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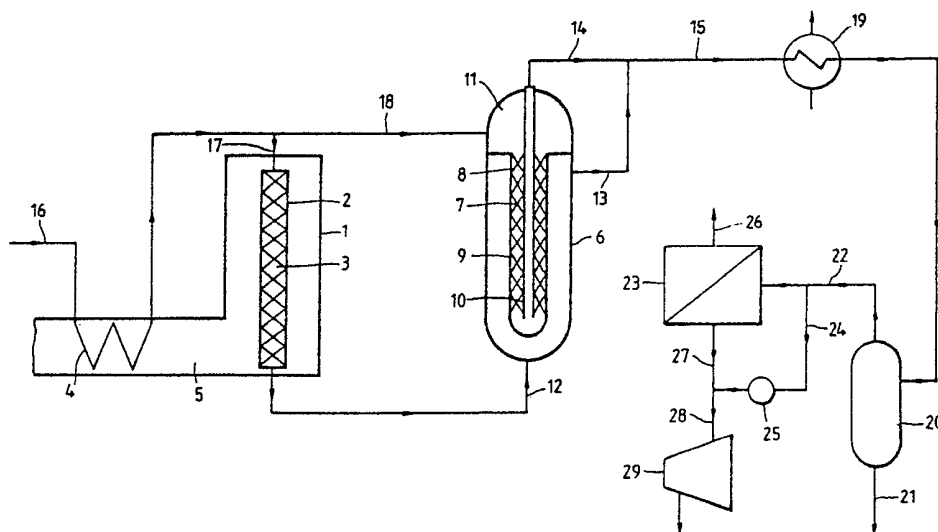
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Methanol synthesis gas production by steam reforming of a hydrocarbon feedstock.

A process for the production of methanol synthesis gas comprises catalytic steam reforming of a major hydrocarbon/steam stream 17 in tubes 2 heated by means of a fired furnace 1 and catalytic steam reforming of a minor hydrocarbon/steam stream 18 in auxiliary reformer tubes 9 heated by the reformed major stream 12, and mixing the reformed minor stream 14 with the reformed major stream, before or after using the reformed major gas stream for heating the auxiliary reformer tubes. The resultant mixed reformed gas 15, after cooling and removal of condensed water, is then subjected to a membrane separation stage 23 to separate a hydrogen-containing permeate stream 26 leaving the synthesis gas as the impermeate stream 27.



EP 0 382 442 A2

Methanol

This invention relates to methanol and in particular to the production of methanol synthesis gas, ie a gas containing hydrogen and carbon oxides, by steam reforming a hydrocarbon feedstock such as natural gas.

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Background to the Invention

The steam reforming process is well known and involves passage of a mixture of the feedstock and steam over a reforming catalyst, usually disposed in externally heated tubes. However, particularly where the feedstock is predominantly methane, eg where the feedstock is natural gas, the synthesis gas contains an excess of hydrogen over that required for methanol synthesis. In synthesis gas having stoichiometric proportions of hydrogen and carbon oxides for methanol synthesis, the ratio (R) of the molar amount of hydrogen (less the molar amount of carbon dioxide) to the total molar amount of carbon oxides equals 2. Typically synthesis gas made by the conventional steam reforming process has a ratio R of the order of 2.5 or more, eg about 3.

It has been proposed in US-A-4337170 to provide a fired reformer and an auxiliary reformer. Part of the feedstock bypasses the primary reformer and is fed to the auxiliary reformer and reformed in catalyst-containing tubes disposed therein. The reformed gas from the auxiliary reformer tubes is mixed with the reformed gas from the fired reformer and the mixture of reformed gases is then fed, in counter-current to the gas undergoing reforming in the auxiliary reformer tubes, past the tubes of the auxiliary reformer so as to supply the heat required for the reforming in the auxiliary reformer tubes. As a result of the use of an auxiliary reformer, the throughput of a steam reforming stage can be increased and so this development is of use for uprating an existing plant.

For metallurgical and efficiency reasons, the pressure at which the reforming stage is conducted is generally in the range 10 to 40 bar abs. However, methanol synthesis is normally conducted at higher pressures, eg 50 to 120 bar abs. or even higher in old processes, and so, after removing unreacted steam but prior to use for methanol synthesis, the synthesis gas has generally to be compressed. Because the reforming process gives a gas containing more hydrogen than is required in the methanol synthesis gas, energy is unnecessarily consumed in the compression of this excess of hydrogen. Furthermore, the provision of an auxiliary reformer giving an increase in the throughput of the reforming stage increases the amount of gas that has to be compressed. Not only does this mean that more power is required to effect the compression, but if an existing plant is being modified, the existing synthesis gas compressor may be inadequate to handle the increased amount of synthesis gas.

It has been proposed in GB-A-2140801 to produce methanol synthesis gas by a process involving partial oxidation of a hydrocarbon feedstock with air, followed by subjecting the resultant gas stream to the shift reaction and then membrane separation to remove most of the nitrogen introduced by the use of air in the partial oxidation step. However such a process, unless employing preliminary preheating, using a fired heater, and adiabatic steam reforming stages, gives a hydrogen-deficient synthesis gas. Furthermore such a process is not amenable to the uprating of a plant having a conventional primary reforming stage.

Brief Description of the Invention.

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We have realised that by the use of a membrane separation technique it is possible to remove most, or all, of the excess of hydrogen from the synthesis gas produced by steam reforming prior to compression. This renders it possible to operate a process using a combination of a fired reformer and an auxiliary reformer such that the volume of synthesis gas fed to the compressor is similar to, or even less than, the amount that would be produced if the auxiliary reformer had not been used.

Accordingly the present invention provides a process for the production of methanol synthesis gas comprising:

- a) forming major and minor streams, each containing a hydrocarbon feedstock and steam;
- b) passing, at a pressure in the range 10-40 bar abs., the major stream over a steam reforming catalyst disposed in tubes heated by means of a fired furnace, thereby producing a reformed major stream;

c) passing, also at said pressure in the range 10-40 bar abs., the minor stream over a steam reforming catalyst disposed in tubes of an auxiliary reformer, thereby forming a reformed minor stream;

5 d) mixing the reformed minor stream with the reformed major stream, thereby forming a combined reformed gas stream;

e) passing the reformed major steam, before or after the mixing thereof with the reformed minor stream, past the exterior of the auxiliary reformer tubes, thereby supplying heat thereto;

f) cooling the combined reformed gas stream to condense unreacted steam therein as water, and separating the condensed water to give a water-depleted gas stream;

10 g) subjecting at least part of the water-depleted gas stream to membrane separation effective to separate a permeate gas stream containing some of the hydrogen from an impermeate gas stream containing hydrogen and carbon oxides, said impermeate gas stream, together with the remainder, if any, of said water-depleted gas stream, forming a synthesis gas stream; and

15 h) compressing the synthesis gas stream to a pressure above 50 bar abs., the amount of hydrogen separated as said permeate stream being such that said synthesis gas stream has a ratio R, as hereinbefore defined, in the range 1.8 to 2.5.

Description of Drawing

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The drawing shows in diagrammatic form a preferred flowsheet of the process of the invention.

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General Description of the Invention

In the process of the invention the feedstock is preferably methane or natural gas containing a substantial proportion, eg over 90% v/v, methane. If the feedstock contains sulphur compounds, prior to feeding to the reformer tubes, the feedstock is subjected to desulphurisation, eg by passage over a hydrodesulphurisation catalyst followed by absorption of hydrogen sulphide using a suitable absorbent, eg a zinc oxide bed. Usually it is desirable to incorporate a hydrogen-containing gas into the feedstock prior to hydrodesulphurisation: this may be achieved by recycling a small amount of the reformed gas, or a hydrogen-containing gas produced therefrom, eg part of the permeate gas stream or purge gas from a methanol loop to which the synthesis gas is fed, to the feedstock prior to passage over the hydrodesulphurisation catalyst.

30 Prior to reforming, steam is mixed with the feedstock: this steam introduction may be effected by direct injection of steam and/or by saturation of the feedstock by contact of the latter with a stream of heated water. The amount of steam introduced is preferably such as to give 2 to 4 moles of steam per gram atom of hydrocarbon carbon in the feedstock. Some of the steam may be replaced by carbon dioxide, where a supply thereof is available, as this decreases the amount of hydrogen that has to be separated as the permeate stream in order to obtain a synthesis gas of approximately stoichiometric composition.

35 The feedstock/steam mixture is preferably preheated by heat exchange with, for example, the combined reformed gas stream and/or the flue gases from the fired reformer and then part thereof is fed as the major stream to the tubes of the fired reformer. The major and minor streams may be preheated separately, eg to different temperatures and/or may contain differing proportions of steam and/or carbon dioxide. For example steam may be introduced separately into the feedstock streams of the major and minor streams. The major stream preferably contains 75-90% of the total amount of feedstock in the major and minor streams. The fired reformer is preferably operated so that the temperature of the reformed major stream leaving the catalyst of the fired reformer is in the range 750 to 950°C, especially 850 to 900°C.

40 In a preferred form of the invention, the auxiliary reformer tubes are of the "double tube" configuration, ie where each tube comprises an outer tube having a closed end and an inner tube disposed concentrically within the outer tube and communicating with the annular space between the inner and outer tubes at the closed end of the outer tube, with the steam reforming catalyst disposed in said annular space. The minor stream is fed to the open end of the annular catalyst-containing space between the inner and outer tubes while the reformed major stream is fed past the external surface of the outer tube. The reformed minor stream leaves the annular space at the end thereof adjacent the closed end of the outer tube and flows back through the inner tube. One form of double-tube reformer is described in EP-A-194067: in this

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reformer insulation is provided to minimise the amount of heat transferred through the walls of the inner tube from the reformed minor stream flowing through the inner tube. However in the present invention it is preferred that such insulation is omitted so that heat transfer takes place through the wall of the inner tube from the reformed minor stream passing through the inner tube to the minor stream undergoing reforming in the annular space containing the catalyst. This heat transfer has a dual effect: firstly it supplies part of the heat required for the reforming of the minor stream and secondly it gives rise to cooling of the reformed minor stream. The latter has the advantage that the resultant reformed gas stream consisting of the mixture of the reformed major and minor streams will be at a lower temperature and hence will contain less heat, thereby reducing the heat recovery necessary therefrom for efficient operation.

The use of this type of reformer wherein a process gas stream, ie the reformed major stream or the mixture thereof with the reformed minor stream, is used to heat the auxiliary reformer tubes has the advantage that the auxiliary reformer tubes can be of thinner gauge material than is customary for reformer tubes since the pressure differential across the auxiliary reformer tubes is relatively small, being essentially that resulting from the pressure drop the major stream experiences as it passes through the fired reformer tubes.

In the present invention, the reformed major and minor gas streams may be combined and the combined gas stream employed for heating the auxiliary reformer tubes as described in the aforesaid US-A-4337170. However it is advantageous, and hence preferred, to combine the reformed minor gas stream with the reformed major gas stream after the latter has been used to heat the auxiliary reformer tubes.

The proportion of feedstock that can be reformed in the auxiliary reformer will depend on the acceptable methane slip in the water-depleted gas and the desired temperature of the combined reformed gas streams. Thus the methane content of the water-depleted gas stream will be the sum of the methane contents of the reformed major and minor streams: for any given reformer, feedstock, pressure, and proportion of steam, the methane content of the reformed major stream will depend on the temperature of the reformed major stream leaving the catalyst in the fired reformer while the methane content of the reformed minor stream will depend on the temperature of the reformed minor stream leaving the catalyst of the auxiliary reformer. The temperature of the reformed minor stream leaving the catalyst of the auxiliary reformer will depend on the temperature of the reformed major stream used to heat the auxiliary reformer, the heat transferred, if any, from the reformed minor stream to the minor stream undergoing reforming, and the relative proportions of the major and minor streams. It is preferred that the reformers are operated so that the overall methane content of the water-depleted gas stream is in the range 2 to 10% by volume on a dry basis.

After reforming, the combined reformed gas stream is cooled to below the dew-point of steam therein to condense unreacted steam as water, which is then separated. This cooling may be effected in conventional manner, eg by indirect heat exchange with reactants to be fed to the tubes of the fired reformer and/or auxiliary reformer, with water, giving hot water and/or steam (which may be used as process steam), and/or with steam giving super-heated steam from which power may be recovered in a turbine. Alternatively, or additionally, at least the final part of the cooling may be by direct heat exchange with water, giving a warm water stream, containing also the condensed water, which may be used, after further heating, as a hot water stream that is contacted with the feedstock to effect saturation thereof to introduce process steam.

After separation of the water, at least part of the water-depleted stream is subjected to a membrane separation process to separate a permeate stream containing hydrogen from an impermeate stream containing hydrogen and carbon oxides. As is well known in the art, a variety of membrane materials may be used: examples of such membrane materials include polyimides and polyethersulphones. It is preferred to employ a membrane that has a relatively low permeability to carbon oxides so that little thereof pass into the permeate stream: for this reason polyimide membranes are preferred.

It is not necessary that all the water-depleted gas is subjected to the membrane separation: thus part thereof may bypass the membrane separation stage. By varying the proportion bypassing the membrane separation stage, control may be effected on the composition of the synthesis gas. The amount of the feedstock that is fed to the auxiliary reformer tubes and the amount of hydrogen removed as the permeate are such that the synthesis gas formed from the impermeate and that part, if any, of the water-depleted gas bypassing the membrane separation stage has a R ratio in the range 1.8 to 2.5, and preferably such that the volume of synthesis gas produced does not exceed the dry gas volume of the reformed major gas stream by more than 10%. In particular it is preferred that the amount of hydrogen removed as the permeate stream is such that the volume of synthesis gas is no greater than the dry gas volume of the reformed major gas stream, so that no additional load is placed upon the synthesis gas compressor.

The permeate stream may be used as fuel for the fired reformer or exported to a user of hydrogen. Part of the permeate stream may be used, as aforesaid, as a hydrogen-containing gas stream added to the

feedstock prior to hydrodesulphurisation of the latter.

It has been the practice to take a purge stream from the methanol synthesis loop and to use this purge as fuel for the fired reformer. Such a purge has been necessary to avoid a build-up in the loop of inerts, eg methane, and possibly nitrogen (which may be present in small amounts in natural gas), and the excess of hydrogen resulting from the use of a hydrogen-rich synthesis gas. By means of the present invention it is possible to recycle some or all of the methane-containing purge to the reforming stage as feedstock as the membrane unit acts to remove some or all of the excess of hydrogen. If the membrane employed is such as to separate nitrogen into the permeate stream, then in some cases it may be possible to recycle all of the purge. That portion, if any, of the purge that is not recycled may be used as fuel for the fired reformer, together with the hydrogen-rich permeate stream from the membrane unit as aforesaid. The recycled purge forms part of the feedstock to the reformer, thus decreasing the amount of fresh feedstock required. Furthermore, since the recycled purge contains hydrogen, it may be used as the hydrogen-containing gas added to the fresh feedstock prior to hydrodesulphurisation of the latter.

Part or all of the recycled purge may be subjected to a further membrane separation step to separate hydrogen as a hydrogen-containing permeate stream. The impermeate stream is then recycled to form part of the feedstock. This has the advantage of reducing the amount of hydrogen that is recycled and so decreases the load on the membrane separation unit treating the water-depleted gas. The hydrogen-containing permeate stream may be used as part of the fuel for the fired reformer. Where there is a need to recycle part of the purge as a hydrogen-containing gas, eg for hydrodesulphurisation, the part to be used for hydrodesulphurisation is desirably not subjected to such a membrane separation step.

In some cases it may be desirable that the major and minor feed streams fed to the reformers contain different proportions of the recycled purge. For example, the major feed stream may contain only a small proportion of the recycled purge, eg merely that required to supply the amount of hydrogen required to ensure satisfactory hydrodesulphurisation, while the remainder is used as feedstock in the minor feed stream. Indeed, in some cases the feedstock of the minor feed stream may consist entirely of recycled purge, preferably after subjecting that purge to a membrane separation step.

Detailed Description of the Invention.

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One form of the invention is illustrated by reference to the drawing which is a diagrammatic flowsheet wherein for simplicity the reformers are shown with only single catalyst tube in each reformer: in practice there will of course generally be a multiplicity of tubes in each reformer.

In the drawing is shown a fired furnace 1 containing a main reformer tube 2 in which a steam reforming catalyst 3 is disposed. A heat exchanger 4 is disposed in the flue gas duct 5 of the fired furnace 1. An auxiliary reformer 6 is provided wherein each catalyst tube is of the "double tube" construction having the catalyst 7 disposed in the annulus 8 between outer tube 9 and inner tube 10. Outer tube 9 is closed at its lower end, while the upper end of the outer tube 9 opens into a plenum chamber 11. At the lower end of reformer 6, a hot gas inlet 12 is disposed, connected to the outlet of the tube 2 of the fired reformer. The reformer 6 is also provided with an outlet 13 for the gas from the space outside the outer tube 9 and an outlet 14 with which the inner tube 10 communicates. Outlets 13 and 14 lead to a reformed gas line 15. A feedstock/steam feed 16 leads to the heat exchanger 4 and a preheated reactants line 17 from heat exchanger 4 to the inlet of tube 2. An auxiliary reformer feed 18 is taken from heat exchanger 4 to the plenum chamber 11 of the auxiliary reformer 6. The reformed gas line 15 leads, via one or more heat exchangers 19, to a catchpot 20 having a drain 21. A water-depleted gas line 22 leads from catchpot 20 to a membrane separation unit 23 provided with a bypass 24 having a flow control valve 25. Membrane separation unit 23 has a permeate line 26 and an impermeate line 27 to which bypass 24 connects forming a synthesis gas delivery line 28 feeding to a synthesis gas compressor 29.

In a typical operation a feedstock/steam mixture at a pressure of about 24 bar abs. is preheated in heat exchanger 4 and a major part stream is then fed to the reformer tube 2, while a minor part stream is fed to plenum chamber 11 via line 18. The major part stream passes over the catalyst 3 and is reformed by heat supplied by the fired furnace 1 giving a reformed major stream which is then fed, via inlet 12 to the space outside the outer tube 9 of the double tube reformer 6, and then via outlet 13 to the reformed gas line 15. The minor part stream is fed, from plenum chamber 11, over the catalyst 7 in the annulus 8 between tubes 9 and 10 wherein it is reformed. The reformed minor stream leaves the lower end of the annulus and then passes up through the inner tube 10 to outlet 14 and thence to reformed gas line 15. The heat required for the reforming of the minor part stream is supplied from the reformed major stream passing past the outside

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of outer tube 9 and from the reformed minor stream passing up through the inner tube 10.

From reformed gas line 15, the combined reformed gas stream is cooled in heat exchanger 19 to below the dew point of the steam therein to condense the unreacted steam as water. The condensed water is separated in catchpot 20 from which it is removed via drain 21. The resultant water-depleted gas is fed, via line 22, to the membrane separation unit 23 and therein separated into a permeate stream 26 and an impermeate stream 27. Part of the water-depleted gas bypasses membrane separation unit via bypass 24. The amount bypassing the membrane unit is controlled by valve 25.

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Example

In a calculated example using the flowsheet described above in relation to the drawing and using a feedstock of desulphurised natural gas and a reforming pressure of 24 bar abs., the gas composition, flow rates, and temperatures at various stages of the reforming operation are as shown in Table 1.

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Table 1

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Position	Temp (°C)	Gas flow rate (kmol.h ⁻¹)				
		CH ₄	H ₂	CO	CO ₂	H ₂ O
17	520	83.4 ^a	2.0	0.0	0.3	250.1
18	520	25.1 ^b	0.6	0.0	0.1	75.2
12	870	14.8	228.6	44.4	24.5	157.3
13	664	14.8	228.6	44.4	24.5	157.3
10*	770	10.4	51.6	6.8	8.0	52.6
14	658	10.4	51.6	6.8	8.0	52.6
15	662	25.2	280.2	51.2	32.5	209.9

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* Inlet, ie bottom.

^{a, b} includes 6.5 and 2.0 kmol.h⁻¹, respectively, of higher hydrocarbons expressed as CH_{2.96}

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In order to achieve the heat transfer across the outer walls of the outer tubes 9 necessary to effect the degree of reforming of the minor feed stream shown in Table 1, it is calculated that, for a given number of tubes of a given diameter, the tubes 9 need to have a length of 7.2 m exposed to the major reformed gas stream 12.

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If the inner tubes 10 were omitted and there were used the same number of outer tubes 9 of the same diameter but with open lower ends so that the reformed minor stream leaving the tubes 9 mixed with the reformed major stream 12 and the resultant mixture used to heat the tubes 9, the temperatures and gas flow rates are calculated to be as set out in Table 2.

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Table 2

Position	Temp (°C)	Gas flow rate (kmol.h ⁻¹)				
		CH ₄	H ₂	CO	CO ₂	H ₂ O
17	520	83.4 ^a	2.0	0.0	0.3	250.1
18	520	25.1 ^b	0.6	0.0	0.1	75.2
12	870	14.8	228.6	44.4	24.5	157.3
9*	762	10.7	50.7	6.5	8.0	52.9
12 + 9*	843	25.5	279.3	50.9	32.5	210.2
15	663	25.5	279.3	50.9	32.5	210.2

* Outlet, ie bottom.

^{a, b} includes 6.5 and 2.0 kmol.h⁻¹, respectively, of higher hydrocarbons expressed as CH_{2.96}

In this case in order to achieve the heat transfer across the outer walls of the outer tubes 9 necessary to effect essentially the same degree of reforming of the minor feed stream, with essentially the same inlet gas flows and temperatures and to give a product stream, ie stream 15, at essentially the same outlet temperature, it is calculated that, because the gas effecting the heating has a lower temperature and because there is no heating of the minor feed stream undergoing reforming by heat transfer from the reformed minor stream passing up through tubes 10, the heat exchange surface area of the outer walls of the tubes 9 needs to be increased by about 14%, eg by increasing the length of tubes 9 exposed to the combined reformed major and minor streams, ie stream 12 plus the stream from the outlet of tube 9, from 7.2 m to 8.2 m.

Table 3 illustrates the formation of an approximately stoichiometric synthesis gas from the combined reformed gas stream 15 of Table 1. It is here assumed that there is no bypass of the membrane unit, that the pressure of the gas fed to the membrane separation unit is about 22 bar abs., and that the permeate has a pressure of about 2 bar abs. It is also assumed that the membrane employed is of the polyimide type having a hydrogen to carbon monoxide permeability ratio of 39, a hydrogen to carbon dioxide permeability ratio of about 5.4, and that the methane permeability is similar to that of carbon monoxide.

Table 3

Position	Temp (°C)	Gas flow rate (kmol.h ⁻¹)				
		CH ₄	H ₂	CO	CO ₂	H ₂ O
15	662	25.2	280.2	51.2	32.5	209.9
22	35	25.2	280.2	51.2	32.5	1.0
26	35	0.3	88.7	0.6	2.5	0.5
27	35	24.9	191.5	50.6	30.0	0.5

The proportion of feedstock that is fed to the auxiliary reformer in the embodiment of Table 1 is about 23% of the total. Consequently, if that system is employed to uprate an existing fired reformer, by the provision of the auxiliary reformer the throughput can be increased by about 25% at the expense of a lower reformed gas temperature and an increase in the methane content (on a dry basis) of the synthesis gas from 4.7% (if no auxiliary reformer and no membrane separation unit were employed) to 6.5% by volume.

Since a small proportion of carbon oxides, principally carbon dioxide, are separated into the permeate stream 26, the full benefit of the increase in the reformer throughput is not realisable in terms of the amount of methanol that can be produced: however it is seen from Table 3 that the synthesis gas stream 27 contains about 17% more carbon oxides than the reformed major stream 12 and so the amount of methanol

that can be produced may be significantly increased.

Further, from Tables 1 and 3 it is seen that the amount of synthesis gas produced, ie stream 27, is about 95% of the amount of dry gas in the reformed major stream 12. Thus not only is the reformer throughput, and hence amount of methanol that can be produced, increased significantly, but also the amount of gas fed to the compressor is slightly reduced, resulting in compression power saving.

Claims

- 10 1. A process for the production of a synthesis gas comprising:
- a) forming major and minor streams, each containing a hydrocarbon feedstock and steam;
 - b) passing, at a pressure in the range 10-40 bar abs., the major stream over a steam reforming catalyst disposed in tubes heated by means of a fired furnace, thereby producing a reformed major stream;
 - 15 c) passing, also at said pressure in the range 10-40 bar abs., the minor stream over a steam reforming catalyst disposed in tubes of an auxiliary reformer, thereby forming a reformed minor stream;
 - d) mixing the reformed minor stream with the reformed major stream, thereby forming a combined reformed gas stream;
 - e) passing the reformed major steam past the exterior of the auxiliary reformer tubes,
 - 20 thereby supplying heat thereto;
 - f) cooling the combined reformed gas stream to condense unreacted steam therein as water, and separating the condensed water to give a water-depleted gas stream; characterised in that, in order to produce a methanol synthesis gas stream,
 - i) the reformed minor stream is mixed with the reformed major stream before or after passing the reformed major stream past the exterior of the auxiliary reformer tubes;
 - 25 ii) at least part of the water-depleted gas stream is subjected to membrane separation effective to separate a permeate gas stream containing some of the hydrogen from an impermeate gas stream containing hydrogen and carbon oxides, said impermeate gas stream, together with the remainder, if any, of said water-depleted gas stream,
 - 30 forming a synthesis gas stream, the amount of hydrogen separated as said permeate stream being such that said synthesis gas stream has a ratio of the molar amount of hydrogen (less the molar amount of carbon dioxide) to the total molar amount of carbon oxides in the range 1.8 to 2.5; and
 - iii) compressing the synthesis gas stream to a pressure above 50 bar abs.
- 35 2. A process according to claim 1 wherein the tubes heated by the fired furnace are disposed within a first shell and the reformed major stream is passed out of said first shell, passed into a second shell in which the auxiliary reformer tubes are disposed, and past the exterior surface of said auxiliary reformer tubes to effect the heating thereof.
3. A process according to claim 1 or claim 2 wherein:
- 40 i) each of the auxiliary reformer tubes comprises an outer tube having a closed end and an inner tube disposed concentrically within the outer tube and communicating with the annular space between the inner and outer tubes at the closed end of the outer tube and the steam reforming catalyst is disposed in said annular space;
 - ii) the minor feed stream is fed to the open ends of the annular catalyst-containing spaces between the inner and outer tubes;
 - 45 iii) the reformed major stream is fed past the external surfaces of the outer tubes in a direction counter-current to the flow of the minor feed stream through said annular catalyst-containing spaces; and
 - iv) the reformed minor stream leaves the annular spaces at the ends thereof adjacent the closed ends of the outer tubes and flows back through the inner tubes,
 - 50 whereby heat transfer takes place between the reformed minor stream passing through said inner tubes and the minor feed stream passing through the annular catalyst-containing spaces.
4. A process according to any one of claims 1 to 3 wherein the major feed stream contains 75-90% of the total amount of hydrocarbon in the major and minor feed streams.
5. A process according to any one of claims 1 to 4 wherein the reforming conditions and proportions of said major and minor feed streams are such that the methane content of the combined reformed streams is in the range 2 to 10% by volume on a dry basis.
- 55 6. A process according to any one of claims 1 to 5 wherein the amount of hydrogen separated in the permeate stream is such that the volume of the methanol synthesis gas stream, prior to compression, does

not exceed the dry gas volume of the reformed major stream by more than 10%.

7. A process according to any one of claims 1 to 6 wherein the separated hydrogen-containing permeate stream is used as fuel for the fired furnace for heating the reformer tubes disposed therein, the methanol synthesis is effected in a synthesis loop from which a methane-containing purge stream is taken, and at least part of this purge stream is recycled to form part of the total feedstock of the major and minor feed streams.

8. A process according to claim 7 wherein at least part of the purge stream is subjected to a membrane separation step to separate a permeate stream containing hydrogen and a methane-containing impermeate stream which is used as part of the total feedstock of the major and minor feed streams.

9. A process according to claim 7 or claim 8 wherein the hydrocarbon of the minor feed stream consists entirely of methane from said recycled purge stream.

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