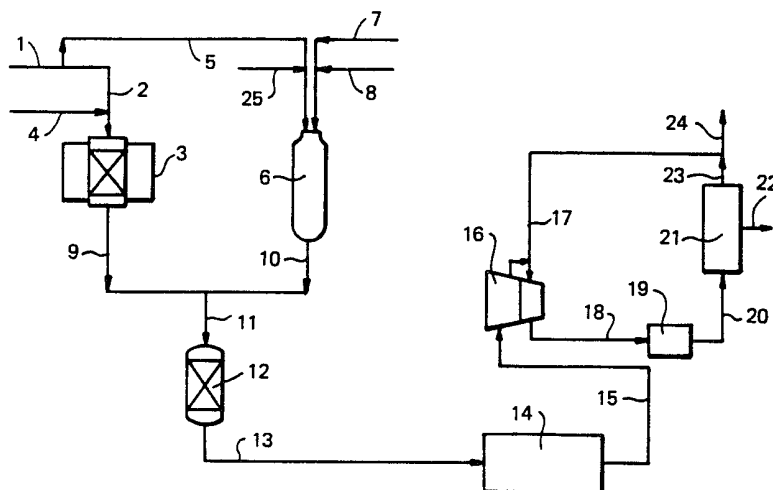




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b>  <b>C01B 3/34</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/15999</b>  <b>(43) International Publication Date:</b> 19 August 1993 (19.08.93)
<b>(21) International Application Number:</b> PCT/GB93/00329 <b>(22) International Filing Date:</b> 17 February 1993 (17.02.93) <b>(30) Priority data:</b> 9203375.2                      18 February 1992 (18.02.92)    GB <b>(71) Applicant (for all designated States except US):</b> DAVY McKEE (LONDON) LIMITED [GB/GB]; Davy House, 68 Hammersmith Road, London W14 8YW (GB). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> HILES, Andrew, George [GB/GB]; 12 Grimsdyke Road, Hatch End, Pinner, Middlesex HA5 4PH (GB). <b>(74) Agent:</b> EYLES, Christopher, Thomas; W.P. Thompson & Co., High Holborn House, 52-54 High Holborn, London WC1V 6RY (GB).		<b>(81) Designated States:</b> AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

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

Synthesis gas is prepared from a hydrocarbon feedstock, e.g. natural gas, liquefied petroleum gas, a naphtha, or a gas oil, by subjecting a part thereof to steam reforming and another part to partial oxidation. The hot gas stream from the steam reformer (3) at a temperature of about 650 °C to about 950 °C and 30 bar to 60 bar contains typically up to 20 % or more of unconverted hydrocarbon and is mixed with the hot gas from the partial oxidation unit (6) which is at the same pressure as the hot gas from the steam reformer (3) and at a temperature of about 1200 °C to about 1500 °C. The mixed stream at a temperature of about 1100 °C to about 1200 °C can be passed through a secondary reforming zone (12) to reduce the methane content in the mixed stream to about 2 % to about 5 % or more on a dry gas basis. The exit gas from the secondary reformer (12) can then be cooled and compressed for use, for example, for methanol synthesis. By adjusting the ratio of the amounts of hydrocarbon feedstock fed to the steam reformer and to the partial oxidation unit, the steam: carbon ratio in the steam reformer, and the oxygen: carbon ratio for the partial oxidation unit, the stoichiometry of the resulting synthesis gas can be adjusted to a desired value.

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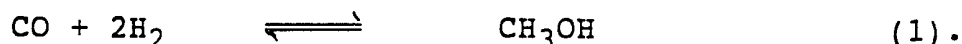
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Process for the production of synthesis gas

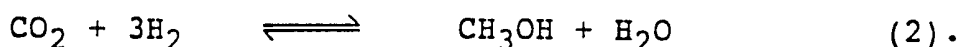
This invention relates to a process for the production of synthesis gas.

Synthesis gas is the name given to mixtures of carbon oxides and hydrogen which are produced on a very large scale from a carbonaceous feedstock, such as natural gas. Such mixtures are used in the manufacture of various industrial chemicals, particularly for production of methanol and ammonia, as well as for production of liquid synthetic fuels by the Fischer-Tropsch process. Synthesis gas is also used in hydroformylation of olefins to yield aldehydes.

For maximum efficiency the composition of the synthesis gas should in most cases be as near stoichiometric as possible for the intended end use thereof. For example, for production of methanol it is desirable to use a synthesis gas which has an approximately 2:1 hydrogen:carbon monoxide molar ratio because this is what the stoichiometry of the methanol synthesis reaction demands:

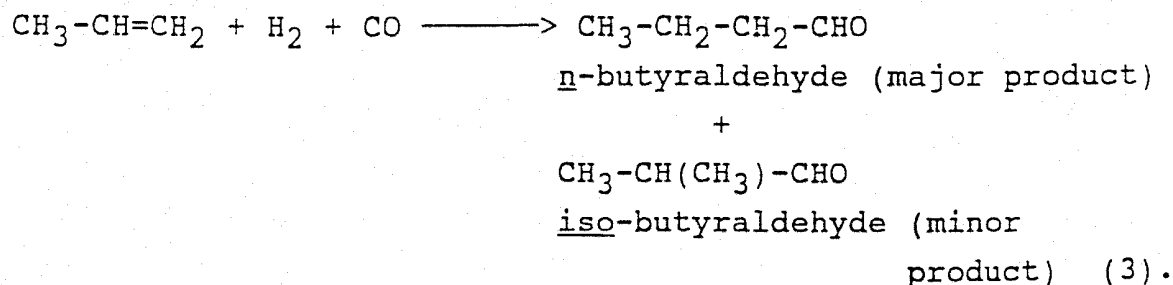


Carbon dioxide also forms methanol but the stoichiometry for this reaction requires a 3:1 hydrogen:carbon dioxide molar ratio:-

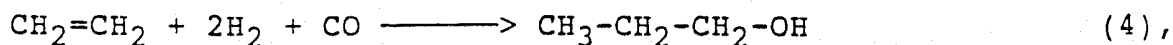


On the other hand a synthesis gas for production of an aldehyde by hydroformylation should have an approximately 1:1  $\text{H}_2$ :CO molar ratio because the stoichiometry requires this ratio. Thus, for example, propylene can be hydroformylated in the presence of a rhodium complex catalyst, e.g.  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ , according to the following reaction:

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If hydroformylation of an olefin to form directly the corresponding alcohol is to be practised, for example:

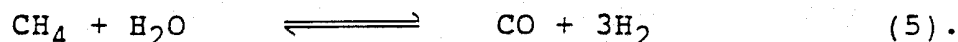


then a synthesis gas with an approximately 2:1 H<sub>2</sub>:CO molar ratio is desirable.

Whilst carbon dioxide can be tolerated in a synthesis gas for production of methanol, its presence in a synthesis gas for hydroformylation or for use in Fischer-Tropsch reactions is undesirable.

Two major routes to synthesis gas are steam reforming of hydrocarbons and partial oxidation of hydrocarbons.

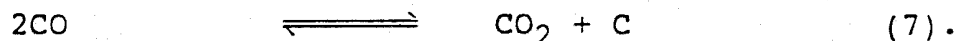
Taking natural gas, the major constituent of which is methane, as an example of a typical hydrocarbon feedstock for steam reforming, the primary reaction concerned is:



In the presence of steam the following reaction occurs:



The potential also exists for the deposition of carbon by the following reaction:



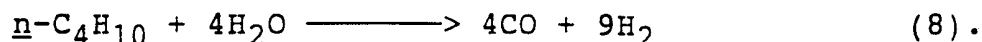
While reactions (6) and (7) are exothermic, reaction (5) is strongly endothermic.

In a commercial plant the hydrocarbon feedstock is desulphurised, if necessary, admixed with steam and passed through catalyst filled tubes mounted in a reforming furnace. In order to convert as much feedstock to synthesis gas as possible it is normal to operate at moderate pressure, e.g.

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about 18 bar to about 20 bar, and at high temperature, e.g. 900°C. Under such conditions the effluent gas typically contains about 2 to 5% or more methane on a dry gas basis. Use of higher pressures or lower temperatures results in more slippage of methane; hence at about 40 bar and 850°C the effluent gas from the steam reformer tubes can contain up to 20% or more methane on a dry gas basis.

If methane is replaced by a higher hydrocarbon feedstock, such as n-butane, then a similar equation can be written for the steam reforming reaction, for example:

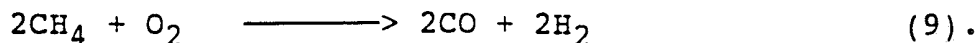


In this case the carbon oxides:H<sub>2</sub> molar ratio is higher than in the case of methane.

It will be appreciated that the temperature and pressure conditions typically used in a steam reformer impose heavy demands upon the materials of construction of the reformer tubes in particular. In practice the tubes are normally operated close to their metallurgical limit and exhibit notable creep with time. Eventually tube failure is unavoidable.

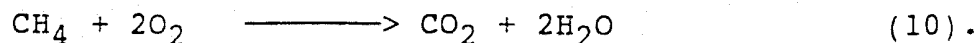
Partial oxidation is an alternative method of producing synthesis gas. Air is commonly used as oxidant in the production of synthesis gas for production of ammonia, since the aim is to produce eventually an approximately 3:1 H<sub>2</sub>:N<sub>2</sub> mixture. On the other hand for production of synthesis gas for hydroformylation, where nitrogen would be an undesirable constituent of the synthesis gas and would accumulate in the conventional gas recycle loop around the hydroformylation reactor, pure oxygen is normally used. Hence an air separation plant is usually located in the vicinity of a partial oxidation plant.

Partial oxidation is an exothermic, non-catalytic process:



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A certain amount of further oxidation is unavoidable which, for the sake of simplicity, can be expressed as:



This process can be carried out at, for example, 40 bar or higher in a pressure vessel with a refractory lining and produces a gas mixture with an exit temperature in the region of 1200°C to 1500°C. Despite the high gas temperatures involved, metallurgical problems do not normally arise in practice due to the use of a refractory lining to the pressure vessel. At the temperatures used, the conversion of methane to carbon oxides and hydrogen according to equations (9) and (10) is essentially complete. Hence the exit gases from the partial oxidation reactor are substantially free from unreacted hydrocarbons, e.g. methane.

In the synthesis of methanol the methanol synthesis loop is typically operated at a pressure of from about 50 bar to about 100 bar. Hence compression from the synthesis gas production pressure to methanol synthesis pressure is necessary. When using natural gas as the hydrocarbon feedstock production of synthesis gas at 40 bar has the advantage that this is a typical pipeline pressure used for transport of natural gas. Hence there is an advantage in generating the synthesis gas at as high a pressure as possible so as to reduce the costs associated with compression of synthesis gas to methanol synthesis pressure.

A synthesis gas for methanol synthesis can be characterised by its SM ratio which is defined as:

$$\text{SM} = \frac{2 \text{ (moles CO)} + 3 \text{ (moles CO}_2\text{)}}{\text{moles H}_2}$$

For methanol synthesis it is desirable to use a synthesis gas with an SM ratio in the range of from about 0.9 to about 1.1 and even more preferably close to one. However, steam

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reforming of natural gas gives a hydrogen-rich gas mixture of carbon oxides and hydrogen which normally contains excess hydrogen for methanol synthesis, while partial oxidation yields a carbon oxides-rich mixture of carbon oxides and hydrogen which is deficient in hydrogen for methanol synthesis. Accordingly there have been a number of proposals to subject part of the feedstock only to steam reforming and the remainder to partial oxidation so as to achieve a mixed synthesis gas of the required composition. A similar variation in the synthesis gas compositions can be achieved from other gaseous or vaporisable liquid hydrocarbon feedstocks containing a higher number of carbon atoms, e.g. naphtha or a gas oil fraction, by the two different processes.

One procedure proposed for production of synthesis gas for methanol production involves use of a pair of essentially separate, parallel plants, one using steam reforming to convert the hydrocarbon feedstock to synthesis gas and the other using partial oxidation. According to this proposal the feedstock for the steam reforming plant is desulphurised, mixed with steam, pre-heated and reformed at a temperature in the region of 900°C and at a pressure in the region of from about 18 bar to about 20 bar in the presence of a steam reforming catalyst to produce a hydrogen rich stream, that is to say a synthesis gas with a higher H<sub>2</sub>:carbon oxides ratio than desired. This is then passed through a reformed gas boiler and through various heat recovery stages, ending with a condenser to remove the process condensate. The resulting gas is typically at a pressure of about 15 bar. This is then compressed to about 40 bar or higher in the first stage of a make-up gas compressor for the methanol synthesis loop. In the parallel plant the natural gas feedstock at about 40 bar or higher is subjected to partial oxidation by reaction with high purity

oxygen. The exit temperature from the partial oxidation reactor is typically in the range of from about 1200°C to about 1500°C. The resulting CO-rich synthesis gas stream, that is to say a synthesis gas stream that is richer in CO than the desired synthesis gas stream with an SM value of one, is typically passed in turn through a waste heat boiler, a carbon scrubber, and further heat recovery stages which may include, for example, a boiler feed water heater and a reboiler for one of the methanol distillation columns, and finally a condenser, before being admixed with the synthesis gas from the steam reforming train which has already been compressed to about 40 bar or higher. The combined stream is then further compressed to methanol synthesis pressure, e.g. to a pressure in the range of from about 50 bar to about 100 bar. By feeding an appropriate proportion of the hydrocarbon feedstock to the two separate synthesis gas trains, a final synthesis gas with the appropriate stoichiometry for methanol synthesis is obtained. However, essentially two separate plants are required, each with its own heat recovery equipment.

In GB-A-1569014 there is proposed a process for producing from a desulphurised hydrocarbon containing feedstock a synthesis gas having essentially the stoichiometric composition required for methanol synthesis in which part of the feedstock is subjected to steam reforming to give an effluent gas containing hydrogen at a temperature between 650°C and 880°C. This gaseous reformer effluent is then admixed with the rest of the feedstock, which has been preheated to over 350°C and has bypassed the steam reformer. The mixture of reformed gas and bypassed hydrocarbon feedstock is then reacted with an oxygen-rich gas in a secondary reforming reactor operating under essentially adiabatic conditions and containing a bed of reforming catalyst so as to produce a synthesis gas at a



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minimum temperature of 880°C and containing less than 7% of methane on a dry gas basis. Operation at a pressure of between about 40 and 120 bar is preferred. In this process the steam reformer is operated at a higher pressure and lower temperature than usual; although this results in a lower conversion of the methane or other hydrocarbon feedstock, the unconverted hydrocarbon feedstock is available as a feedstock for the subsequent partial oxidation step which occurs in the secondary reforming reactor.

There are, however, a number of significant problems with the process proposed in GB-A-1569014. For example, when a hot reformer gas is mixed with fresh feed gas which has bypassed the steam reformer, a mixed feedstock is obtained for the oxygen blown secondary reformer which contains a significant proportion of hydrogen, small proportions of carbon oxides, and excess steam, as well as the fresh hydrocarbon feed. This mixture is then burnt with high purity oxygen. The design of the burner and of the combustion zone is critical because there is the risk of impingement of the extremely hot flame on the vessel wall, which could cause a reactor failure and hence pose a very major safety hazard, and because there is also the risk of flame or radiant heat impact on the catalyst, which is somewhat less serious from a safety standpoint but is still an important operating criterion.

It is believed that both of these problems, i.e. impingement of the hot flame on the vessel wall and damage to the catalyst, have occurred in practice in commercial plants built and operating according to the teachings of GB-A-1569014.

The burner design for such a plant is complicated by the fact that it has to operate with a wide mixture of combustible gases in the feed gas thereto, ranging from

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hydrogen to methane and higher hydrocarbons, which have significantly different burning velocities and combustion kinetics. Moreover the effluent gas from the steam reformer is subject to variations in flow rates and composition due to control fluctuations, changes in catalyst performance, and reaction equilibria. Hence there is the added problem of controlling the feedstock composition to the burner, which is obtained by mixing hot gas from the steam reforming reactor with fresh gas, which is at a substantially different temperature, prior to combustion.

There is accordingly a need to provide an improved process for the production of synthesis gas of a desired stoichiometry from a hydrocarbon feedstock, such as methane, natural gas, liquefied petroleum gas, naphtha or a gas oil fraction. There is a further need to provide a process for producing synthesis gas of desired stoichiometry in which the risks to the safety of the plant and of damage to the catalyst associated with mixing a hot hydrogen-rich stream, fresh hydrocarbon feed and an oxygen-containing gas are obviated.

The present invention accordingly seeks to provide an improved process for the production of synthesis gas in which the risks associated with mixing of oxygen-containing gases with a hot hydrogen-containing gas are substantially obviated. It further seeks to provide a process for production of synthesis gas of desired stoichiometry using a combination of steam reforming and partial oxidation in which a single set of heat recovery equipment can be used. It further seeks to provide a process for the production of synthesis gas of desired stoichiometry from natural gas or other hydrocarbon feedstock which can be operated efficiently at higher than normal reforming pressures, thereby reducing the costs associated with further compression to the pressure required for a subsequent

synthesis step, such as methanol synthesis.

According to the present invention there is provided a process for the production of a synthesis gas comprising:

(a) providing (A) a primary reforming zone containing a charge of a steam reforming catalyst, and (B) a partial oxidation zone;

(b) supplying to the primary reforming zone at a first predetermined rate a first stream of a hydrocarbon feedstock;

(c) supplying steam to the primary reforming zone in a first predetermined ratio relative to the hydrocarbon feedstock of the first stream;

(d) maintaining the primary reforming zone under temperature and pressure conditions conducive to formation, by steam reforming of the hydrocarbon feedstock, of a gaseous mixture comprising carbon oxides and hydrogen;

(e) recovering from the primary reforming zone a first gaseous product stream comprising carbon oxides, hydrogen, methane, and steam at a first elevated pressure and at a first elevated temperature;

(f) supplying to the partial oxidation zone at a second predetermined rate a second stream of the hydrocarbon feedstock;

(g) supplying an oxygen containing gas to the partial oxidation zone in a second predetermined ratio relative to the hydrocarbon feedstock of the second stream and in an amount corresponding to at least the stoichiometric amount required for partial oxidation of the second stream of the hydrocarbon feedstock;

(h) maintaining the partial oxidation zone under partial oxidation conditions;

(i) recovering from the partial oxidation zone a second gaseous product stream comprising carbon oxides, hydrogen

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and steam at a second elevated temperature in excess of the first elevated temperature and at a second pressure which is substantially the same as the first pressure;

(j) admixing the first and second gaseous product streams to form a mixed gaseous stream at a third temperature intermediate the first and second temperatures and at a third pressure substantially the same as the first and second pressures; and

(k) selecting the ratio of the first and second rates in dependence upon the composition of the hydrocarbon feedstock, the first predetermined ratio and the second predetermined ratio to provide a desired carbon oxides:hydrogen ratio in the mixed gaseous stream in dependence upon the intended use thereof as a source of synthesis gas.

It will be appreciated by those skilled in the art that, in the process of the present invention, a hydrocarbon feedstock is treated in a steam reforming plant and in a partial oxidation plant connected in parallel, the hot gaseous exit streams from the steam reforming plant and from the partial oxidation plant then being mixed before any attempt is made to recover any significant amount of heat from either gaseous exit stream. In this process the relative amounts of hydrocarbon feedstock fed to the respective plants, the steam:carbon ratio of the supply to the steam reforming plant (i.e. the first predetermined ratio), and the carbon:oxygen ratio of the supply to the partial oxidation plant (i.e. the second predetermined ratio) are selected to produce a mixed gas stream with a desirable SM value at a desired temperature and pressure.

In a particularly preferred process the mixed gaseous stream of step (j) is contacted with a reforming catalyst in a secondary reforming zone to yield a final synthesis gas stream which is lower in unreacted

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hydrocarbons than mixed gaseous stream of step (j).

Preferably the temperature and pressure conditions used in the primary reforming zone include use of an inlet temperature of from about 350°C to about 750°C, more preferably from about 400°C to about 650°C, and an inlet pressure of from about 30 bar to about 60 bar. Normally the temperature and pressure conditions used in the primary reforming zone are selected to provide an exit temperature of from about 750°C to about 950°C and an exit pressure of from about 30 bar to about 60 bar.

Preferably the second gaseous product stream is recovered from the partial oxidation zone at a second temperature of from about 1200°C to about 1500°C. If further reforming of the mixed gaseous stream of step (j) is required, then it is preferred to select the second predetermined ratio so as to produce a second temperature of from about 1300°C to about 1500°C. On the other hand, if no further reforming is required, a lower second temperature may be preferred, e.g. from about 1200°C to about 1400°C, in which case the second predetermined ratio is adjusted accordingly.

In step (j) the first and second gaseous product streams are preferably mixed to form a mixed gaseous stream at a third temperature of from about 900°C to about 1200°C. If the mixed gaseous stream of step (j) is to be subjected to further reforming in a secondary reforming zone, then the third temperature is preferably from about 1000°C to about 1200°C, whereas the third temperature may be lower if no secondary reforming zone is included.

The hydrocarbon feedstock may, for example, comprise a natural gas having a methane content of from about 65% to 100%. Alternatively it may be a liquid hydrocarbon feedstock, such as a liquefied petroleum gas, a naphtha or a gas oil.

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The oxygen containing gas is normally a high purity oxygen stream obtained from an air separation plant.

In the process the SM ratio is preferably from about 0.90 to about 1.10.

If the mixed gaseous stream of step (j) is to be used directly as a source of synthesis gas without further reforming, then it is desirably cooled prior to use by passage through one or more heat recovery zones connected in series, typically selected from heat recovery units such as a waste heat boiler, a reformed gas boiler, a feed gas pre-heater, a boiler feed water heater, a heat exchanger for a distillation column reboiler, and a condenser. The cooled mixed gaseous stream, which still contains some untreated hydrocarbon feedstock, can then be compressed, as and if necessary, and/or further treated, e.g. subjected to CO<sub>2</sub> removal, ready for use in a subsequent chemical synthesis step, e.g. methanol synthesis, a Fischer-Tropsch reaction, or hydroformylation.

Alternatively the mixed gaseous stream of step (j) can be passed through a secondary reforming zone prior to passage through one or more heat recovery zones, as outlined in the preceding paragraph, prior to possible compression ready for use in a subsequent chemical synthesis step.

A further possibility is to cool the mixed gaseous stream of step (j) by direct quench.

Alternatively the mixed gaseous stream of step (j) can be contacted with a reforming catalyst in a secondary reforming zone to yield a final synthesis gas stream. This final synthesis gas stream can be passed through a heat recovery train comprising one or more heat recovery units connected in series or it can be cooled by direct quench.

It will thus be seen that the output from both the steam reforming zone and the partial oxidation zone, after mixing and possibly also secondary reforming, are passed

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though a common heat recovery system.

For large plants it may be more economic to provide two or more steam reforming zones and/or partial oxidation zones connected in parallel.

As outlined above, the process may include a secondary reforming zone through which the mixed gaseous steam of step (j) is passed. The decision whether to include a secondary reforming zone in a particular plant or not will normally be taken on economic grounds. Thus it may be more economic, under certain circumstances, to accept a certain methane slippage in the mixed gaseous stream and to feed this as synthesis gas into the methanol synthesis loop and then to recover untreated methane in the purge gas stream from the methanol synthesis loop for recycle to the synthesis gas plant. An advantage of such a procedure is that the third temperature can be reduced to a value of, for example, from about 1200°C to about 1400°C, with a consequent saving in high purity oxygen and that no secondary reforming reactor is necessary; on the other hand, the disadvantage of such a procedure is that, because of the presence of unreacted methane in the mixed gaseous stream of step (j), the volume flow rate of gas through the heat recovery train and the gas compressor for the methanol synthesis loop is correspondingly higher. For a given plant the designer can assess these factors and reach a decision on economic grounds whether it is preferable, either by reason of capital cost savings or operating cost savings or a combination of both, to include a secondary reforming reactor or to include provision for recycle of unreacted hydrocarbons from the inert gas purge from the methanol synthesis loop.

In order that the invention may be clearly understood and readily carried into effect, three preferred processes in accordance with the invention for the

production of a synthesis gas of stoichiometry suitable for methanol synthesis will now be described, by way of example only, with reference to the accompanying drawings, Figures 1 to 3 of which are each a flow diagram of a respective methanol synthesis plant.

Referring to Figure 1 of the drawings, a desulphurised natural gas is supplied to the plant in line 1 at a pressure of about 40 bar or more. Part flows on in line 2 to a steam reforming furnace 3 after having been mixed with steam supplied in line 4. The rest of the natural gas is fed by line 5 to a partial oxidation reactor 6 which is also supplied with high purity oxygen in line 7. If desired, or as necessary, steam or water can be supplied to partial oxidation reactor 6 in line 8.

The proportions of the natural gas supplied in lines 2 and 5 depend upon its composition. For example, if the natural gas has a methane content of about 70%, then approximately 60% thereof is supplied in line 2 and about 40% thereof in line 5. On the other hand if a natural gas with a methane content approaching 100% is used, then as little as about 25% of it may be fed, under appropriate circumstances, in line 2 whilst the remainder passes through line 5. Typically, however, the proportion fed in line 2 to the steam reformer when the purity of the natural gas approaches 100% methane ranges from about 40% to about 50% of the total feedstock. In accordance with conventional practice the volume of steam supplied in line 4 is significantly in excess of the stoichiometric amount required by equation (5) above (and by the analogous equations, such as equation (8), in which higher hydrocarbons replace methane) in order to suppress carbon laydown by the reaction of equation (7). Similarly slightly in excess of the stoichiometric amount of oxygen required to satisfy the requirements of equation (9) (or the analogous



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equations in which higher hydrocarbons replace methane) is supplied in line 7 to the partial oxidation reactor 6 in order to achieve the desired exit temperature.

Reforming furnace 3 is operated with a tube internal pressure of about 40 bar or higher and the exit temperature from the catalyst filled reformer tubes is typically about 750°C to about 850°C. Under these conditions the effluent gas stream in line 9 can contain up to 20% or more methane on a dry gas basis.

The catalyst in the tubes of steam reforming furnace 3 can be any of the catalysts conventionally used for steam reforming of hydrocarbons. Typical catalysts include those containing one or more of the following active components: nickel, nickel oxide, cobalt oxide, chromia and molybdenum oxide. Such an active component or components may be supported on a suitable refractory support. As examples of suitable refractory supports there can be mentioned aluminium oxide, alkaline earth oxides, zirconium oxide, and mixtures thereof. The catalyst may further include a promoter, such as thorium, cerium, caesium, an alkali metal oxide, or a mixture of two or more thereof. Further disclosure of suitable catalysts will be found, for example, in US-A-3264066, US-A-3442613, US-A-3763205, and US-A-4079017.

Partial oxidation reactor 6 is also operated at about 40 bar or higher and with an exit gas temperature of about 1350°C to about 1450°C. The quantity of oxygen admitted in line 7 is matched to the quantity of hydrocarbon feedstock supplied in line 5 so as to give the required exit temperature to achieve by equilibrium the desired composition of the gas exiting partial oxidation reactor 6 in line 10. The hot gases in lines 9 and 10 are mixed and pass on in line 11. The temperature of the gaseous mixture in line 11 is controlled to lie within the range of from

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about 1000°C to about 1200°C. Under normal circumstances this can be achieved by adjusting the conditions in the steam reforming furnace so as to produce an appropriate exit gas temperature in line 9, raising or lowering this in dependence on the mass flow in line 9 relative to the temperature and mass flow of the gas in line 10. An alternative and preferred method of adjusting the temperature of the gas mixture in line 11 involves altering the oxygen feed rate in line 7 (or the hydrocarbon feedstock rate in line 5) so as to alter the oxygen:carbon feed ratio to the partial oxidation reactor 6, thereby changing the temperature of the gases exiting in line 10. If necessary the gas in line 11 can be passed through a heater in order to raise its temperature.

The gas in line 11 can be passed to a secondary catalytic reactor 12 containing a charge of catalyst. Since it still contains both steam and methane further reforming according to equation (5) above can take place. Since the temperature is sufficiently high further reaction of methane with steam can occur to form more carbon oxides and hydrogen in passage through secondary catalytic reactor 12, which operates essentially adiabatically.

The catalyst in reactor 12 can be any of the catalysts conventionally used for steam reforming of hydrocarbons, such as those mentioned above. Preferably, however, it is one of the catalysts recommended for effecting high temperature secondary reforming.

The resulting synthesis gas in line 13 has an SM value close to one and a methane content on a dry gas basis of approximately 2 to 5% or more. It is passed through heat recovery train 14, which may include a waste heat boiler or a reformed gas boiler, a feed gas pre-heater, a boiler feed water heater, a heat exchanger for a distillation column reboiler, or other heat recovery means, and a condenser to

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remove process condensate, which is mainly condensed steam. The cooled gas passes via line 15 to a make up gas compressor 16 in which it is brought up to methanol synthesis pressure, e.g. 100 bar. Recycled gas may be fed in line 17 to a separate stage of gas compressor 16 or to a separate circulating gas compressor. The compressed gas passes on in line 18 to methanol synthesis reactor 19. A mixture of methanol and unreacted gas passes on in line 20 to methanol recovery section 21 from which product methanol is passed to purification and storage in line 22. Uncondensed material and gas pass on in line 23 to form the recycle stream in line 17. A purge gas stream is taken in line 24 to remove inert gases from the plant.

A portion of the purge gas stream in line 24 may be recycled and fed, for example, to a desulphurisation reactor (not shown) used to desulphurise the hydrocarbon feedstock. In this case the purge gas can supply any hydrogen needed in that desulphurisation reactor.

Line 25 permits steam to be admixed with the natural gas in line 5, if desired, prior to admission to partial oxidation reactor 6.

In an alternative procedure part or all of the purge gas stream in line 24 can be subjected to a physical separation method, e.g. pressure swing absorption, in order to obtain a stream rich in hydrocarbon feedstock for recycle to line 2 or line 5 and/or a stream rich in hydrogen for recycle, for example, to line 15, besides a stream relatively high in inert gases, such as nitrogen and/or argon, which is purged from the plant.

The plant of Figure 2 is similar to that of Figure 1. However, secondary reforming reactor 12 is omitted and the mixed gas stream in line 11 is fed directly to heat recovery train 14. Hence the gas feed to the gas compressor 16 in line 15 still has a significant methane content, e.g.

about 5 to about 10% on a dry gas basis, since secondary reforming has not been used. Another significant difference is that the gas stream purged from the methanol synthesis loop in line 24 is passed to a gas separation train 30. Train 30 can include a cryogenic unit which can be integrated into the air separation plant used to produce the high purity oxygen in line 7, and/or a gas separation unit using a membrane, and/or a pressure swing absorption unit. Gas separation train 30 provides separation of the gas in line 24 into a methane rich stream which is recycled in line 31, a hydrogen rich stream in line 32 (which can be used, if desired, as a source of hydrogen for use in desulphurisation of the natural gas feedstock), and an inerts rich stream in line 33 which is purged from the plant.

In Figure 3 of the drawings a natural gas stream in line 101 at pipeline pressure, e.g. 40 bar or more, is passed through a desulphurisation reactor 102 which is supplied with a hydrogen containing stream in line 103. The desulphurised natural gas in line 104 is fed by lines 105 and 106 to respective banks of catalyst filled reformer tubes 107 and 108 in a steam reforming furnace 109. Reference numeral 110 indicates the common flue gas duct for the two banks 107 and 108 of reformer tubes. Prior to entry to its respective bank of reformer tubes 107 or 108, each of the natural gas streams in lines 105 and 106 is admixed with steam from lines 111 and 112 respectively so as to provide a predetermined steam: carbon ratio in the feed mixture to the steam reformer tubes.

Further desulphurised natural gas from line 104 is fed by way of lines 113 and 114 to respective partial oxidation reactors 115 and 116 which are also fed with a mixture of high purity oxygen and steam; the oxygen supply lines are numbered 117 and 118 respectively, while the relevant steam supply lines are indicated at 119 and 120.

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Reforming furnace 109 is operated at approximately 40 bar and so as to produce an exit gas stream in each of lines 121 and 122 which is at approximately 825°C; this gas stream in each case still contains up to 20% methane on a dry gas basis besides hydrogen, carbon oxides and steam.

Partial oxidation reactors 115 and 116 are each operated at essentially the same pressure as steam reforming furnace 109 and with a carbon:oxygen ratio in the supply thereto such that the exit gas temperature in the gas streams in each of lines 123 and 124 is about 1450°C; these gas streams contain a mixture of carbon oxides, hydrogen and steam but essentially no unconverted hydrocarbon from the natural gas feedstock.

The exit gas streams in lines 121 and 123 are mixed and pass on in line 125 to a secondary reforming reactor 126. The temperature of the mixed stream in line 125 is typically about 1180°C. Similarly the streams from lines 122 and 124 are mixed to form a common feed stream in line 127, typically at a temperature of about 1180°C, for a further secondary reforming reactor 128. In passage through secondary reforming reactors 126 and 128 unconverted hydrocarbons in the gas streams in lines 125 and 127 are further converted to carbon oxides and hydrogen. Hence the methane content in the gas streams exiting the secondary reforming reactors 126 and 128 in lines 129 and 130 respectively is typically about 2% to 5% or more on a dry gas basis. These gas streams are passed through respective heat recovery units 131 and 132, e.g. reformed gas boilers, and the resulting partially cooled streams in lines 133 and 134 are combined to form a common feed stream in line 135 for a heat recovery section 136. This heat recovery section 136 can include one or more heat recovery units connected in series, such as a waste heat boiler, a boiler feed water heater, and/or a heat exchanger for a distillation column

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boiler, and finally through a condenser.

The cooled gas in line 137 is fed to a gas compressor 138 for a methanol synthesis loop in order to raise the pressure to methanol synthesis gas pressure, e.g. approximately 100 bar. The compressed make up gas in line 139 is admixed with recycled gas in line 140 and fed to the final stage of the gas compressor 138. The compressed gas is fed in line 141 to methanol synthesis reactor 141 which contains a charge of a suitable methanol synthesis catalyst, e.g. a reduced CuO/ZnO catalyst, maintained at a methanol synthesis temperature, e.g. 250°C. The resulting methanol-containing vaporous mixture flows on in line 143 to a methanol recovery section 144 which includes a condenser. Liquid crude methanol is recovered in line 145 and is passed on for refining and storage. Uncondensed material is recovered in line 146; part is recycled in line 140 whilst a purge stream from the loop is supplied in line 147 to a pressure swing absorption unit 148 to separate untreated hydrogen therefrom. Such hydrogen is supplied by way of line 103 to the desulphurisation reactor 102. Gas is purged from the plant in line 149.

Steam can be admixed with the hydrocarbon feed to the partial oxidation reactors 115 and 116 by means of lines 150 and 151.

Although the process of the invention has been described in relation to methanol synthesis, it will be readily recognised by those skilled in the art that the teachings of the invention can be applied also to the production of synthesis gas for ammonia synthesis. In this case air or a mixture of air and oxygen is used in place of the high purity oxygen in line 7 in the plant of Figure 1 and methanol synthesis reactor 19 is replaced by an ammonia synthesis reactor, the gas in line 11 being subjected to a shift reaction and CO<sub>2</sub> removal prior to compression and the

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gas in line 15 having an approximately 3:1  $H_2:N_2$  molar ratio. Alternatively methanol synthesis reactor 19 can be replaced by a hydroformylation reactor supplied with a suitable  $\alpha$ -olefin, such as propylene; in this case the proportion of natural gas supplied in line 2 and 5 and the conditions in steam reformer 3 and partial oxidation reactor 6 are chosen to provide an approximately 1:1  $H_2:CO$  molar mixture in line 15, whilst an aldehyde, e.g. n-butyraldehyde, is recovered in line 22 in place of methanol. In this case a  $CO_2$  removal zone may be included in line 15.

The invention is further illustrated in the following Examples.

#### Example 1

A natural gas containing 96% methane with the balance comprising ethane, propane, carbon dioxide and nitrogen is supplied to a plant of the type illustrated in Figure 1 in line 1 at a rate of 100 kmol/h at 40 bar. 45 kmol/h of this stream is fed to primary reforming furnace 3 in line 2 after having been admixed with steam from line 4. The gas in line 9 is at 40 bar and at a temperature of 750°C. Its composition is:

<u>Component</u>	<u>% by volume</u>	<u>Flow rate (kmol/h)</u>
$H_2O$	45.6	96.4
$H_2$	32.6	69.0
CO	3.4	7.2
$CO_2$	6.0	12.6
$CH_4$	12.2	25.9
$N_2 + Ar$	0.2	0.5

The remaining 55 kmol/h of the natural gas is fed in line 5 to partial oxidation reactor 6 which is also supplied in line 7 with 46.2 kmol/h of oxygen and in line 8 with 92.3 kmol/h of steam. There exits from partial oxidation reactor 6 a gas stream in line 10 at 1450°C. Upon mixing the two streams in lines 9 and 10 the resulting mixture in line 11

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is at 1135°C. This flows through secondary reformer 12. The resulting synthesis gas exits at 38 bar and 930°C in line 13 with the following composition:

<u>Component</u>	<u>% by volume</u>	<u>Mass rate (kmol/h)</u>
H <sub>2</sub> O	37.0	186.5
H <sub>2</sub>	42.7	215.0
CO	11.5	58.1
CO <sub>2</sub>	6.9	34.8
CH <sub>4</sub>	1.7	8.6
N <sub>2</sub> + Ar	0.2	1.2

This stream has an SM value of 1.03 and a methane content (on a dry gas basis) of 2.7%.

#### Example 2

In this Example a plant of the type illustrated in Figure 1 is used. The feedstock is a natural gas having the following composition:

<u>Component</u>	<u>% by volume</u>
CH <sub>4</sub>	71.3
CO <sub>2</sub>	1.6
C <sub>2</sub> H <sub>6</sub>	11.2
C <sub>3</sub> H <sub>8</sub>	8.8
<u>n</u> -C <sub>4</sub> H <sub>10</sub>	1.9
<u>i</u> -C <sub>4</sub> H <sub>10</sub>	3.5
<u>n</u> -C <sub>5</sub> H <sub>12</sub>	1.0
<u>n</u> -C <sub>8</sub> H <sub>18</sub>	0.4
N <sub>2</sub> + Ar	0.3

The flow rate in line 1 is 100 kmol/h, 60% of which is supplied in line 2 to steam reformer 3, whilst 40% of the natural gas is fed in line 5 to partial oxidation unit 6. The exit temperature and pressure of the gas in line 9 from the steam reformer 3 are 850°C and 40 bar respectively; its composition is:



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<u>Component</u>	<u>% by volume</u>	<u>Mass flow (kmol/h)</u>
H <sub>2</sub> O	37.7	165.4
H <sub>2</sub>	41.6	182.4
CO	8.0	35.2
CO <sub>2</sub>	6.4	27.9
CH <sub>4</sub>	6.3	27.8
N <sub>2</sub> + Ar	Trace	0.2

O<sub>2</sub> is supplied to partial oxidation unit 6 in line 7 at a rate of 44.8 kmol/h in admixture with 89.7 kmol/h steam from line 8. The gas from the partial oxidation unit 6 in line 10 is at 1450°C and 40 bar. After admixture of the two hot gas streams from lines 9 and 10 the temperature of the mixed stream in line 11 is 1067°C. The gas in line 13 is at 944°C and 38 bar and its composition is:

<u>Component</u>	<u>% by volume</u>	<u>Mass flow (kmol/h)</u>
H <sub>2</sub> O	34.7	249.7
H <sub>2</sub>	44.1	317.5
CO	12.7	91.2
CO <sub>2</sub>	6.6	47.8
CH <sub>4</sub>	1.7	12.5
N <sub>2</sub> + Ar	Trace	0.5

This stream has an SM value of 1.03 and a methane content (on a dry gas basis) of 2.7%.

It will be appreciated by those skilled in the art that the apparatus illustrated in the drawings has the following advantages compared with a conventional steam reforming plant:

(1) it can be operated at a higher pressure (e.g. 40 bar) than a conventional steam reforming plant, which is typically limited to 20 bar or so, and the otherwise unacceptably high slippage of methane or other hydrocarbon feedstock through the steam reforming tubes, corresponding to an effluent gas analysis comprising up to 20% or more methane on a dry gas basis, can be tolerated;

(2) it replaces a significant part of the catalyst duty of the steam reformer by incorporating a secondary reforming reactor downstream from where the two gas streams mix, i.e. one from the steam reformer and the other from the partial oxidation reactor, and this secondary reactor can be an adiabatic reactor, which is much cheaper than a multi-tube furnace reactor of the type normally used for steam reforming;

(3) use of combined steam reforming and partial oxidation can offer improved economics, particularly in large capacity plants, and produces lower emissions of carbon dioxide and nitrogen oxides compared to steam reforming alone by virtue of reducing the reforming furnace heat load and consequently reducing the flue gas emissions therefrom.

In addition, compared to the proposals of GB-A-1569014, because the combustion step is separated from the secondary catalytic reforming step, the invention:

(a) avoids the risks associated with the use of a flame in proximity to the secondary reforming catalyst by physically separating the combustion zone from the catalytic zone and thereby avoids the potential for flame impingement upon the catalyst or radiant heat damage to the catalyst; and

(b) avoids the need for the primary steam reformer outlet stream to pass through the partial oxidation combustion zone and hence there is less danger of flame instability. Thus hydrogen in the steam reformer outlet gas is not mixed with fresh hydrocarbon feedstock prior to mixing with the oxygen used for partial oxidation. Instead only hydrocarbon feedstock, e.g. natural gas, is fed to the burner of the partial oxidation reactor in accordance with conventional partial oxidation practice which has been built up over the last 30 years or more. By mixing the effluent

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gas from the steam reformer with the exit gas from the partial oxidation reactor only after combustion has occurred, the effects of variation in composition of the respective exit streams caused by control fluctuation and variations in the feedstock composition are of little consequence. Moreover the degree of mixing of the two exit gas streams is not critical to the operation of any downstream secondary reforming reactor and/or heat recovery equipment. Also higher temperatures and longer residence times can be achieved in the partial oxidation reactor for a given reactor size thereby reducing the potential for carbon and soot formation. Furthermore the duty imposed on the secondary catalyst bed is significantly reduced.

Another benefit of using the process of the invention compared with that of GB-A-1569014 is that it minimises or substantially avoids the potential for carbon or soot formation. A potential problem with both steam reforming and partial oxidation of natural gas is the formation of carbon. This potential to form carbon increases with feedstocks that are rich in higher hydrocarbons and particularly when the feedstock composition is liable to change, for instance if the feedstock comes direct from a pipeline. The potential for forming carbon in a partial oxidation reactor supplied with natural gas is very low when operated at the high temperatures proposed for use in the process of the present invention since there is virtually no hydrocarbon remaining after the combustion step in the partial oxidation reactor.

CLAIMS

1. A process for the production of a synthesis gas comprising:
  - (a) providing (A) a primary reforming zone containing a charge of a steam reforming catalyst, and (B) a partial oxidation zone;
  - (b) supplying to the primary reforming zone at a first predetermined rate a first stream of a hydrocarbon feedstock;
  - (c) supplying steam to the primary reforming zone in a first predetermined ratio relative to the hydrocarbon feedstock of the first stream;
  - (d) maintaining the primary reforming zone under temperature and pressure conditions conducive to formation, by steam reforming of the hydrocarbon feedstock, of a gaseous mixture comprising carbon oxides and hydrogen;
  - (e) recovering from the primary reforming zone a first gaseous product stream comprising carbon oxides, hydrogen, methane, and steam at a first elevated pressure and at a first elevated temperature;
  - (f) supplying to the partial oxidation zone at a second predetermined rate a second stream of the hydrocarbon feedstock;
  - (g) supplying an oxygen containing gas to the partial oxidation zone in a second predetermined ratio relative to the hydrocarbon feedstock of the second stream and in an amount corresponding to at least the stoichiometric amount required for partial oxidation of the second stream of the hydrocarbon feedstock;
  - (h) maintaining the partial oxidation zone under partial oxidation conditions;
  - (i) recovering from the partial oxidation zone a second gaseous product stream comprising carbon oxides, hydrogen and steam at a second elevated temperature in excess of the

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first elevated temperature and at a second pressure which is substantially the same as the first pressure;

(j) admixing the first and second gaseous product streams to form a mixed gaseous stream at a third temperature intermediate the first and second temperatures and at a third pressure substantially the same as the first and second pressures; and

(k) selecting the ratio of the first and second rates in dependence upon the composition of the hydrocarbon feedstock, the first predetermined ratio and the second predetermined ratio to provide a desired carbon oxides:hydrogen ratio in the mixed gaseous stream in dependence upon the intended use thereof as a source of synthesis gas.

2. A process according to claim 1, in which the mixed gaseous stream of step (j) is passed through a heat recovery section comprising one or more heat recovery units connected in series to form a final synthesis gas stream.

3. A process according to claim 1, which includes the step of cooling the mixed gaseous stream of step (j) by direct quench.

4. A process according to claim 1, in which the mixed gaseous stream of step (j) is contacted with a reforming catalyst in a secondary reforming zone to yield a final synthesis gas stream.

5. A process according to claim 4, in which the final synthesis gas stream is passed through a heat recovery train comprising one or more heat recovery units connected in series.

6. A process according to claim 4, in which the final synthesis gas stream is cooled by direct quench.

7. A process according to any one of claims 1 to 6, in which the temperature and pressure conditions used in the primary reforming zone include use of an inlet temperature from about 350 °C to about 750 °C and an inlet pressure of from about 30 bar to about 60 bar.

8. A process according to any one of claims 1 to 7, in which the temperature and pressure conditions used in the primary reforming zone are selected to provide an exit temperature of from about 650°C to about 950°C and an exit pressure of from about 30 bar to about 60 bar.

9. A process according to any one of claims 1 to 8, in which the second gaseous product stream is recovered from the partial oxidation zone at a second temperature of from about 1200°C to about 1500°C.

10. A process according to any one of claims 1 to 9, in which in step (j) the first and second gaseous product streams are mixed to form a mixed gaseous stream at a third temperature of from about 900°C to about 1200°C.

11. A process according to any one of claims 1 to 10, in which the hydrocarbon feedstock comprises a natural gas having a methane content of from about 65% to 100%, a liquefied petroleum gas, a naphtha, or a gas oil.

12. A process according to any one of claims 1 to 11, in which the oxygen containing gas is essentially pure oxygen.

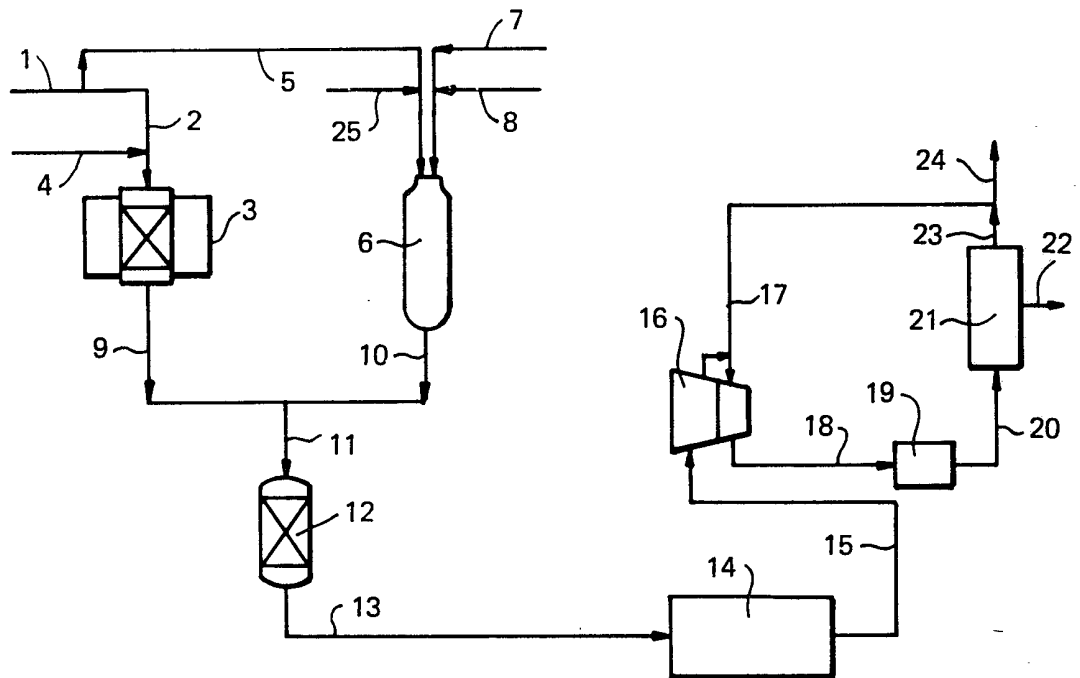
- 29 -

13. A process according to any one of claims 1 to 12,  
in which the SM ratio, where

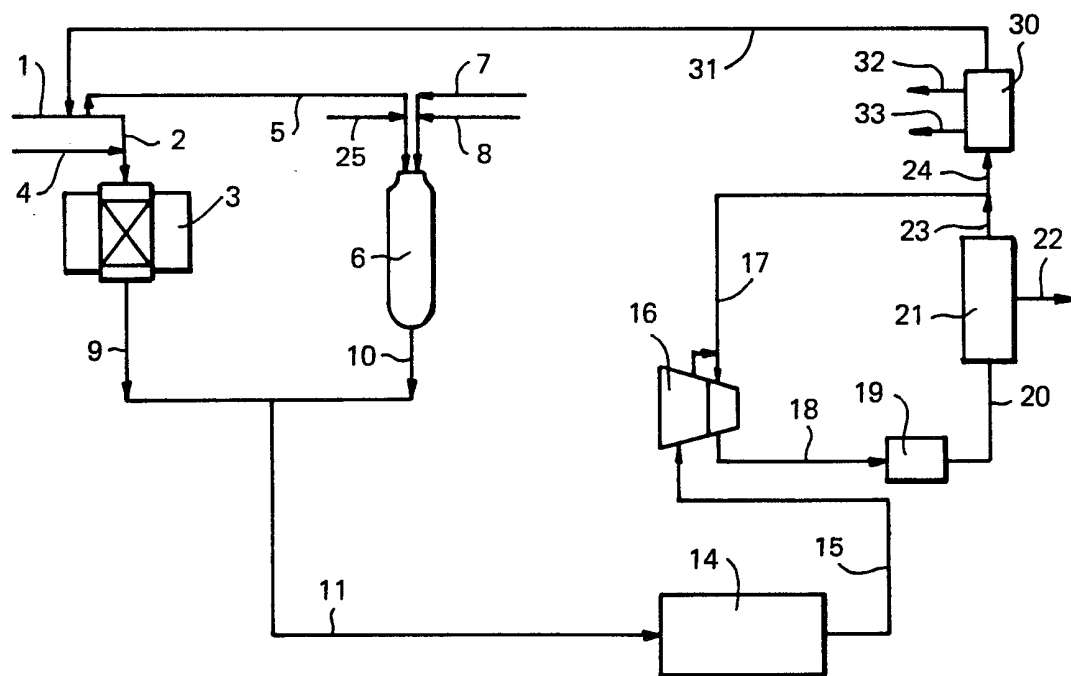
$$SM = \frac{2 \text{ (moles CO)} + 3 \text{ (moles CO}_2\text{)}}{\text{moles H}_2}$$

is from about 0.90 to about 1.10.

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**FIG. 1**



**FIG. 2**



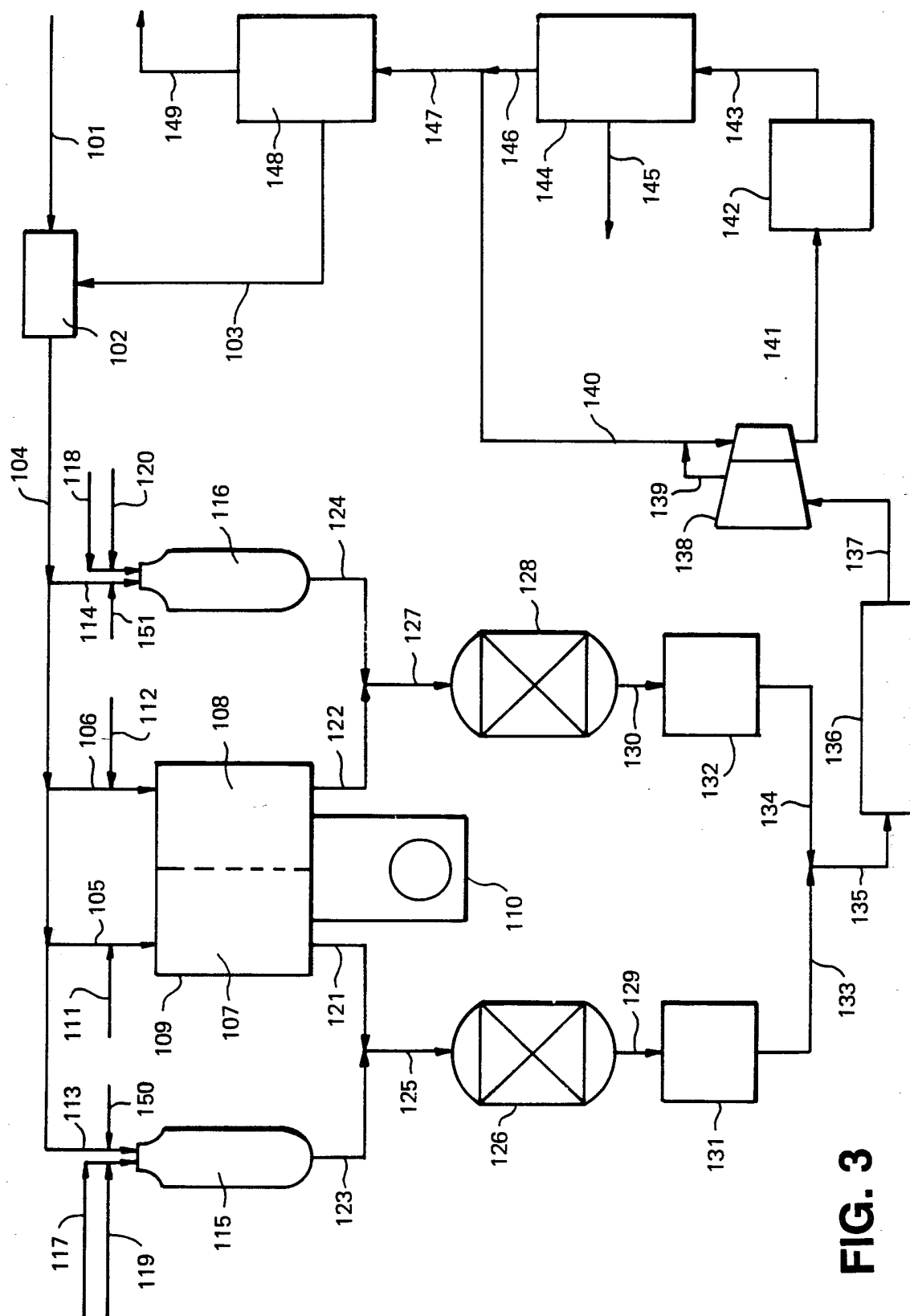


FIG. 3

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/00329

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>4</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>5</sup>: C 01 B 3/34

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System

Classification Symbols

IPC<sup>5</sup> : C 01 B

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	GB, A, 1 569 014 (BANQUY) 11 June 1980 (11.06.80), claim 1. ---	1
A	US, A, 3 264 066 (QUARTULLI & KAO) 02 August 1966 (02.08.66), the whole document. ---	1
A	US, A, 3 442 613 (GROTZ) 06 May 1969 (06.05.69), the whole document. ----	1

\* Special categories of cited documents: <sup>14</sup>

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

"E" earlier document but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"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

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

17 May 1993

Date of Mailing of this International Search Report

09.06.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

MARCHART e.h.

## ANHANG

## ANNEX

## ANNEXE

zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

to the International Search  
Report to the International Patent  
Application No.

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/GB 93/00329 SAE 70211

In diesem Anhang sind die Mitglieder  
der Patentfamilien der im obenge-  
nannten internationalen Recherchenbericht  
angeführten Patentdokumente angegeben.  
Diese Angaben dienen nur zur Unter-  
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family  
members relating to the patent documents  
cited in the above-mentioned inter-  
national search report. The Office is  
in no way liable for these particulars  
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of information.

La présente annexe indique les  
membres de la famille de brevets  
relatifs aux documents de brevets cités  
dans le rapport de recherche inter-  
national visée ci-dessus. Les renseigne-  
ments fournis sont donnés à titre indica-  
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Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
GB A 1569014	11-06-80	AU A1 30252/77 AU B2 512311 CA A1 1076361 DE A1 2758395 DE C2 2758395 EG A 13184 ES A1 467603 ES A5 467603 FR A1 2372116 FR B1 2372116 IT A0 7847841 IT A 1105173 JP A2 53116294 JP B4 55046961 MX U 5666 MY A 100/84 NO A 774416 NO B 153564 NO C 153564 US A 4888130 US A 4999133	10-05-79 02-10-80 29-04-80 28-09-78 27-01-83 31-12-80 16-10-78 14-11-78 23-06-78 27-05-83 30-01-78 28-10-85 11-10-78 27-11-80 06-12-83 31-12-84 25-09-78 06-01-86 16-04-86 19-12-89 12-03-91
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