

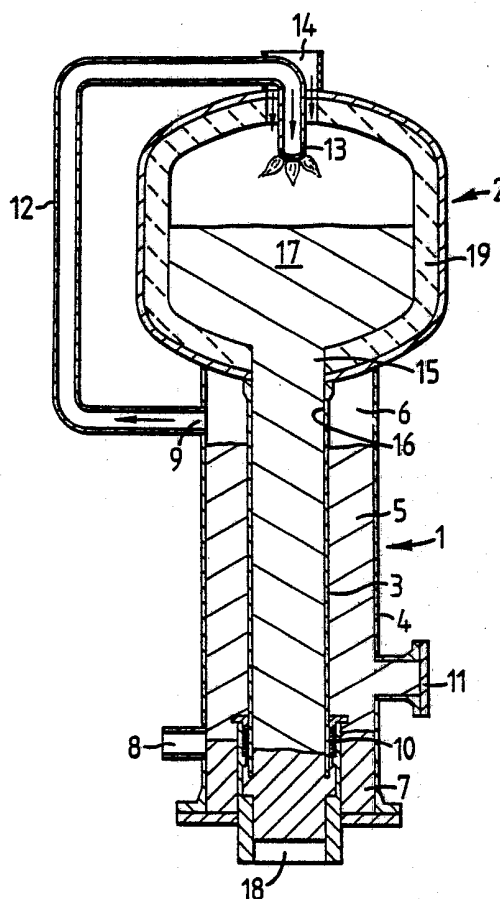


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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**(54) Title:** PROCESS AND APPARATUS FOR THE PRODUCTION OF SYNTHESIS GAS**(57) Abstract**

Synthesis gas (carbon monoxide and hydrogen) is produced by the sequence of primary and secondary reforming comprising; (a) feeding hydrocarbon-containing gas (8) and steam (8) to a primary reforming zone (1) containing a primary steam reforming catalyst (5) under reforming conditions wherein the hydrocarbon gas (8) is partially reformed to produce a primary reformer effluent (9), (b) feeding the primary reformer effluent (9) and oxygen-containing gas (14) to a secondary reforming zone (2) containing secondary reforming catalyst (17) and reforming conditions wherein a secondary reformer effluent is produced (18), (c) passing the secondary reformer effluent to the primary reforming zone (1) as indirect heating medium, and (d) removing the secondary reforming effluent (18) from the primary reforming zone (1) and recovering the raw synthesis gas, wherein the primary reforming zone (1) comprises at least one double-pipe heat exchanger-reactor, the primary steam reforming catalyst (5) being positioned either in the central core (16) of the double-pipe heat exchanger or in the annulus (6) thereof and in that the secondary reformer effluent is passed through whichever of the central core (16) or annulus (6) does not contain the primary steam reforming catalyst (5) countercurrently to the hydrocarbon-containing gas and steam.



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PROCESS AND APPARATUS FOR THE PRODUCTION OF SYNTHESIS GAS

The present invention relates to a process and apparatus for the production of synthesis gas.

Synthesis gas is the name generally given to a gaseous mixture principally comprising carbon monoxide and hydrogen, but also  
5 possibly containing carbon dioxide and minor amounts of methane and nitrogen. It is used, or is potentially useful, as feedstock in a variety of large-scale chemical processes, for example the production of methanol, the production of gasoline boiling range hydrocarbons by the Fischer-Tropsch process and the production of  
10 ammonia.

Processes for the production of synthesis gas are well known and generally comprise steam reforming, autothermal reforming, non-catalytic partial oxidation of light hydrocarbons or non-catalytic partial oxidation of any hydrocarbons. Of these  
15 methods, steam reforming is generally used to produce synthesis gas for conversion into ammonia or methanol.

Modifications of the simple steam reforming processes have been proposed. In particular, there have been suggestions for improving the energy efficiency of such processes in which the heat available  
20 from a secondary reforming step is utilised for other purposes within the synthesis gas production process. For example, processes are described in GB-A-1550754, US-A-4479925 and GB-A-2153382 in which heat from a secondary reformer is used to provide heat to a primary reformer.

25 GB-A-1,550,754 describes a process for the steam reforming of

hydrocarbons by the sequence of primary and secondary reforming, which comprises the steps of

- (a) heating a first mixture of hydrocarbons in the presence of a steam reforming catalyst to form a first partially reformed effluent,
- (b) heating a second mixture of hydrocarbon feed and steam to conditions at which primary reforming occurs by indirect heat exchange with the process gas as hereinafter defined and reforming said hydrocarbons in the presence of a steam reforming catalyst to form a second partially reformed effluent,
- (c) introducing said first and second partially reformed effluents to a secondary reformer to carry out said secondary reforming in the presence of oxygen and forming a secondary reforming effluent, and passing said secondary reforming effluent as the process gas in indirect heat exchange with said second mixture of hydrocarbon feed as set forth in (b) above.

The primary reformer which is heated by the effluent from the secondary reformer is a shell and tube heat exchanger-reactor.

US-A-4479925 discloses a process for producing ammonia synthesis gas in a reactor-exchanger primary reformer, followed by an autothermal secondary reformer in which the primary reformer is heated by synthesis gas from the secondary reformer. The primary and secondary reformers are separate units, the primary unit being a shell and tube heat exchanger-reactor.

GB-A-2153392 discloses an autothermal process for producing a synthesis gas in which a mixture of steam and hydrocarbon feed gas is reacted by passing the mixture through a catalyst in counter-current flow to the combustion reaction effluent of the process, to cool the reaction effluent and to provide heat for the reaction of the steam-hydrocarbon feed gas mixture and introducing oxygen or oxygen-enriched air to form said combustion reaction effluent. The patent application also discloses a reactor for carrying out the process which essentially comprises a shell and tube heat exchanger-reactor as the primary reformer.

The present invention provides a process and apparatus for the production of synthesis gas by the sequence of primary and secondary reforming in which the available heat of the effluent from the secondary reforming is efficiently used to provide heat for the primary reforming. The apparatus has the advantage that it is mechanically relatively simple. The apparatus is of a modular design which allows the heat requirement to be easily changed and which also provides operational and maintenance advantages.

Thus, according to the present invention a process for producing synthesis gas by the sequence of primary and secondary reforming comprising;

- (a) feeding hydrocarbon-containing gas and steam to a primary reforming zone containing a primary steam reforming catalyst under reforming conditions wherein the hydrocarbon gas is partially reformed to produce a primary reformer effluent,
  - (b) feeding the primary reformer effluent and oxygen-containing gas to a secondary reforming zone containing secondary reforming catalyst under reforming conditions wherein a secondary reformer effluent is produced,
  - (c) passing the secondary reformer effluent to the primary reforming zone as indirect heating medium, and
  - (d) removing the secondary reforming effluent from the primary reforming zone and recovering the raw synthesis gas,
- characterised in that the primary reforming zone comprises at least one double-pipe heat exchanger-reactor, the primary steam reforming catalyst being positioned either in the central core of the double-pipe heat exchanger-reactor or in the annulus thereof and in that the secondary reformer effluent is passed through whichever of the central core or annulus does not contain the primary steam reforming catalyst countercurrently to the hydrocarbon-containing gas and steam.

The present invention includes apparatus suitable for producing synthesis gas by the process as hereinbefore described which apparatus comprises a primary reforming zone and a secondary reforming zone, characterised in that the primary reforming zone

comprises at least one double-pipe heat exchanger-reactor capable of containing a primary steam reforming catalyst in either the central core or annulus, the double-pipe heat exchanger-reactor having at least one inlet for introducing steam and hydrocarbon-containing gas into whichever of the central core or annulus contains the primary steam reforming catalyst, an outlet for conveying primary reformer effluent to the secondary reforming zone and an inlet for introducing secondary reformer effluent into whichever of the central core or annulus does not contain the primary steam reforming catalyst, countercurrently to the steam and hydrocarbon-containing gas, the secondary reforming zone which is capable of containing secondary reforming catalyst has an inlet for primary reformer effluent, an inlet for oxygen-containing gas and an outlet for conveying the secondary reformer effluent to the primary reforming zone.

If the primary steam reforming catalyst is positioned in the inner core of the double-pipe heat exchanger-reactor, the outer pipe tends to be subjected to a higher temperature and would have to have a relatively thick wall unless insulated. Preferably, therefore, in operation the primary steam reforming catalyst of the primary reforming zone is positioned in the annulus of the (or each) double-pipe heat exchanger-reactor(s).

Generally, the primary reforming zone will comprise a plurality of double-pipe heat exchanger-reactors. Each double-pipe heat exchanger-reactor may be associated with a separate secondary reforming zone. However, in a preferred embodiment, a plurality of double-pipe heat exchanger-reactors, typically 2 to 10, are associated with a single secondary reforming zone. Thus, for example, apparatus according to the present invention may comprise 7 secondary reforming zones each of which is associated with 6 double-pipe heat exchanger-reactors i.e. the total number of double-pipe heat exchanger-reactors is 42.

Suitably, the apparatus according to the present invention may be constructed as a single unit in order to reduce piping and ancillary units.

In a preferred embodiment of the present invention a plurality of double-pipe heat exchanger-reactors are arranged peripherally about the circumference of a single secondary reforming zone and are close-coupled thereto by, for example, interconnecting pipes.

5 Typically, the secondary reforming zone may be of about 4m diameter and may have about 12 double-pipe heat exchanger-reactors arranged around the periphery thereof. Advantages of the arrangement of the preferred embodiment are that it is more compact, i.e. it occupies a smaller area, and it facilitates the removal of one or more  
10 exchanger-reactors for maintenance purposes without substantially affecting operation of the remaining exchanger-reactors. Furthermore, it simplifies operation because it reduces the number of control operations, there being only one secondary reforming zone to control.

15 Whichever of the central core or annulus of each double-pipe heat exchanger-reactor is not being used for the primary reforming catalyst may be used to contain secondary reforming catalyst. Generally, the geometry of the double-pipe heat exchanger-reactor will not accommodate all of the secondary reforming catalyst, but by  
20 utilising the volume of the double-pipe heat exchanger-reactor, the volume of the second reforming reactor may be reduced.

The hydrocarbon-containing gas may suitably be any hydrocarbon capable of undergoing a steam reforming reaction, such as, for example, at least one hydrocarbon ranging from methane to naphthas  
25 having an end point of about 220°C, including natural gas, ethane, propane and LPG. A preferred hydrocarbon-containing gas is natural gas. If required, the hydrocarbon-containing gas may first of all be desulphurised using technology known in the art and pressurised e.g. to about 40 to 80 atmospheres.

30 The feed to the primary reforming zone may optionally also include carbon dioxide.

The hydrocarbon-containing gas, steam and optionally carbon dioxide may suitably be preheated for example to a temperature in the range 400 to about 650°C before being introduced into the  
35 primary reforming zone. This preheating may suitably be

accomplished at least in part by using waste heat from elsewhere in the process and/or by, for example a fired heater. At least the hydrocarbon-containing gas portion of the feed may then be passed through a catalyst guard bed for the purpose of removing impurities therein, for example sulphur, which may be undesirable downstream to, for example, the steam reforming catalyst.

The preheated feed is then passed to the primary reforming zone which comprises at least one double-pipe heat exchanger reactor containing a primary steam reforming catalyst in either the central core or, preferably, the annulus under steam reforming conditions.

Double-pipe heat exchangers are known and comprise two pipes one positioned inside the other, generally substantially concentrically. A packed stuffing box may be used to allow differential movement and removal of the inner pipe for cleaning or maintenance purposes.

The primary steam reforming catalyst used in the primary reforming zone may be any suitable catalyst including conventional steam reforming catalysts such as, for example, nickel, nickel oxide, chromia, molybdenum, or mixtures thereof, either supported or unsupported.

The primary reformer effluent which comprises unchanged hydrocarbon, carbon monoxide and hydrogen leaves the primary reforming zone at a temperature which is typically in the range from 650 to 950°C and is fed to the secondary reforming zone. The secondary reforming reactor contains secondary reforming catalyst which may be a catalyst of the same type as used in the primary reforming zone.

The oxygen-containing gas which is fed to the second reforming zone is suitably air, oxygen-enriched air or oxygen and is preferably preheated to a temperature in the range 100 to 300°C. The oxygen-containing gas is preferably oxygen if the synthesis gas is to be converted to methanol and air or oxygen-enriched air if it is to be converted to ammonia.

Steam, hydrocarbon-containing gas and/or carbon dioxide may also be fed to the second reforming zone. The



hydrocarbon-containing gas, if used, is preferably obtained by dividing the feed to the primary reforming zone suitably after preheating.

5 The secondary reforming zone suitably takes the form of a refractory lined reactor operable under essentially adiabatic conditions. Part of the hydrocarbon is combusted in order to provide the heat required for reformation. Suitably, the temperature in the second reforming zone is maintained in the range from 900 to 1400°C, typically about 1200°C. The second reformer  
10 effluent is then passed to the primary reforming zone as the indirect heat exchange medium. The available heat of the second reformer effluent is used to provide heat for the endothermic reforming reactions by passing the second reformer effluent through one or more double-pipe heat exchanger-reactors counter-currently to  
15 the hydrocarbon-containing gas and steam feed mixture.

In an embodiment of the present invention, whichever of the central core or annulus of each double-pipe heat exchanger-reactor does not contain primary reforming catalyst may contain a carbon monoxide shift catalyst.

20 The carbon monoxide shift catalyst may suitably be either or both a conventional high temperature shift catalyst, for example Fe/Cr, or a steam reforming catalyst. An advantage of using this catalyst disposition is that, as the gas from the secondary reformer is cooled as it passes through the primary reforming zone, an extra  
25 exotherm is given out as the shift reaction:-



proceeds to the right hand side of the equation to maintain chemical equilibrium. This extra heat can be used to increase the gas outlet temperature, all other things being equal, thereby increasing the  
30 temperature driving force at the cooler end of the exchanger.

This enables operation with a lower steam consumption than would be possible without shift equilibrium. Another advantage of maintaining shift equilibrium as the gas is cooled is that the possible formation of carbon by the reaction:-



which can lead to blockage of the heat exchanger, is eliminated. For similar reasons, a shift catalyst may be included in downstream equipment, for example waste heat boilers.

5       The secondary reformer effluent is removed from the primary reforming zone at a temperature which may be for example in the range from 450 to 700°C and preferably cooled, thereby raising some or all the steam required in the process. After cooling, carbon dioxide may be recovered from the effluent. Methods for removing  
10 carbon dioxide from such compositions are well known in the art. Any suitable method may be used, but it is preferred to use a physical solution process in order to avoid a demand for large quantities of steam for regeneration.

Carbon dioxide recovered from the secondary reformer effluent  
15 may be fed to the primary and/or secondary reforming zones, if required.

The process and apparatus according to the present invention can have a number of advantages over known processes and apparatus. The apparatus is relatively simple and can be manufactured using  
20 standard pipe sections. Thus the capital cost of the apparatus is low. Also the apparatus can be designed in the form of modules which allows the heat requirement and/or capacity of the process to be relatively easily changed by adding or removing double-pipe heat exchanger-reactors and/or secondary reforming reactors. This  
25 modular approach enables the apparatus to be easily transported and installed. It also allows individual double-pipe heat exchanger-reactors and/or secondary reactors to be shut-down for maintenance or replacement without having to shut-down the whole process. The use of double-pipe heat exchanger reactors also  
30 provides more uniform heating than shell and tube heat exchangers in which tubes at the edge of the tube bundle may be subjected to a different rate of heat exchange than tubes at the centre of the tube bundle.

The process and apparatus according to the present invention  
35 will now be further described with reference to the accompanying

drawings in which;

Figure 1 is a schematic sectional view of one embodiment of the apparatus according to the present invention.

Figure 2 is a schematic sectional view of a second embodiment  
5 of the apparatus according to the present invention and

Figure 3 is a schematic plan view of a preferred arrangement of a plurality of double-pipe heat-exchanger reactors and a secondary reforming zone.

Figure 4 is a schematic elevation view of the arrangement of  
10 Figure 3.

Figure 5 is a flow diagram of a process according to the present invention

Figure 1 illustrates an integral primary and secondary reformer comprising a primary reforming zone 1 and a secondary reforming  
15 zone 2. The primary reforming zone 1 comprises a double-pipe heat exchanger-reactor having an inner pipe 3 and an outer pipe 4, the two pipes are substantially concentric. A primary reforming catalyst 5 is packed into the annulus 6 formed between the inner pipe 3 and outer pipe 4 which catalyst is supported by packing 7.  
20 The feed for the primary reforming zone enters through inlet 8 and the primary reformer effluent leaves through outlet 9. Thus the feed passes along the length of the annulus 6 of the double-pipe heat exchanger-reactor. A packed gland 10 is provided to permit relative movement between the inner pipe 3 and outer pipe 4. The  
25 primary reforming zone is also provided with an access port 11. The secondary reforming zone 2 comprises a reactor, lined with a refractory material 19, attached to the primary reforming zone 1 at the opposite end to the feed inlet 8. Pipe 12 conveys the primary reformer effluent from the primary reforming zone 1 to the inlet 13  
30 of the secondary reforming zone 2. Oxygen-containing gas and optionally steam, hydrocarbon-containing gas and/or carbon dioxide can be introduced via inlet 14. It will be appreciated that inlet 14 may be replaced by a number of separate inlets. The secondary reformer effluent leaves the secondary reforming zone 2 via outlet  
35 15 which is connected to the inner core 16 of the primary reforming

zone 1. The secondary reforming catalyst is shown as being contained in the secondary reforming zone 2 and also in the inner core 16 of the primary reforming zone.

5 The secondary reformer effluent passes along the length of the central core 16 of the primary reforming zone 1, countercurrently to the primary reformer feed, and leaves through outlet 18.

The pipes 3,4 of the double-pipe heat exchanger-reactor may be of any suitable size. For example in an embodiment of the present invention, the inner pipe 3 may have a nominal bore of 6 inches (152  
10 mm) and the outer pipe 4 may have a nominal bore of 10 inches (254 mm). In another embodiment the inner pipe 3 may have a nominal bore of 8 inches (203 mm) and the outer pipe may have a nominal bore of 12 inches (305 mm).

The inner wall of the outer pipe 4 may be insulated e.g. with a  
15 refractory material in order to reduce heat loss. Insulating the inner wall of the outer pipe 4 may also allow a lower specification, lower cost material to be used for the pipe wall.

Since the temperatures to which the material of the pipes 3,4 will be exposed will be different at different positions along the  
20 length of the double-pipe heat exchanger-reactor, different materials can be used at different positions. For example, a metal suitable for use in a high temperature environment may be required adjacent the inlet for the secondary reformer effluent 15 whereas a lower specification, lower cost metal may be adequate adjacent the  
25 outlet 18 for the secondary reforming effluent.

Figure 2 illustrates a second embodiment of the apparatus according to the present invention in which the same reference numerals as used in Figure 1 are used to identify the same elements. The second embodiment differs from the first embodiment  
30 in that in place of the pipe 12 for conveying the primary reformer effluent from the primary reforming zone 1 to the secondary reforming zone 2 a shell 20 is used which encloses the second reforming zone, this shell 20 is directly connected to the annulus 6 of the primary reforming zone and together with the secondary  
35 reforming zone forms an annulus for conveying the primary reforming

effluent about the secondary reforming zone. The primary reforming effluent enters the secondary reforming zone via openings 21. In this embodiment, the secondary reforming catalyst 22 is shown as a bed which is wholly contained within the secondary reforming zone 2. The central core 16 of the double-pipe heat exchanger reactor may be packed with a carbon monoxide shift catalyst if desired.

Figure 3 illustrates a preferred embodiment of the apparatus according to the invention in which the same reference numerals as used in Figure 1 are used to identify the same elements. In this embodiment a plurality of double-pipe heat exchanger-reactors 1 are peripherally arranged around the circumference of the secondary reforming zone 2, being close-coupled thereto by interconnecting pipes 12.

Figure 4 illustrates an elevation view of the arrangement of Figure 3 in which the same reference numerals as used in Figure 1 are used to identify the same elements. In this embodiment, instead of a single large diameter outlet 18 for the secondary reforming effluent there may be used a number of smaller diameter outlets. It will be readily appreciated that different arrangements of inlets 13 and 14 and pipes 12 are possible.

A process for producing synthesis gas according to the present invention is illustrated in Figure 5. In Figure 5, 32 represents a preheater, 33 represents a fired heater, 36 is a guard bed, 38 is an integrated primary and secondary reformer according to the present invention such as illustrated in Figure 1 or Figure 2, 48 is a boiler for generating steam and 49 is a carbon dioxide recovery plant.

Desulphurised natural gas is fed through line 31 to the preheater 32 and thereafter through the fired heater 33. After exiting through line 34, it is passed through the guard bed 36 wherein poisons detrimental to the operation of the reforming catalysts are removed. A proportion of the natural gas is then passed through line 37 to the primary reforming zone of the integrated primary and secondary reformer 38. Carbon dioxide may also be fed to the primary reforming zone through line 40.

Superheated steam is introduced via line 39.

The gas at exit from the primary reformer which may contain a considerable proportion of unconverted methane is passed through line 41 to the secondary reforming zone of the integrated reformer 38. Also passed to the secondary reformer is a proportion of the preheated fresh natural gas through line 43, steam through line 44 and preheated oxygen through line 45. The facility also exists for adding carbon dioxide through line 51.

The gaseous stream exiting from the secondary reforming zone is passed as the indirect heating medium to the primary reforming zone of the integrated primary and secondary reformer 38 which may contain a catalyst to promote the shift reaction. In cooling and reacting it heats the primary reaction gases.

The secondary reformer effluent is then passed out of the primary reforming zone through line 47 and is cooled in the boilers 48. The steam raised thereby can be used in the process. Carbon dioxide can be recovered from the cooled gas stream in the carbon dioxide removal plant 49 using conventional technology. Recovered carbon dioxide can be recycled through line 50 to the reformer 38, optionally via a gas compressor.

The heat available from the secondary effluent may not be sufficient for all of the primary reforming. Additional primary reformer effluent may therefore be provided by a conventional radiant steam reforming furnace (not shown). Additional heat may be provided to the primary reforming zone of the apparatus according to the present invention. For example, the double-pipe heat exchanger-reactors may be positioned in a radiant furnace (not shown).

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## Claims:

1 A process for producing synthesis gas by the sequence of primary and secondary reforming comprising:

- 5 (a) feeding hydrocarbon-containing gas and steam to a primary reforming zone containing a primary steam reforming catalyst under reforming conditions wherein the hydrocarbon is partially reformed to produce a primary reformer effluent,
- (b) feeding the primary reformer effluent and oxygen-containing gas to a secondary reforming zone containing secondary reforming catalyst under reforming conditions wherein a secondary reformer effluent is produced,
- 10 (c) passing the secondary reformer effluent to the primary reforming zone as indirect heating medium, and
- (d) removing the secondary reforming effluent from the primary reforming zone and recovering the raw synthesis gas,

15 characterised in that

the primary reforming zone comprises at least one double-pipe heat exchanger-reactor, the primary steam reforming catalyst being positioned either in the central core of the double-pipe heat exchanger-reactor or in the annulus thereof and in that the

20 secondary reformer effluent is passed through whichever of the central core or annulus does not contain the primary steam reforming catalyst countercurrently to the hydrocarbon-containing gas and steam.

2 Apparatus suitable for use in a process for the production of synthesis gas as claimed in claim 1 which apparatus comprises a primary reforming zone and a secondary reforming zone characterised in that

- 5 the primary reforming zone comprises at least one double-pipe heat exchanger-reactor(s) capable of containing a primary steam reforming catalyst in either the central core or annulus, the double-pipe heat exchanger-reactor having at least one inlet for introducing steam and hydrogen-containing gas into whichever of the central core or
- 10 annulus contains the primary steam reforming catalyst, an outlet for conveying primary reformer effluent to the secondary reforming zone and an inlet for introducing secondary reformer effluent into whichever of the central core or annulus does not contain the primary steam reforming catalyst, countercurrently to the steam and
- 15 hydrocarbon-containing gas, the secondary reforming catalyst having an inlet for primary reformer effluent, an inlet for oxygen-containing gas and an outlet for conveying the secondary reformer effluent to the primary reforming zone.

- 3 Apparatus according to claim 2 wherein in operation the primary steam reforming catalyst of the primary reforming zone is positioned
- 20 in the annulus of the (or each) double-pipe heat exchanger-reactor(s).

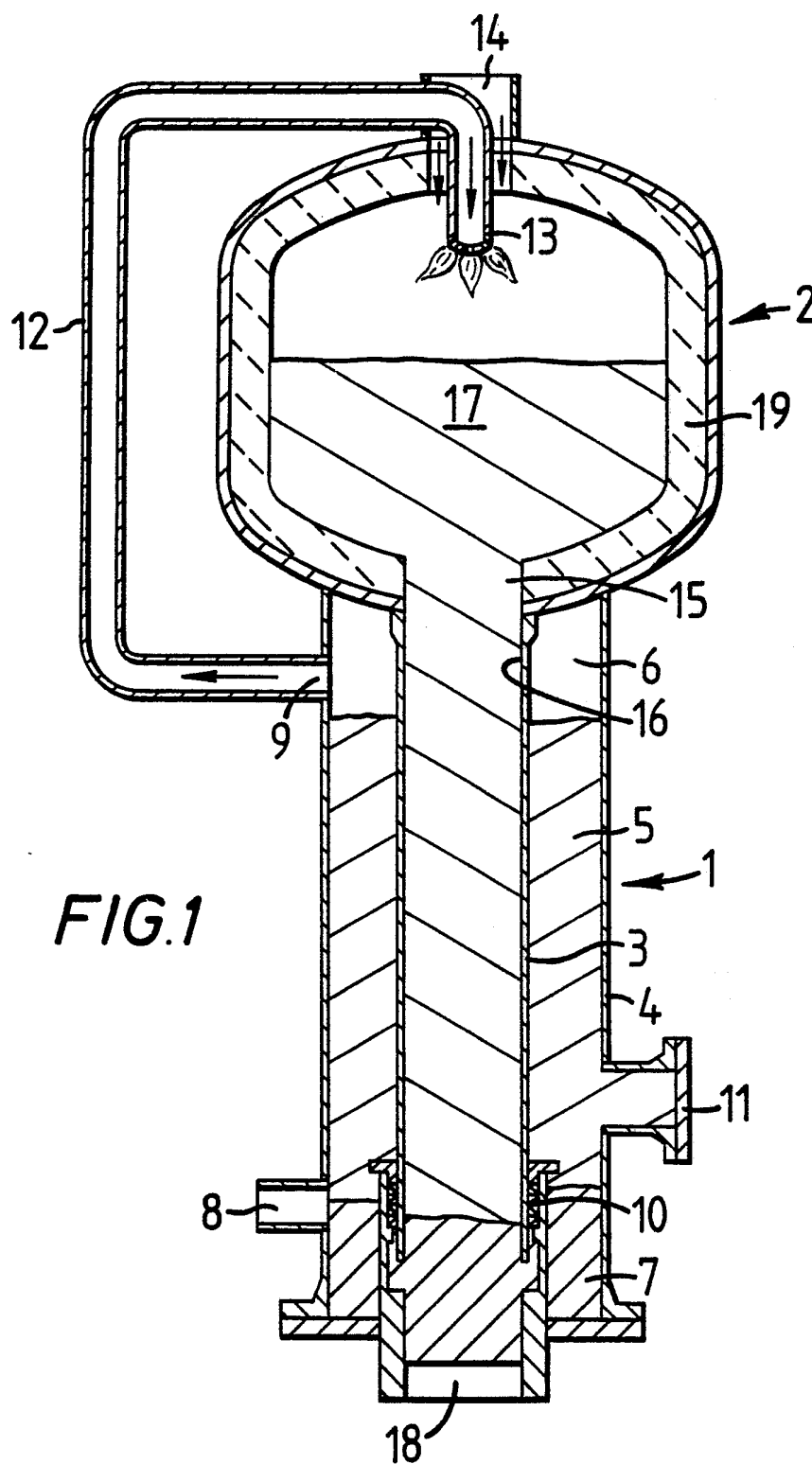
- 4 Apparatus according to either claim 2 or claim 3 wherein the primary reforming zone comprises a plurality of double-pipe heat
- 25 exchanger-reactors.

5 Apparatus according to claim 4 wherein each double-pipe heat exchanger-reactor is associated with a separate secondary reforming zone.

- 6 Apparatus according to claim 2 wherein the apparatus is
- 30 constructed as a single unit.

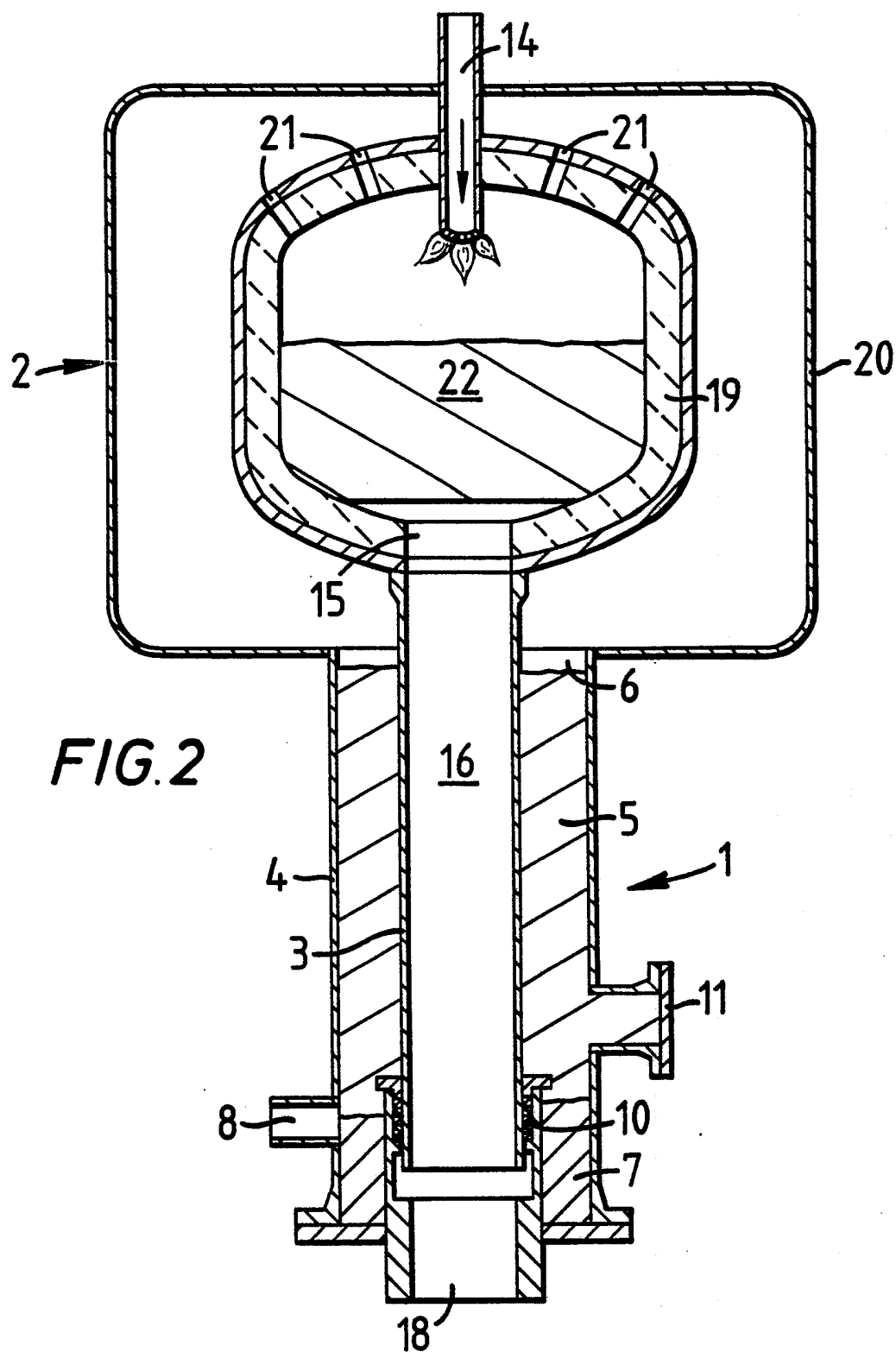
7 Apparatus according to claim 4 wherein the plurality of double-pipe heat exchanger-reactors are arranged peripherally about the circumference of a single secondary reforming zone and are close-coupled thereto.



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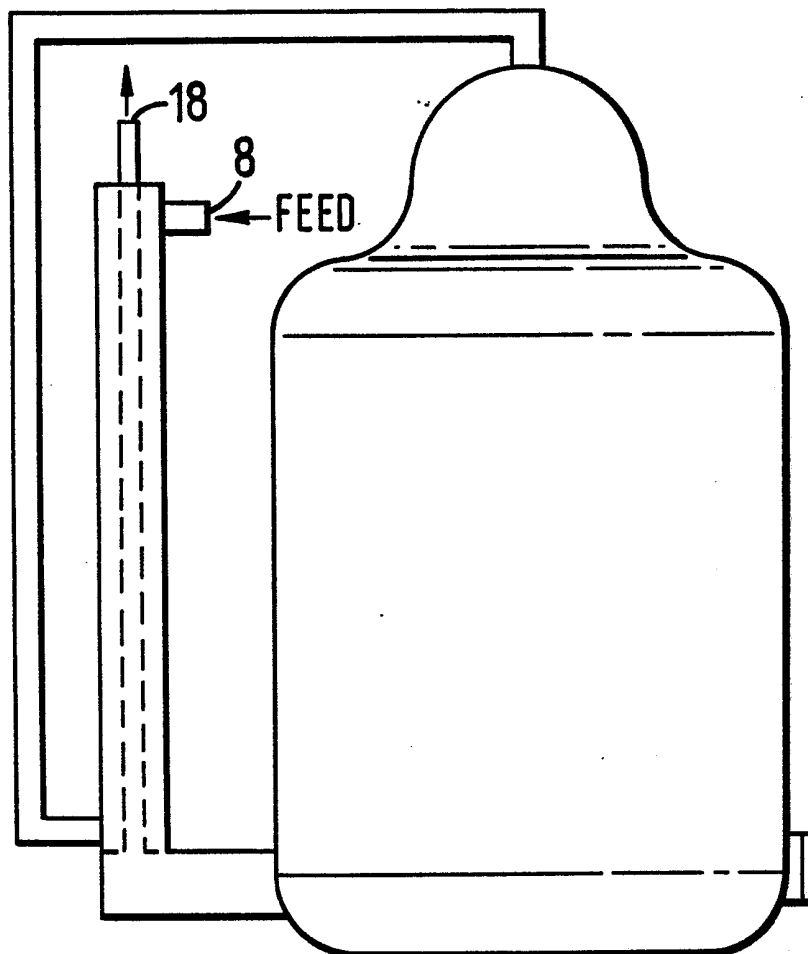
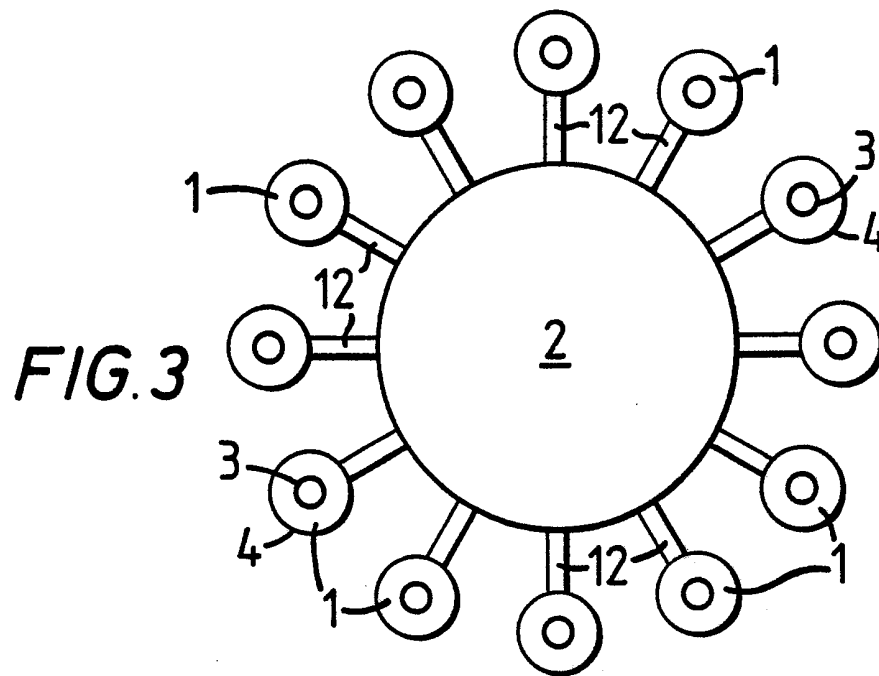
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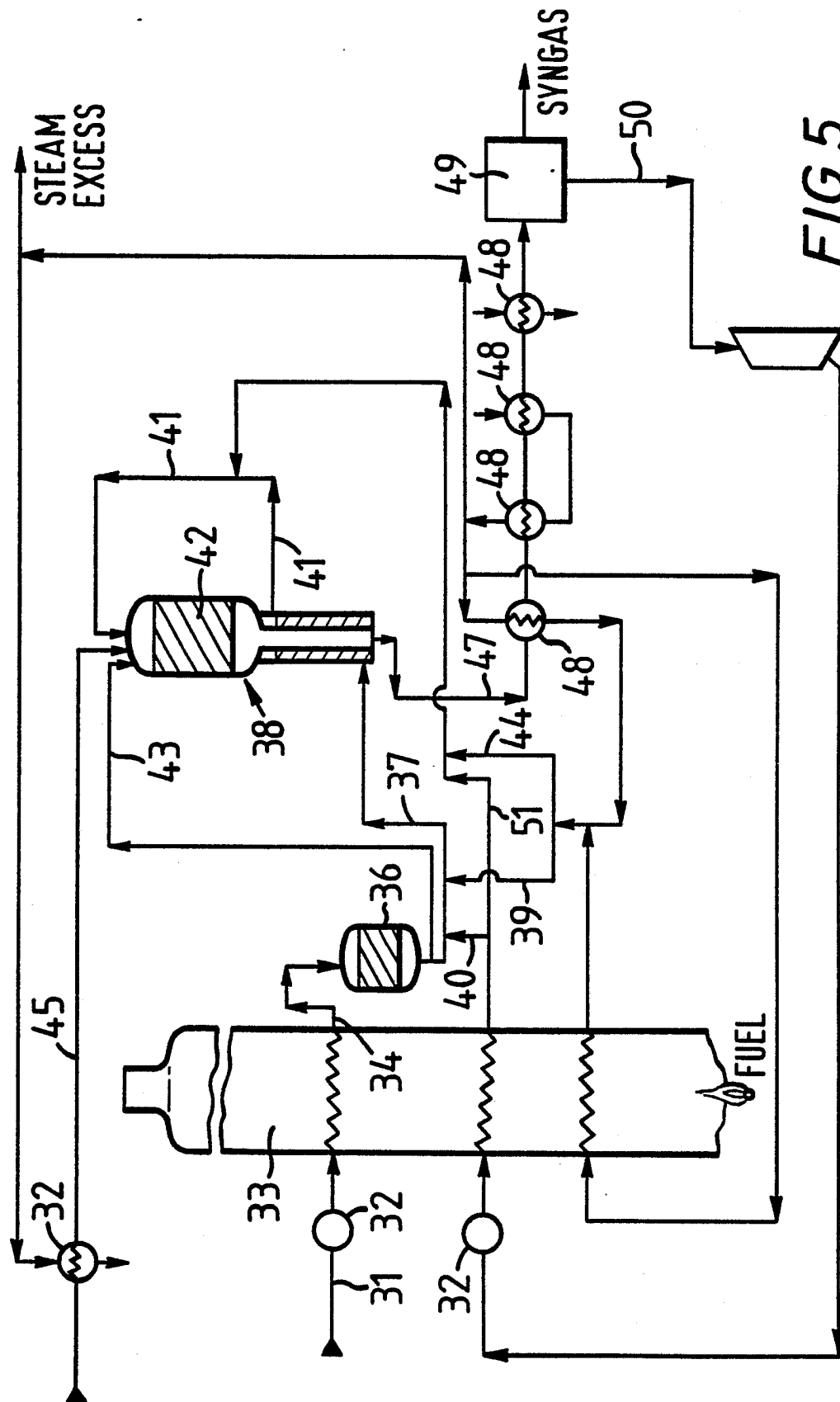


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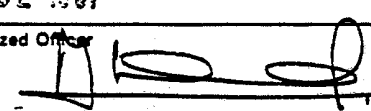
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**SUBSTITUTE SHEET**

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00252

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> :            C 01 B 3/38; B 01 J 8/06		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>4</sup>	C 01 B; B 01 J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> *		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US, A, 3450514 (SINFELT et al.) 17 June 1969 see figure 3; column 4, lines 47-74; claims 1,2	1,2,6
Y	Chemical Abstracts, volume 103, no. 24, 16 December 1985, (Columbus, Ohio, US), see page 144, abstract 198441f, & JP, A, 60103001 (MITSUBISHI HEAVY INDUSTRIES, LTD) 7 June 1985	1,2
P,Y	GB, A, 2179366 (THE BRITISH PETROLEUM CO.) 4 March 1987 see claims 1,2,13	1,6
A	GB, A, 2153382 (FLUOR CORP.) 21 August 1985 see figure 1 cited in the application	1
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
2nd July 1987	8 JUL 1987	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	M. VAN HOLL 	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 87/00252 (SA 16932)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 17/07/87

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