part of the gas containing at least 40 mol. % carbon dioxide using CO_2 removal (13, 18) and possibly a methanation process.

10. Process according to any preceding claim wherein the CO_2 removal unit (13, 18) is a washing unit, an adsorption unit or a permeation unit.

11. Process according to Claim 9 or 10 comprising sending a gas containing at least carbon monoxide and hydrogen (23, 24, 34, 42) from the CO_2 removal unit (13, 18) to the synthesis unit (16) and/or to a methanation unit (22) and/or to a permeation unit (43).

12. Process according to Claim 11 comprising sending a gas containing at least carbon monoxide and hydrogen from the $C0_2$ removal unit (13, 18) to a permeation unit (43), said gas constituting a third mixture, and sending a hydrogen enriched gas (46) from the permeation unit to an adsorption unit (13) and/or a hydrogen depleted gas (47) to the synthesis unit (16).

13. Process according to Claim 12 comprising sending part (24) of the third mixture to the synthesis unit (16).

14. Process according to Claim 11, 12 or 13 comprising sending at least part of the gas containing carbon monoxide and hydrogen from the CO_2 removal unit (13, 18) to a permeation unit (43) and sending a fourth mixture (47) depleted in hydrogen from the permeation unit to the synthesis unit (16).

15. Process according to any preceding claim wherein the first reactor (1) is a catalytic or non-catalytic partial oxidation reactor.

16. Process according to any preceding claim wherein the first reactor (1) is not fed by an air stream and the second reactor (2) is not fed by an oxygen enriched stream.

17. Installation for the production of at least one synthesis gas for a process taking place within a synthesis unit (16) consuming a mixture of at least carbon monoxide and hydrogen with a hydrogen/carbon monoxide ratio of between 1.8:1 and 3:1 comprising: first and second reactors (1, 2), said first reactor being a partial oxidation unit and said second reactor being a steam methane reformer each having a respective inlet and outlet, means for sending oxygen having a concentration of at least 99 mol. % to the inlet of the first reactor, means for sending at least one of natural gas, coal and petroleum residues (5) to the inlet of the first reactor, means for sending steam and natural gas (5) to the inlet of the second reactor, means for producing a first mixture (11) containing at least carbon monoxide and hydrogen constituting a synthesis gas at the outlet of the first reactor, means for producing at least one second mixture (12) containing at least hydrogen, carbon dioxide and carbon monoxide at the outlet of the second reactor, means (7, 13, 18) for deriving at least one gas containing at least carbon dioxide from the outlet of the second reactor and means (19) for sending at least part of the at least one gas containing carbon dioxide to the inlet of the first reactor and possibly to an inlet of the second reactor.

18. Installation according to Claim 17 wherein said means comprising a cryogenic air separation unit, means for removing liquid oxygen from a column of the air separation unit, means for pumping the liquid oxygen to an operating pressure of the first reactor , means for vaporising the pumped liquid and means for sending the pressurised gas thus produced to the inlet of the first reactor, there being no means for sending air to the inlet of the first reactor.

19. Installation according to Claim 17 or 18 wherein the first reactor (1) is a partial oxidation reactor, including or without a catalyst bed.

20. Installation according to one of Claims 17, 18 or 19 wherein the means for deriving a gas containing at least carbon dioxide (15, 25, 35, 145) from the outlet of the second reactor (2) include a CO_2 removal unit (13, 18), means for sending a gas (9, 12, 28) from the outlet of the second reactor to the CO_2 removal unit and means for sending at least part of the gas containing at least carbon dioxide from the CO_2 removal unit to the inlet of the first reactor (1).

21. Installation according to Claim 20 comprising means for sending a gas (24, 34, 42) containing at least carbon monoxide and hydrogen from the CO_2 removal unit (13, 18) to the outlet of the first reactor (1) and/or to the synthesis unit (16).

22. Installation according to Claim 20 or 21 comprising a permeation unit (43) and means for sending a third mixture from the CO_2 removal unit (18) to the

permeation unit and means for sending a gas (47) containing hydrogen and carbon monoxide from the permeation unit (43) to the synthesis unit (16).

23. Installation according to one of Claims 17 to 22 wherein the means for deriving a gas (15) containing at least carbon dioxide from the outlet of the second reactor include an adsorption unit (13) and optionally a shift reactor (7) upstream the adsorption unit, means for sending gas from the outlet of the second reactor (2) to the adsorption unit, optionally via the shift reactor and/or via the CO_2 removal unit (18) and the permeation unit (43), and means (19) for sending a gas containing at least carbon dioxide from the adsorption unit to the inlet of the first reactor (1).

24. Installation according to Claim 23 comprising means for sending a gas containing at least hydrogen from the adsorption unit (13) to the synthesis unit (16).

25. Installation according to one of Claims 23 or 24 comprising a synthesis unit (16) consuming a mixture of at least carbon monoxide and hydrogen with a hydrogen/carbon monoxide ratio of between 1.8:1 and 3:1, a finishing unit (17), means for sending gas from the outlet of the first reactor (1) to the synthesis unit, means for sending gas from the outlet of the synthesis unit to the finishing unit and means for sending a gas (14) containing at least hydrogen from the adsorption unit or a methanation unit (22) to the finishing unit.

26. Installation according to Claim 25 wherein the gas containing at least hydrogen sent from the adsorption unit (13) to the finishing unit (17) is purer in hydrogen than the gas containing at least hydrogen sent from the adsorption unit (13) to the outlet of the first reactor or to the synthesis unit (16).

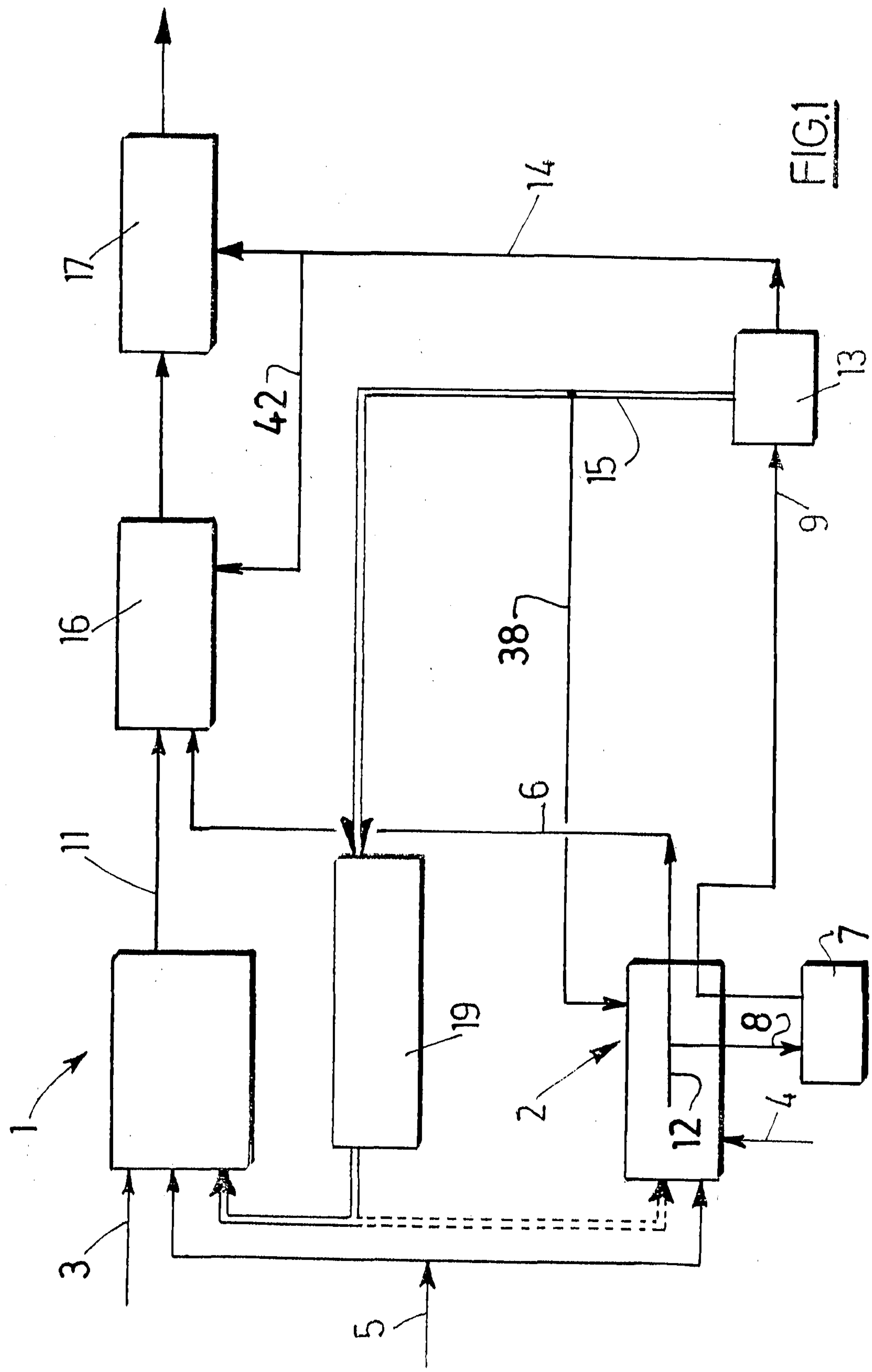

FIG.1

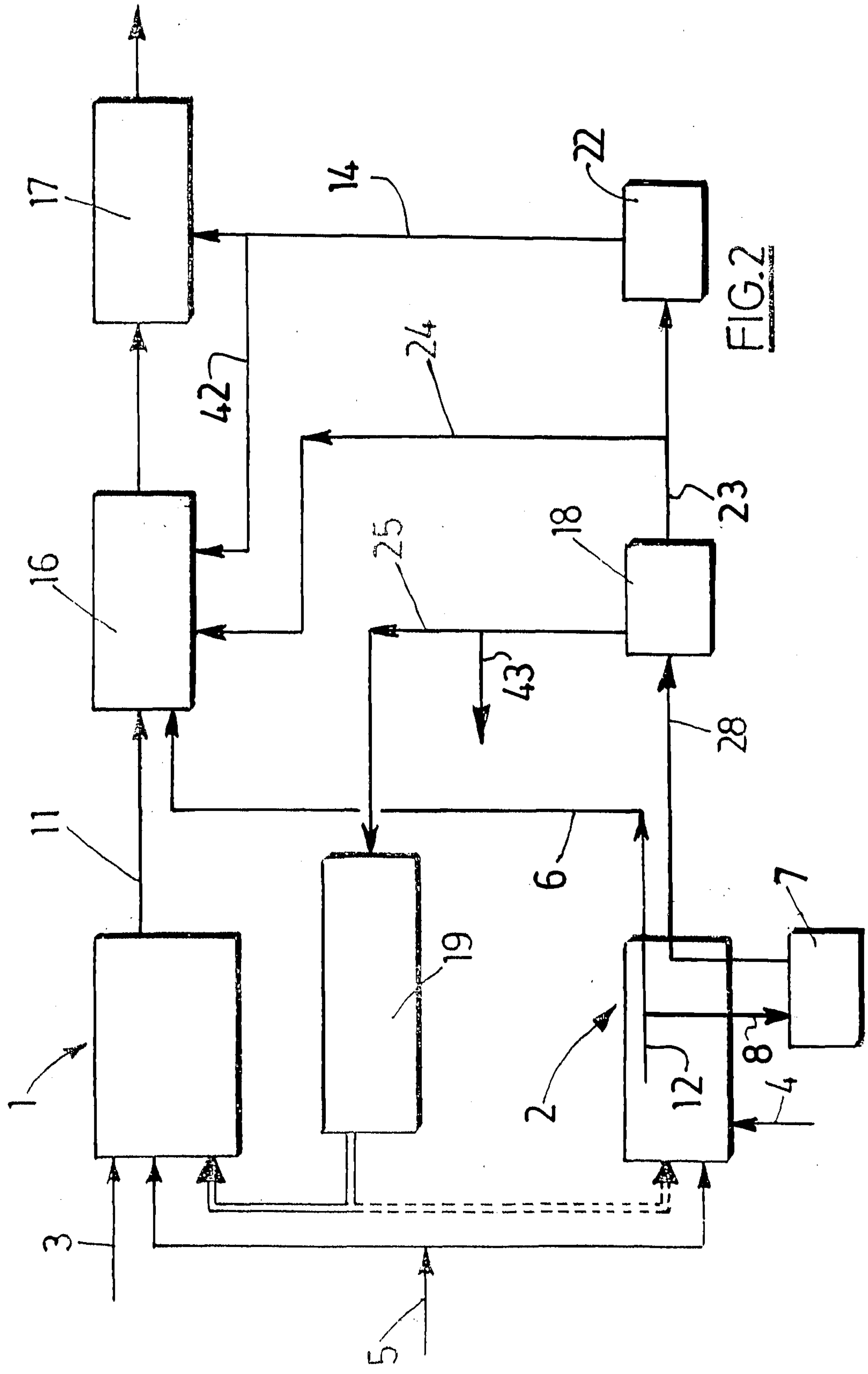

FIG.2

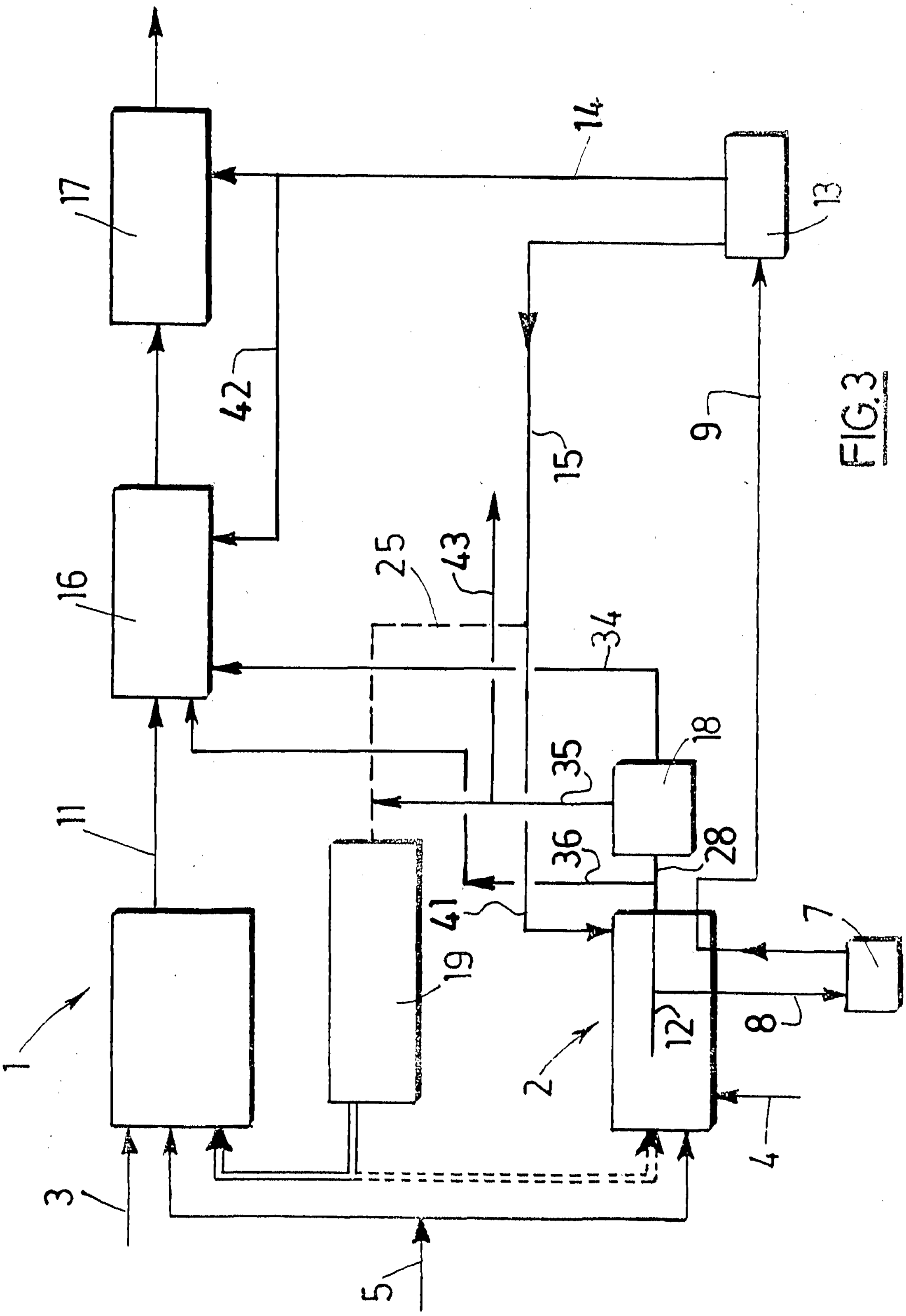

FIG.3

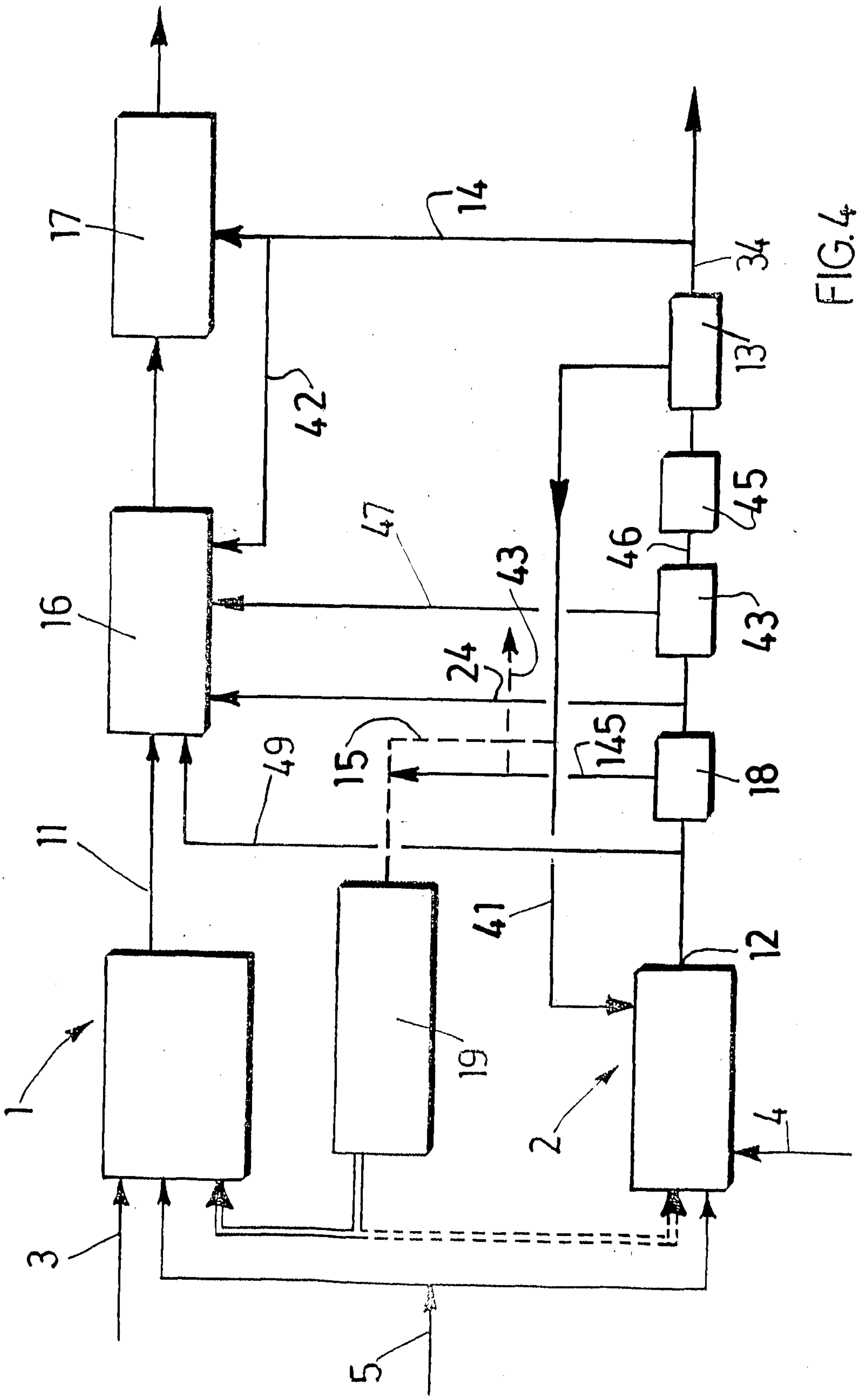

FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 01/02615

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B3/38 C01B3/36 C01B3/56 C01B3/50 C01B3/48
C10G2/00 F25J3/04

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 7 C01B C10G F25J

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)

WPI Data, PAJ, INSPEC, COMPENDEX, EPO-Internal, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 58242 A (SYNTROLEUM CORP) 5 October 2000 (2000-10-05) page 7, line 22 -page 11, line 22 page 14, line 7 -page 15, line 12 figures	1-26
A	EP 0 930 268 A (AIR PROD & CHEM) 21 July 1999 (1999-07-21) page 4, line 53 -page 5, line 11	1,2,17, 18
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 March 2002	04/04/2002

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 01/02615

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 522 744 A (ICI PLC) 13 January 1993 (1993-01-13) page 10, line 43 -page 19, line 48 figures 1,2 ---	1,17
A	EP 0 212 758 A (SHELL INT RESEARCH) 4 March 1987 (1987-03-04) column 3, line 10 -column 4, line 20 figures -----	1,17

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Information on patent family members

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