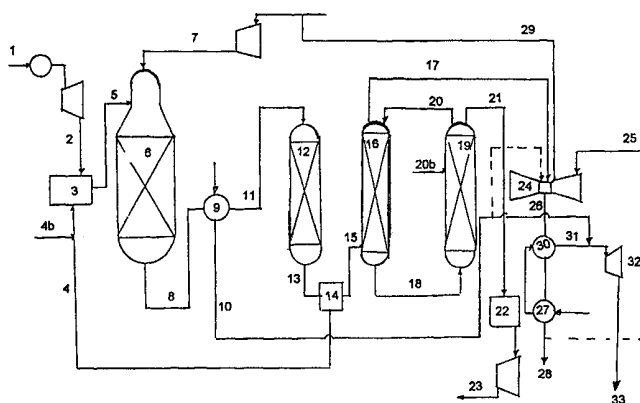




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/NO98/00213</p> <p>(22) International Filing Date: 13 July 1998 (13.07.98)</p> <p>(71) Applicant (for all designated States except US): NORSK HYDRO ASA [NO/NO]; N-0240 Oslo (NO).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): FJELLHAUG, Henrik, O. [NO/NO]; Tyrihansv. 26, N-1370 Asker (NO). NILSEN, Henning, Reier [NO/NO]; Elveveien, N-3400 Lier (NO). SOYEZ, Werner [DE/BE]; Schuitenlaan 6, B-3080 Vossem (BE). SAIGNE, Michel [FR/BE]; Avenue Astrid 32, B-1640 Rhode-St.-Genese (BE).</p> <p>(74) Agent: SUNDNES, Arne; Norsk Hydro ASA, N-0240 Oslo (NO).</p>		<p>(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, GM, HR, HU, ID, 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, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, 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), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report.</p>

(54) Title: PROCESS FOR GENERATING ELECTRIC ENERGY, STEAM AND CARBON DIOXIDE FROM HYDROCARBON FEEDSTOCK



## (57) Abstract

The present invention relates to a process for production of electric energy, steam and carbon dioxide in concentrated form from a hydrocarbon feedstock comprising formation of synthesis gas in an air driven autothermal thermal reactor unit (ATR), heat exchanging the formed synthesis gas and thereby producing steam, treating at least part of the synthesis gas in a CO-shift reactor unit and carbon dioxide separation unit for formation of concentrated carbon dioxide and a lean hydrogen containing gas which combusted in a combined cycle gas turbine for production of electric energy, and where air from said turbine unit is supplied to the ATR unit. The exhaust from the gas turbine is heat exchanged for production of steam which together with steam generated upstream is utilized in a steam turbine for production of substantially CO<sub>2</sub>-free electric energy. Steam may be fed to the gas turbine for diluting the hydrogen containing gas mixture. The process may also be combined with production of synthesis gas products such as methanol and/or ammonia. Part of the gas from the carbon dioxide removal unit may be utilized in a fuel cell.

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## **Process for generating electric energy, steam and carbon dioxide from hydrocarbon feedstock**

The invention relates to a process comprising production of electric energy, steam and carbon dioxide in concentrated form from a hydrocarbon feedstock. The invention further comprises optional production of synthesis gas based products combined with said process.

The electric energy is produced in a combined cycle power plant integrated with the reforming plant where the gas turbine is fuelled by the hydrogen containing gas. (Integrated Reforming Combined Cycle (IRCC)). A major problem in such a process is to operate the gas turbine at conditions giving minimum nitrogen oxide emission and simultaneously achieving optimal electric energy and steam production.

A process for producing electric power, steam and concentrated carbon dioxide is published on Internet, <http://www.hydro.com/konsern/news/eng/1998/980423e.html>. In this publication there is described a process comprising reacting natural gas with steam subsequently resulting in a hydrogen containing gas which is combusted in a combined cycle gas turbine producing electric power.

From Japanese patent application JP 608041 it is further known to apply a hydrogen fired turbine for production of electric energy. According to this application natural gas and oxygen in a mol ratio 1:0.5 to 1:0.7 is reacted by partially oxidizing said fuel to generate hydrogen and carbon monoxide. Air is supplied to a pressure swing

absorption oxygen separator (PSA) and the oxygen is then delivered to an autothermal reactor (ATR) where the natural gas is transformed to hydrogen and carbon monoxide. The reformed gas enters a shift reactor in which the carbon monoxide is converted to carbon dioxide. The gas mixture is then introduced into a membrane separator in which hydrogen is separated from the carbon dioxide. The separated  $\text{CO}_2$  is washed-out and desorbed later on. The hydrogen substantially free from carbon compounds is used in a gas turbine for generating electric power. This process requires oxygen, demanding a power consuming PSA unit. According to the application flow sheet the natural gas must be decompressed nearly to ambient pressure to permit addition of oxygen. After the PSA separation the oxygen must be compressed a second time. All these extra compressions reduce the efficiency of the process.

The main object of the invention is to provide an improved process for generating power using steam reforming of a hydrocarbon feedstock, in which a substantial part of the generated  $\text{CO}_2$  is separated as a highly concentrated  $\text{CO}_2$ -gas stream and where the emission of nitrogen oxides is within acceptable levels for conventional gas turbines.

Another object of the invention is to utilise at least part of the formed synthesis gas of said power generating process for production of synthesis gas products, especially ammonia, methanol and/or dimethylether.

With regard to electric energy generation, the present process will compete with conventional power plants based on combustion of hydrocarbon feedstock, such as natural gas. However, one major disadvantage of simply combusting hydrocarbons is the emission of carbon dioxide as the exhaust from the combustion only contain

minor amounts of carbon dioxide which at present can not be recovered economically. The emission of nitrogen oxides (NOX) which varies depending on operating conditions may also constitute an emission problem.

A major problem when reducing the emission of carbon dioxide and NOX is to obtain the desired emission reduction without unacceptable reduction of efficiency of the process with regard to power generation. The first step in evaluating the basic process in view of the above requirements was the synthesis gas production step. Having considered various methods the inventors found that an ATR would give several advantages and it was decided to investigate further the best way of running the ATR. Contrary to that taught by the above Japanese patent application it was found that the ATR should be an air driven reactor, i.e. not an oxygen driven reactor. Application of ATR seemed to offer several advantages in terms of degrees of freedom. Thus operating pressure could be chosen in view of the overall economy of the concept. The methane slip could be varied in view of operation of downstream units and finally the synthesis gas produced in the ATR would be a relatively lean gas suitable for the gas driven turbine and comparable to fuel mixtures being used in proven, large scale combined cycle plants (IRCC).

Useful hydrocarbon feedstock for such a process will be natural gas, nafta, various petroleum distillates etc. By applying a pre-reformer ahead of the ATR the flexibility with regard to feedstock will be fairly great. Preferred feedstock will be natural gas.

The NOX problem was found to be strongly related to operating conditions of the gas turbine. The NOX-formation is correlated to the flame temperature in this turbine. Accordingly provisions for regulating said flame temperature should be made. The range of gas mixture to be combusted in said turbine could be selected through design of the process in order to keep the flame temperature at a desired level and

still maintain an acceptable power generation. The flame temperature in the turbine is largely determined by the composition of the fuel gas. It was found that an air-driven ATR would provide a lean hydrogen based fuel gas mixture compatible to gases being used in IGCC-plants. It was found advantageous to extract process air for the ATR at the discharge of the gas turbine's air compressor and boost to the required ATR-injection pressure. Further, the air flow could be adjusted to meet the agreeable level of methane slip, and the composition of the fuel-gas mixture compatible with acceptable level of NOX-formation in the gas turbine combustion system. The nitrogen extracted with the air from the gas turbine is returned to the turbine part as a component of the fuel gas mixture, thus largely maintaining the turbine mass flow.

If need be, moderate steam injection can be applied to reduce the NOX-formation in the turbine. Optimal design of the burner design can also reduce the NOX-emission.

One alternative within the concept of the invention is to combine the ATR with a reformer exchanger. It was found that this option could increase the recovery of CO<sub>2</sub> in concentrated form.

In order to obtain maximum flexibility, the basic power generating concept could be combined with production of various products based on the existing process streams. Thus a methanol unit could utilize some of the synthesis gas from the ATR and an ammonia plant could utilize some of the hydrogen/nitrogen gas separated from the carbon dioxide subsequent to the shift reaction of the synthesis gas. The only extra units required for the ammonia plant would be a conventional membrane separation unit and a methanator upstream the ammonia synthesis reactor.

The scope of the invention comprises formation of synthesis gas in an air driven ATR unit, heat exchanging the formed synthesis gas and thereby producing steam. At least part of the cooled synthesis gas is then treated in a CO-shift reactor, which may be one single unit or two CO-shift reactors, one low temperature and one high temperature reactors. Said gas stream is further treated in a carbon dioxide unit for formation of a concentrated stream of carbon dioxide and one stream being a lean hydrogen containing gas which at least partly is combusted in a combined cycle gas turbine for production of electric energy. Air from said turbine is supplied to the ATR unit. The exhaust from the gas turbine is heat exchanged for production of steam which together with steam generated upstream is utilized in a steam turbine for production of electric energy.

The ATR unit can be combined with a reformer exchanger and the feedstock can be split between these two units, preferably 50-80% of the feedstock is fed to the ATR.

A pre-reformer can be arranged upstream the ATR unit.

A minor part of the steam generated in the process can be fed to the gas turbine for diluting the hydrogen containing gas and thereby lowering the flame temperature in the gas turbine.

At least part of the exhaust from the gas turbine can be recycled to the ATR as oxygen source or combined with the air supply to the gas turbine.

Part of the synthesis gas can be utilized for methanol production and this production can be performed in various ways as described above in connection with figure 1.

Part of the gas from the carbon dioxide separation unit can be utilized for ammonia production. In that case one stream is fed to a membrane separation unit for separating out hydrogen which is mixed with another hydrogen containing gas stream whereby the mixed stream will have a nitrogen:hydrogen ratio of 1:3. The nitrogen from the membrane unit is returned to the main hydrogen containing gas stream subsequently fed to the gas turbine.

The invention will be further explained and elucidated in connection with the examples and the description of the attached figures.

Figure 1 shows a simplified flow sheet of the basic power generating concept.

Figure 2 shows a simplified flow sheet of the basic concept combined with a methanol plant and/or an ammonia plant.

Figure 1 shows an example for performing the invention. Gaseous hydrocarbon feedstock, for instance natural gas, is supplied as stream 1, heated and compressed before it through conduit 2 is conducted to a saturator 3 where it is mixed with process water 4 and demineralised make up water supplied through line 4b. The hydrocarbon feed which is at least partly saturated with water is then fed to the ATR unit 6 as stream 5. Compressed air is supplied through conduit 7 to the ATR unit 6. Optionally a pre-reformer may be arranged upstream the ATR. This will give increased flexibility with regard to hydrocarbon feedstock. Increased content of heavier hydrocarbons can then be accepted. At least part of the air supply 29 can be supplied from the gas turbine air compressor and boosted to necessary injection pressure. The unit 6 can also be a combined unit comprising an ATR and a reformer exchanger. How much of the hydrocarbon feedstock shall be fed to the respective



units can be varied within wide limits. A practical split will be 50-80% of the feedstock to the ATR and the remaining part to the reformer exchanger. The synthesis gas 8 from the ATR unit 6 is cooled in a boiler (steam generator) 9 before being supplied to a shift converter unit 12 as stream 11. This unit may comprise two conventional CO-shift reactors, a low temperature (LT) reactor and a high temperature (HT) reactor, or just one single CO-shift reactor. The resulting gas mixture 13 is cooled, condensed water is removed in unit 14 and the resulting gas mixture is then supplied as stream 15 to a CO<sub>2</sub> absorber 16 from which the CO<sub>2</sub> and absorbent is supplied through conduit 18 to a desorber 19. Make up absorbent can be supplied to unit 19 as stream 20b. The regenerated absorbent, for instance an amine solution, is recycled to the absorber 16 through conduit 20. Water is removed in unit 22 from the CO<sub>2</sub> stream 21. The process water from the units 22 and 14 are recycled to the saturator 3. The highly concentrated CO<sub>2</sub> stream can then be compressed and delivered through line 23 for further use, for instance as injection gas in an oil or gas field. The gas stream 17 from the CO<sub>2</sub> absorber 16 consists mainly of hydrogen and nitrogen, with minor amounts of CO, CO<sub>2</sub>, CH<sub>4</sub>. This stream 17 will then be used as fuel for a combined cycle gas turbine 24 to which air 25 is supplied. Optionally steam 10 can be supplied to the turbine 24 for NOX-abatement. At least part of the stream 17 can be utilized in a fuel cell for generating direct current electric power. If the electric power shall be used for electrolysis there will be no need for a rectifier with this optional electric power generation. The exhaust 26 from the turbine 24 is heat exchanged with water in a steam generator 27 and the steam therefrom may be superheated in heat exchanger 30 before the stream 31 is supplied to a power generator 32 to which also steam 10 may be supplied. The exhaust 28 may be recycled to the reformer unit 6 or combined with the air supply 25 to the gas turbine 24.

In figure 2 an ammonia plant and a methanol plant are integrated in the basic process according to figure 1. The combined process may comprise both of said plants or one of them. Synthesis gas 34 can be taken from stream 11 and supplied to a methanol synthesis 35. Unconverted synthesis gas 37 can be recycled to the synthesis gas stream 11 and product methanol is drawn off through conduit 36. The synthesis gas 34 may alternatively be treated in a gas separation membrane unit for removing hydrogen and carbon dioxide for feed to the methanol synthesis. This feed may be supplied with additional carbon dioxide from stream 23. The other fraction from said membrane unit will then be recycled to stream 11.

Feed for an ammonia synthesis may be drawn from line 17. One side stream 38 is first fed to a membrane gas separation unit 40 for supplying hydrogen 42 to line 39 for adjusting the  $H_2 : N_2$  ratio to 3:1 before this gas mixture is treated in a methanation unit 43 prior to the ammonia synthesis 44 producing ammonia 45. Nitrogen from the membrane unit 40 is recycled through line 41 to the feed 17 for the hydrogen turbine 24.

### Example 1

This example shows the effect of the present invention with regard to electric power production, efficiency and recovery of carbon dioxide as a concentrated stream in a process within figure 1. The example further shows the efficiency, recovery of concentrated carbon dioxide and total power production of the process compared to the same for a process applying a primary-secondary reformer for production of synthesis gas. This illustrative example shows the effects of exhaust recycle to the ATR and it also shows the effects of combining the ATR with a reformer exchanger. In the following table said combination is ATR-RE. The process according to the invention is compared with utilization of a combination of a secondary-primary

reformer for producing the synthesis gas, SR/PR in the table. The molar steam : carbon ratio in the feed to the reformer unit is stated as Steam:C in the table.

Table 1

	ATR Basis Two CO-shift	ATR Basis One CO-shift	ATR Exhaust gas recycle No cooling	ATR Exh. gas recycle Cooling 30°C	ATR Exh. gas recycle No cooling Reduced process steam	ATR-RE	SR/PR Two CO-shift
Natural gas. LVH(MW)	823.2	823.2	823.2	823.2	823.2	823.2	882.71
Steam:C	2.0:1	2.0:1	2.6:1	2.6:1	2.0:1	3.2:1	2.8:1
Gas. comp. Turb. fuel:							
CH <sub>4</sub>	0.0175	0.0173	0.0095	0.017	0.0109	0.0023	0.0328
CO	0.0052	0.0118	0.0024	0.0028	0.0039	0.0034	0.0038
CO <sub>2</sub>	0.0006	0.0006	0.0005	0.0005	0.0005	0.0007	0.001
H <sub>2</sub>	0.5611	0.5476	0.4216	0.4015	0.4282	0.6272	0.7697
N <sub>2</sub>	0.4106	0.4055	0.5592	0.5713	0.5757	0.3621	0.1846
Ar	0.0049	0.0048	0.0067	0.0069	0.0069	0.0043	0.0021
Gas flow kmol/hr.	17.176	17.390	23.648	23.148	22.971	17.641	15.520
Power.MW gas turbine	287.42	287.87	298.82	295.25	298.39	302.03	289.77
Power.MW Steam	139.54	137.9	143.64	135.28	154.38	113.10	149.11
Power.MW Exp.comp.	4.34	4.34	4.34	4.34	4.34	4.34	4.46
Power.MW Air compr.	33.82	33.82	80.66	61.12	80.64	30.61	12.55
Total power. MW	397.48	396.29	366.14	373.75	376.47	388.86	430.79
Efficiency %	48.3	48.1	44.5	45.4	45.7	46.9	48.8
CO <sub>2</sub> recovery %	88.8	85.7	91.7	87.3	90.3	95.8	84.5

From the above results it can be seen that the process according to the invention can recover as much as 95.8 % of the CO<sub>2</sub> produced. The results further shows that within the inventive concept the efficiency, power production and CO<sub>2</sub> varies depending upon operating conditions and that the process have great flexibility. NOX-formation will generally be a function of the hydrogen % in the gas fed to the gas turbine.

The present invention provides a process producing clean carbon dioxide suitable as driving gas for injection in oil reservoirs. The IRCC-plant will thus operate with minimal emission of carbon dioxide. Further, the process provides a lean combustion fuel gas mixture based on hydrogen, suitable for combustion in current gas turbines technology . Moderate dilution with steam of the gas mixture fed to the gas turbine can be applied as the only NOX- abatement required.

### Claims

1. A process for production of electric energy, steam and carbon dioxide in concentrated form from a hydrocarbon feedstock comprising formation of synthesis gas in an air driven autothermal thermal reactor unit (ATR), heat exchanging the formed synthesis gas and thereby producing steam, treating at least part of the synthesis gas in a CO-shift reactor unit and carbon dioxide separation unit for formation of concentrated carbon dioxide and a lean hydrogen containing gas which at least partly is combusted in a combined cycle gas turbine for production of electric energy, and where air from said turbine unit is supplied to the ATR unit, that the exhaust from the gas turbine is heat exchanged for production of steam which together with steam generated upstream is utilized in a steam turbine for production of substantially CO<sub>2</sub>- free electric energy.
2. A process according to claim 1, comprising utilization of a reformer unit comprising an ATR combined with a reformer exchanger.
3. A process according to claim 1, comprising that 50-80 % of the hydrocarbon feedstock is supplied to the ATR and the remaining feedstock to the reformer exchanger.
4. A process according to claim 1, comprising utilization of a pre-reformer ahead of the ATR unit.

5. A process according to claim 1, comprising utilization of a single CO-shift reactor unit.
6. A process according to claim 1, comprising feeding steam to the gas turbine for diluting the hydrogen containing gas mixture.
7. A process according to claim 1, comprising recycling of exhaust gas from the gas turbine to the ATR unit.
8. A process according to claim 1, comprising combining at least part of the exhaust from the gas turbine with the air supply to said turbine.
9. A process according to claim 1, comprising utilization of part of the synthesis gas for production of methanol and that the remaining synthesis gas is further treated in the downstream units before utilization for electric energy production.
10. A process according to claim 1, comprising utilization of part of the hydrogen containing gas from the carbon dioxide removal unit for production of ammonia comprising separating said gas in a membrane unit for adjusting the nitrogen :hydrogen ratio to ammonia conditions and returning separated nitrogen to the main hydrogen containing gas stream, and where the stream containing nitrogen:hydrogen in a ratio of 1:3 is treated in a methanator unit prior to the ammonia synthesis.
11. A process according to claim 1, comprising feeding part of the hydrogen containing gas from the carbon dioxide removal unit for utilization as fuel for a fuel cell producing electric energy.

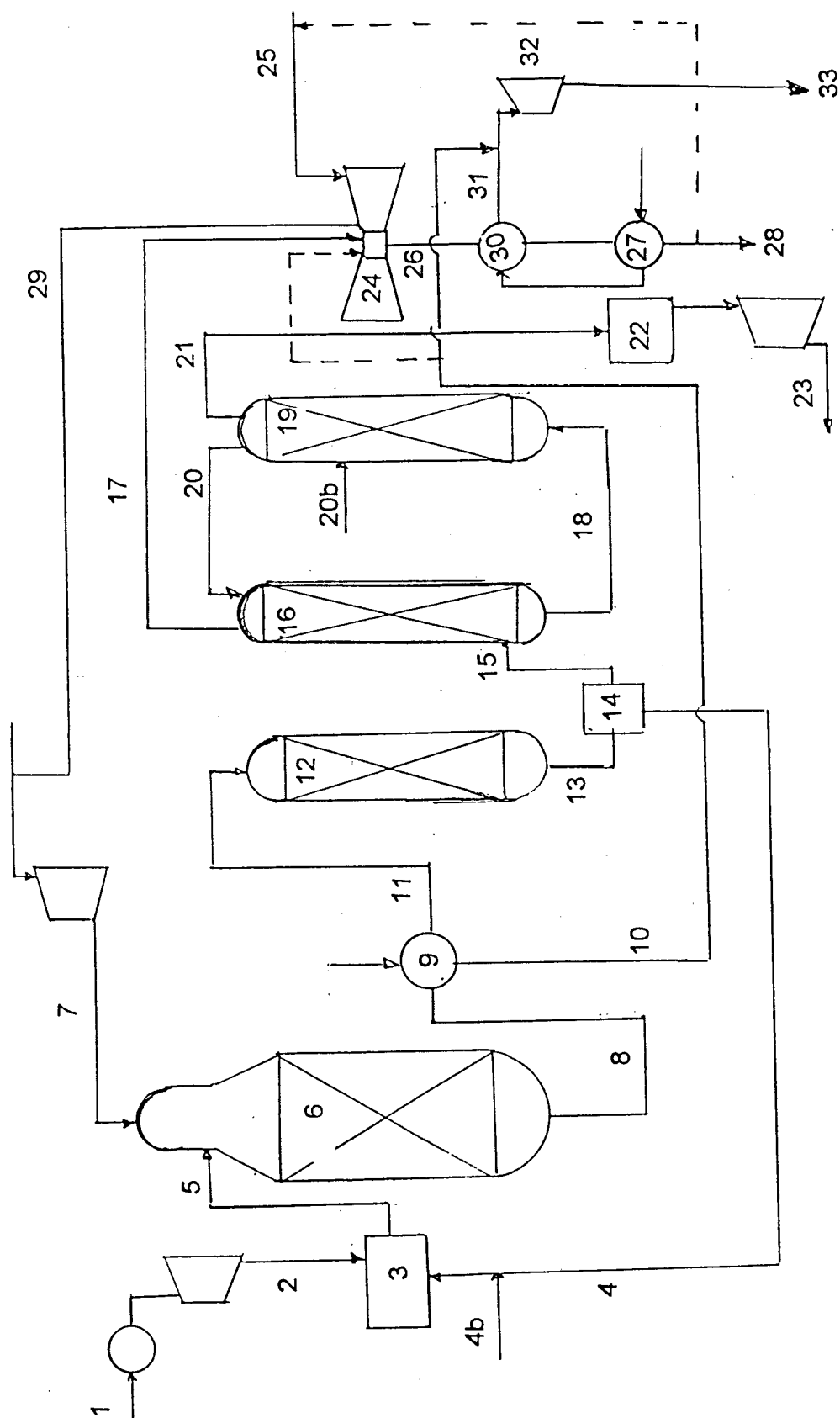


Fig. 1

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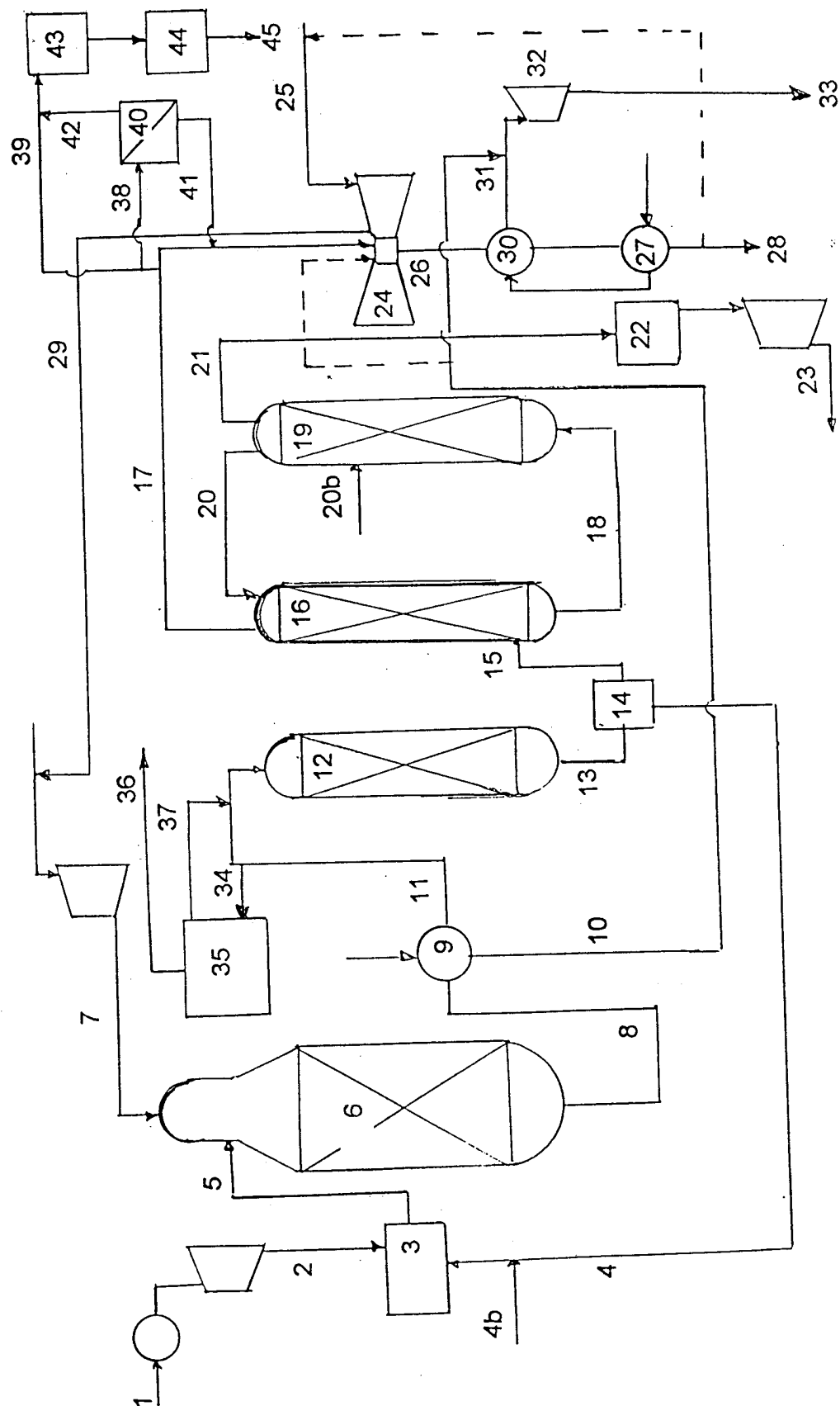


Fig. 2



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 98/00213

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: F01K 23/10 // C01B 3/36, F02C 6/18

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)

IPC6: C01B, F01K, F02C

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

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

WPI, EDOC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9801514 A1 (SYNTROLEUM CORPORATION), 15 January 1998 (15.01.98)  -- -----	1-8

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9801514 A1	15/01/98	AU 3601297 A	02/02/98
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