

APPLICATION ACCEPTED AND AMENDMENTS

FORM 1

ALLOWED 24-1-90

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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

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APPLICATION FOR A STANDARD PATENT

Shell Internationale Research Maatschappij B.V., a Netherlands Company, of Carel van Bylandtlaan 30, 2596 HR, The Hague, THE NETHERLANDS, hereby apply for the grant of a standard patent for an invention entitled:

Process and Apparatus for Producing Hydrogen

which is described in the accompanying complete specification.

Details of basic application(s):-

<u>Basic Applic. No:</u>	<u>Country:</u>	<u>Application Date:</u>
8629031	UNITED KINGDOM	4 December 1986

The address for service is:-

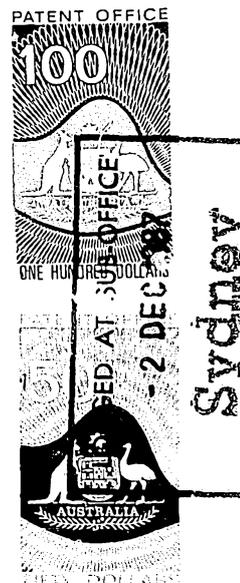
Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this FIRST day of DECEMBER 1987

Shell Internationale Research Maatschappij B.V.

By:

Registered Patent Attorney



TO: THE COMMISSIONER OF PATENTS
OUR REF: 43418
S&F CODE: 61750

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PATENTS ACT 1952

DECLARATION IN SUPPORT OF A
CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

Process and apparatus for producing hydrogen

I, Onno Aalbers, of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands, do solemnly and sincerely declare as follows:-

1. I am authorised by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., the applicant for the patent to make this declaration on its behalf.
2. The basic application(~~s~~) as defined by Section 141 of the Act was/~~were~~ made in the United Kingdom on 4th December, 1936 by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
3. Johannes BERENDS and JOHANNES DIDERICUS DE GRAAF, both Netherlands nationals of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands

(respectively), ~~is~~are the actual inventor(s) of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The Applicant is the assignee of the actual inventor(s).

4. The basic application(~~s~~) referred to in paragraph 2 of this Declaration was/~~were~~ the first application(~~s~~) made in a Convention country in respect of the invention the subject of the application.

DECLARED at The Hague this 27th day of October 1907

.....
Onno Aalbers

TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

This document contains the
specification made under
Section 49.

and is correct for printing.

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
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Priority:

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Related Art:

Name and Address
of Applicant:

Shell Internationale Research Maatschappij B.V.
Carel van Bylandtlaan 30
2596 HR
The Hague
THE NETHERLANDS

Address for Service:

Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Process and Apparatus for Producing Hydrogen

The following statement is a full description of this invention, including the best method of performing it known to me/us

PROCESS AND APPARATUS FOR PRODUCING HYDROGEN

The invention relates to a process for producing hydrogen and to an apparatus suitable for carrying out such a process.

5 It is well known to prepare a hydrogen-containing gas such as synthesis gas (which mainly contains hydrogen and carbon monoxide, and in addition carbon dioxide, nitrogen and (unconverted) hydrocarbons and steam) by means of steam reforming or (non) catalytic partial oxidation of a hydrocarbonaceous feed.

10 It is furthermore known to remove hydrogen from a hydrogen-containing product gas e.g. by means of pressure swing adsorption, thus obtaining substantially pure hydrogen and in addition hydrogen-depleted off gas.

It has now been found that said hydrogen-preparation and -separation steps can be efficiently integrated by employing energy produced by
15 combusting in a combustion zone hydrogen-depleted off gas obtained from the latter step in at least one of the steps of the integrated process itself, e.g. for the compression of oxygen-containing gas required in at least the former step of the process.

The invention therefore relates to a process for producing hydrogen
20 which comprises the following steps:

(a) converting a hydrocarbonaceous feed in a reaction zone at elevated temperature and pressure at least partly into a gas mixture containing hydrogen and carbon monoxide,

(b) removing hydrogen from product gas obtained from step (a), and

25 (c) applying the hydrogen-depleted off gas obtained from step (b), as fuel for convective heating in step (a) and/or for a gas-turbine driving a feed gas and/or air compressor.

The process according to the present invention will be elucidated hereinafter with the use of the Figures in which various preferred options
30 of the process have been incorporated without having the



intent of limiting said process to those particular embodiments as depicted in the Figures.

5 Figure 1 relates to a preferred embodiment of the present process wherein hydrogen-depleted off gas is heat-exchanged with flue gas, before use as fuel gas in a convective reforming zone.

Figure 2 relates to another preferred embodiment of the process according to the invention in which off gas is used as fuel gas in a gas turbine.

10 Reference numerals relating to similar process steps and/or equipment are the same in the two Figures.

In Figure 1 the essential process steps (a), (b) and (c) are carried out in reforming zone (1) of convective reformer (2), in pressure swing adsorption unit (3), and in combustion zone (4), respectively.

15 A hydrocarbonaceous feed, preferably containing normally liquid and/or gaseous hydrocarbons, in particular C_1-C_4 hydrocarbons such as those present in natural gas, is introduced via line (5) into reforming zone (1) together with steam introduced via line (6). In zone (1) step (a) of the present process is suitably carried out at a temperature from 600 to 1600 °C and a pressure from 2 to 200 bar. The reforming zone preferably comprises catalyst in order to operate said zone at a relatively low temperature from 600 to 20 1100 °C and at a pressure from 5-50 bar.

25 The reactor which contains said reforming zone (1) and optionally combustion zone (4) (which may also be spaced apart from the reforming zone and be located outside the reactor) preferably contains internals in order to improve heat exchange between said zones and ensure optimal use of catalyst, if any.

30 The reactor internals suitably comprise double concentric tubes with catalyst in the annular space between the tubes. The outer tubes are suitably mounted substantially vertically in a horizontal inlet manifold for hydrocarbon/steam feed distribution. The lower ends of the outer tubes are preferably closed in order to reverse the flow of gas having passed downwardly through the 35 annular catalyst bed. The inner tubes into which the hydrogen-

containing product gas is subsequently passed, are suitably connected to a product outlet manifold. Advantageously, the combustion gas (having a temperature of e.g. 900-1200 °C) enters the reforming reactor below or near the lower ends of the tubular reaction zone and leaves the reactor below the horizontal inlet manifold, situated at the relatively cold (e.g. 500-800 °C) upper part of the reactor. When the concentric tubes are mounted in the above-described manner, their hot lower ends can expand freely and thermal expansion in the manifolds is kept to a minimum.

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A gas mixture containing hydrogen and carbon monoxide is removed from reforming zone (1) through line (7). In order to produce additional hydrogen, at least part and preferably all of said gas mixture is preferably directed to carbon monoxide conversion zone (8) in which at least part of the carbon monoxide present in the gas mixture is catalytically converted in the presence of steam at the appropriate carbon monoxide conversion conditions in one or more steps into carbon dioxide. Conversion zone (8) is suitably maintained at a temperature from 180 to 450 °C and a pressure from 2 to 200 bar.

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Hydrogen-containing product gas obtained from conversion zone (8) and/or reforming zone (1) is directed via line (9) to pressure swing adsorption unit (3) from which a substantially pure hydrogen gas stream is withdrawn via line (10). Unit (3) preferably comprises a plurality of vessels containing molecular sieve beds which are sequentially in the adsorption-, desorption- and purge-stage. However, it is also possible to substitute a liquid absorption unit (wherein carbon monoxide and/or carbon dioxide are selectively absorbed by a liquid which is subsequently regenerated) or a hydrogen-permeable membrane unit for pressure swing adsorption unit (3) in order to recover hydrogen from the product gas obtained via line (9).

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Hydrogen-depleted off gas (which may still contain up to 5 or even up to 30% by volume of hydrogen, depending on the type of adsorption unit and pressure employed) obtained from unit (3) is

preferably directed via line (11) to compressor (15) and subsequently via line (14) to heat exchanger (12) wherein heat is exchanged with the effluent gas stream (13) from combustion zone (4) which gas stream generally has a higher temperature (e.g. from 150 to 1000 °C) than the off gas. Accordingly, the energy efficiency of the process according to the invention is substantially improved, thus enabling optimal use of the hydrogen-depleted off-gas in one or more process steps.

The heat exchanged off-gas is directed via line (16) to combustion zone (4). As the energy-content of the off-gas is in many cases not sufficient to employ said gas as the only fuel source for a combustion zone, additional fuel is preferably provided via line (18).

In a preferred embodiment of the process according to the invention as depicted in Figure 1 the combustion zone (4) as applied in step (c) provides thermal energy for the reforming reaction zone (1) of step (a) by means of convective heat transfer. A main advantage of such an arrangement is that the reaction zone will as a result be heated substantially uniformly instead of risking local overheating by a number of burners located in the reaction zone, as in previous reforming processes.

Effluent gas from combustion zone (4) applied in steps (a) and (c) as discussed hereinbefore is suitably (after heat exchange) directed via line (19) to a separate combustion zone (20) to be used as moderator gas together with fuel gas supplied via line (21). Optionally, part of the heat-exchanged effluent gas is recycled via line (17) to combustion zone (4). Effluent gas emanating from the latter combustion zone (20) is preferably directed via line (30) to turbo-expander (22) wherein the gas is expanded to provide mechanical energy to compress oxygen-containing gas (e.g. air) supplied via line (23) to compressor (24). In some cases sufficient oxygen is present in the expanded effluent gas obtained via line (27) from turbo-expander (22) to enable the use of said gas as oxygen-containing gas for the combustion zone (not depicted in Figure 1).

Turbo-expander (22), compressor (24) and generator (33) are preferably coupled (e.g. by means of axis (25)) and optionally combined with one or more other compressors (15).

5 Compressed oxygen-containing gas (e.g. the gas provided via line (26)) is preferably employed in at least one of the steps (a) and (c) of the present process, in particular in combustion zone (4) (via line (28)) and via line (29) in combustion zone (20). The use of compressed, and thereby preheated, oxygen-containing gas is preferred in the process according to the invention in order to improve the thermal efficiency of the combustion zone(s) and thus of the entire process.

10 The process and apparatus which are schematically depicted in Figure 2 will be described hereinafter only in so far as features different from those depicted in Figure 1 are included.

15 A significant difference is the use of a catalytic or non-catalytic partial oxidation zone (31) in the embodiment depicted in Figure 2. Such a zone is generally operated at a temperature from 600 to 1600 °C and preferably at a temperature from 1000 to 1500 °C, whereas the pressure in said zone is generally from 1 to 250 bar and preferably from 10 to 100 bar. Zone (31) constitutes the reaction zone employed in step (a) as well as a combustion zone as employed in step (c) of the process according to the invention.

20 A further difference with the process and apparatus as depicted in Figure 1 is that in Figure 2 the hydrogen-depleted off gas obtained from hydrogen separation unit (3) through line (11) is used as fuel gas in combustion zone (20) of a gas turbine instead of in a combustion zone (4) of a reforming apparatus. Expanded effluent gas from turbo-expander (22) is optionally at least partly used in a combustion zone (not depicted in Figure 2).

25 30 Oxygen-containing gas is advantageously provided by compressor (24) via line (26) to combustion zone (20). Substantially pure oxygen gas is supplied via line (34) to compressor (32) and subsequently directed via line (35) to partial oxidation zone (31).

35 The invention further relates to an apparatus suitable for producing hydrogen which comprises a reactor having feed inlet

means and product outlet means communicating with heat exchanger reactor internals, a combustor which is in heat exchange relation with said internals, a pressure swing adsorption unit communicating with the product outlet means and having separate hydrogen- and off-gas outlet means, and a gasturbine which is in communication

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The process according to the invention is illustrated by way of the following Example.

EXAMPLE

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The process substantially as depicted in Figure 2 is carried out by introducing 872 tons/day of feed gas (containing substantially methane) at a temperature of 50 °C and a pressure of 51 bar in catalytic partial oxidation zone (31) and reacting the feed gas with 2490 tons/day of substantially pure oxygen gas introduced via line (35) at a temperature of 100 °C and a pressure of 48 bar.

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The hydrogen-containing synthesis gas obtained via line (7) at 380 °C and 30 bar is subjected in carbon monoxide conversion zone (8) to a catalytic steam shift together with steam having a temperature of 380 °C and a pressure of 61 bar. 2160 tons/day of mainly hydrogen- and carbon dioxide-containing product gas from zone (8) is led to Pressure Swing Adsorption unit (3) at a temperature of 40 °C and a pressure of 26 bar; from unit (3) 200 tons/day of substantially pure hydrogen is obtained at 40 °C and 25 bar in addition to 1960 tons/day offgas containing carbon dioxide and hydrogen as major components at 40 °C and 1.6 bar. Said offgas is led via line (11) to compressor (15) from which an outlet gas stream (14) is obtained at a temperature of 310 °C and a pressure of 17 bar and combined with 344 tons/day of methane-containing gas at a pressure of 51 bar and a temperature of 50 °C having a similar composition as the feed gas to zone (31).

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The combined gas stream (16) is directed to a gas turbine comprising combustion zone (20), compressor (24) and turbo expander (22). In said gas turbine 76 Megawatt electric power is generated by generator (33) of which 18 Megawatt is required for operating

compressors (15) and (32), leaving 58 Megawatt nett power export, excluding additional electricity generation by means of waste heat recovery from the expanded effluent gas stream (27).

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The claims defining the invention are as follows:

1. A process for producing hydrogen which comprises the following steps:

(a) converting a hydrocarbonaceous feed in a reaction zone at elevated temperature and pressure at least partly into a gas mixture containing hydrogen and carbon monoxide,

(b) removing hydrogen from product gas obtained from step (a), and

(c) applying the hydrogen-depleted off gas obtained from step (b), as fuel for convective heating in step (a) and/or for a gas-turbine driving a feed gas and/or air compressor.

2. The process as claimed in claim 1 wherein energy produced in step (c) is employed to compress oxygen-containing gas.

3. The process as claimed in claim 2 wherein compressed oxygen-containing gas is employed in at least one of steps (a) and (c).

4. The ~~process~~^{process} as claimed in any one of the preceding claims wherein step (a) is carried out in the presence of steam at a temperature from 600 to 1600°C and a pressure from 2 to 200 bar.

5. The process as claimed in any one of the preceding claims wherein at least part of the carbon monoxide present in the gas mixture obtained from step (a) is catalytically converted in the presence of steam at carbon monoxide conversion conditions into carbon dioxide and hydrogen.

6. The process as claimed in any one of the preceding claims wherein step (b) is carried out by passing hydrogen-containing gas to a pressure swing adsorption zone.

7. The process as claimed in claim 6 wherein hydrogen-depleted gas obtained from the pressure swing adsorption zone is heat exchanged with effluent gas from a combustion zone.

8. The process as claimed in any one of the preceding claims wherein effluent gas from the combustion zone applied in step (c) is used as moderator gas for the combustion zone employed in step (a).

9. An apparatus suitable for carrying out the process as claimed in any one of claims 1-8 comprising a reactor having a feed inlet means and product outlet means communicating with heat exchanger reactor internals, a combustor which is in heat exchange relation with said internals, a pressure swing adsorption unit communicating with the product outlet means and having separate hydrogen- and off-gas outlet means, and a gas turbine which is in communication with the combustor and/or the off-gas outlet means.

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10. A process for producing hydrogen, substantially as hereinbefore described with reference to any one of the Examples and/or the accompanying drawings.

11. An apparatus suitable for carrying out the process as claimed in claim 10 and as substantially as hereinbefore described with reference to Figure 1 or Figure 2.

DATED this TWENTY-FIRST day of NOVEMBER 1989
Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

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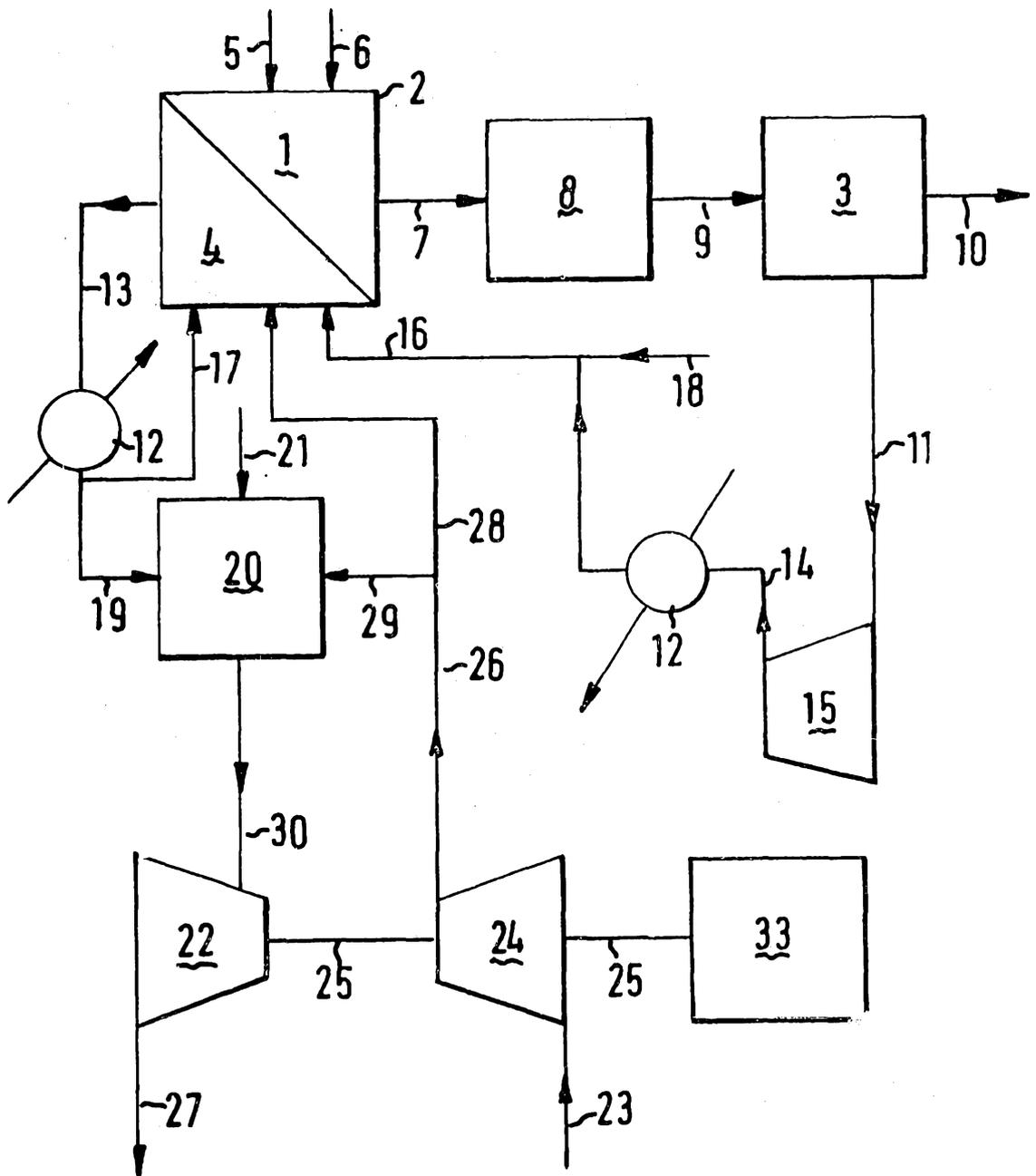


FIG. 1

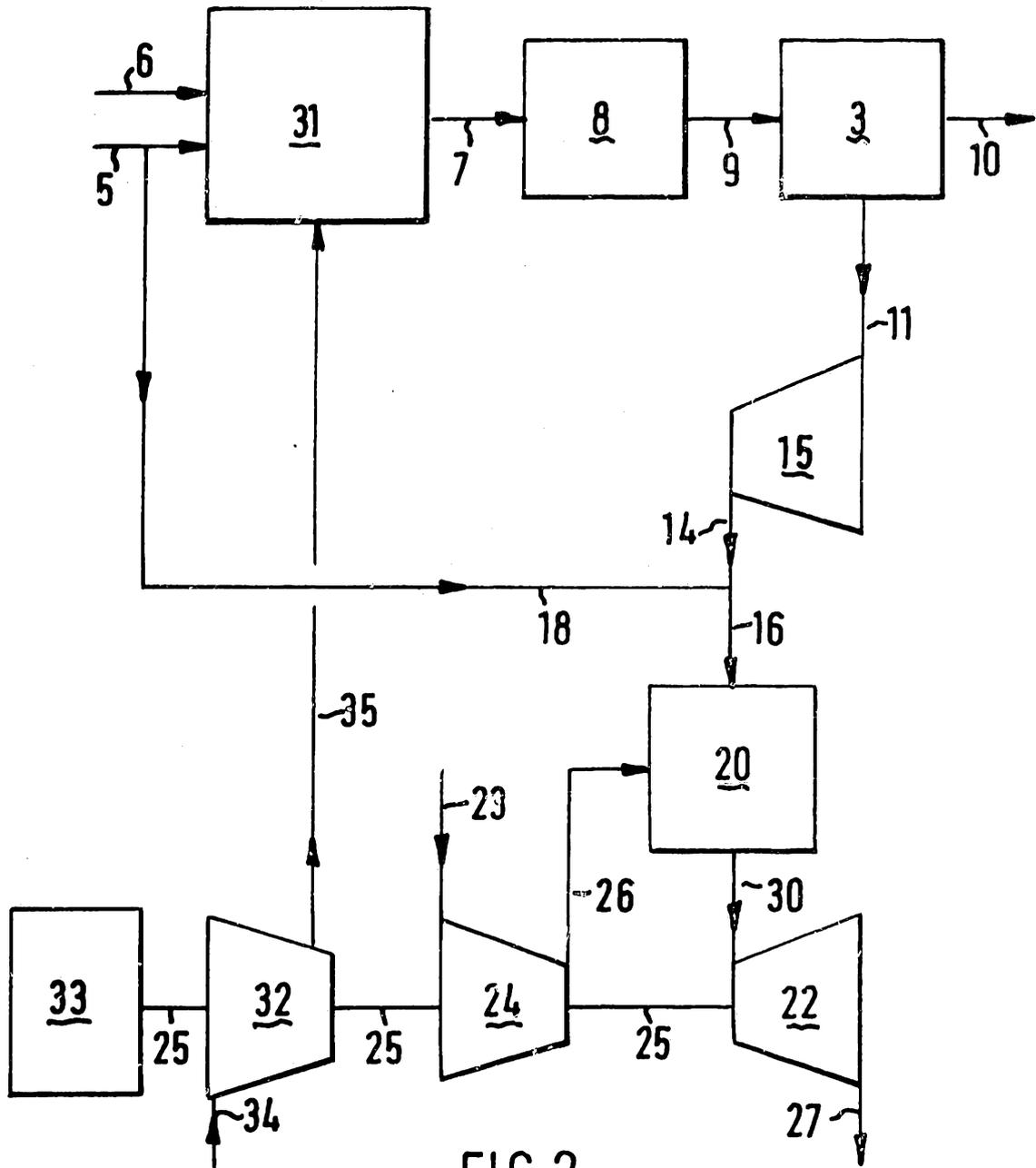


FIG. 2