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(54) Process for the production of synthesis gas

(57) Synthesis gas having a stoichiometric composition desirable for subsequent conversion into methanol or Fischer-Tropsch products from a substantially sulphur-free gaseous hydrocarbon feedstock is produced by the steps of:

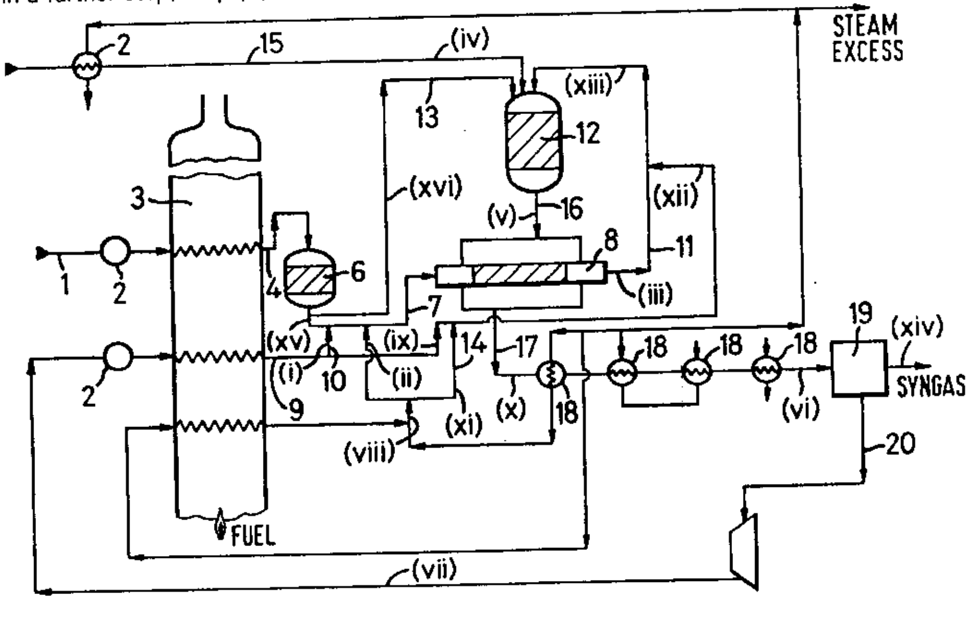
(I) feeding substantially sulphur-free hydrocarbon-containing gas 7, steam from boiler 18 and carbon dioxide 10 to a single primary reforming zone 8 comprised of an exchanger reactor containing a steam reforming catalyst under reforming conditions wherein hydrocarbon gas is partially reformed to produce a primary reformer effluent 11,

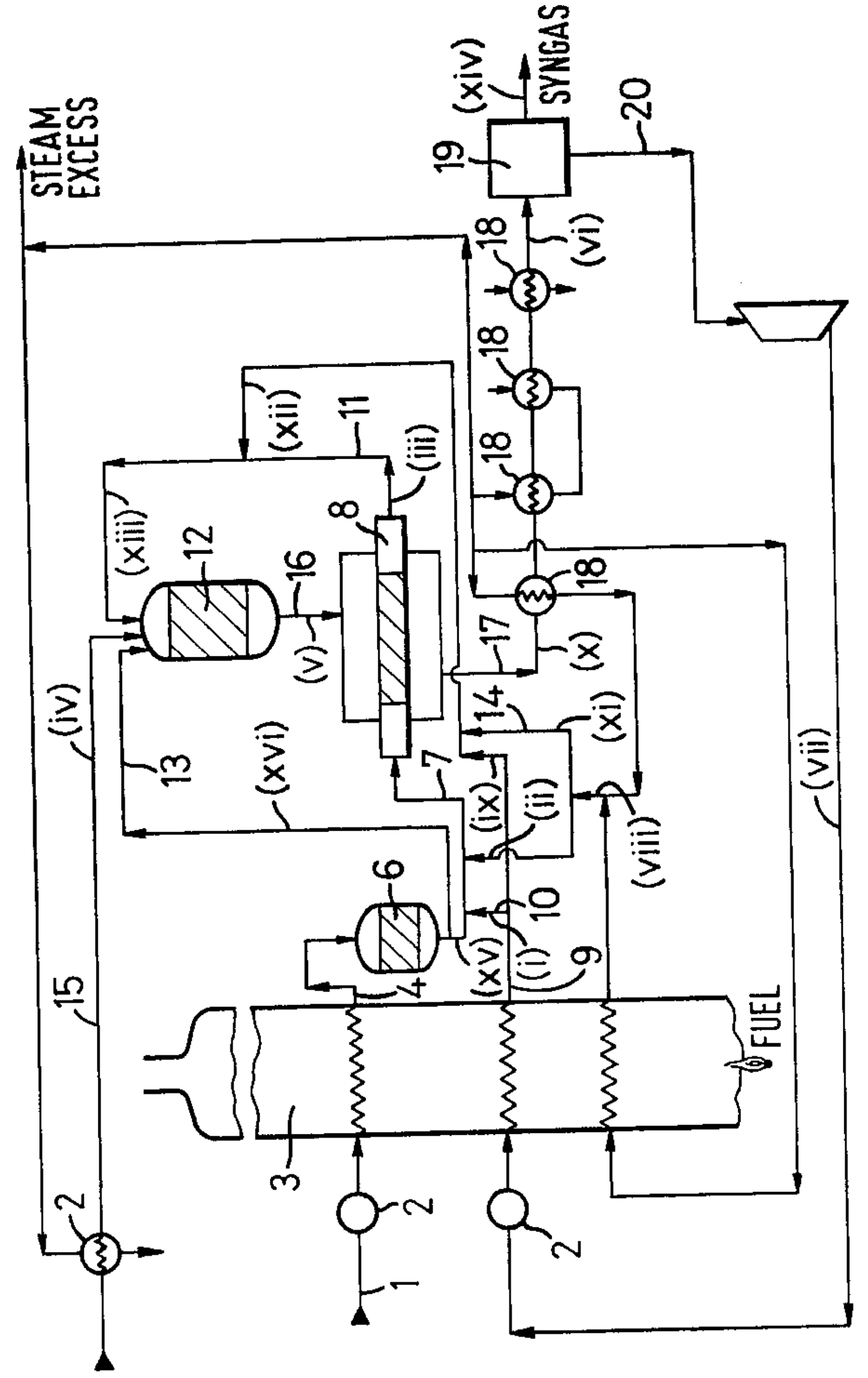
(II) feeding substantially sulphur-free hydrocarbon-containing gas 13, oxygen-containing gas 15, steam from boiler 18, carbon dioxide 9 and primary reformer effluent 11 to a secondary reformer 12 containing reforming catalyst under reforming conditions wherein hydrocarbon gas is reformed to produce a secondary reformer effluent,

(III) passing secondary reformer effluent 16 from step (II) to the primary reforming zone as indirect heating medium for the exchange reactor,

(IV) removing the secondary reforming effluent 17 from the primary reforming zone.

Preferably carbon dioxide is removed wholly or partially from the secondary reformer effluent and recycled in a further step, step (V), as feed to steps (I) and (II) of the process.




STEAM EXCESS
SYNGAS
(xiv)
19
20
18
18
18
18
18
(vi)
(xii)
11
(iii)
8
(xiii)
12
16
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(x)
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6
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(xv)
(i)
9
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FUEL
3
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1

SPECIFICATION

Process for the production of synthesis gas

The present invention relates in general to the production of synthesis gas and in particular to a process for the production of a synthesis gas from a substantially sulphur-free hydrocarbon-containing feedstock, the synthesis gas having a molar ratio of hydrogen to carbon monoxide substantially equal to 2 which ratio is desirable for methanol or Fischer-Tropsch synthesis.

Synthesis gas is the name generally given to a gaseous mixture principally comprising carbon monoxide and hydrogen, but also 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 ammonia. In order to improve the economics of such processes, it is desirable that the synthesis gas be of the optimum stoichiometric composition desirable for the particular reaction and/or be in a condition with particular regard to its temperature and pressure especially adapted for the reaction, with a minimum of intervening processing. In the production of methanol, for example, the synthesis gas suitably has a composition given by the formula:–

$$(H_2-CO_2)/(CO+CO_2)=2$$

so that when CO_2 in the formula=0, H_2:CO=2. Similar compositions, possibly free from carbon dioxide, are useful for Fischer-Tropsch conversions, whereas much higher hydrogen ratios are desirable for ammonia production. Moreover, since methanol is generally produced from synthesis gas by reaction at a pressure in the range from 30 to 100 atmospheres in the so-called low-pressure process and a temperature in the range from about 200 to 300°C, the synthesis gas production process should ideally produce the gas at temperatures and pressures as near as possible to these values.

The production of synthesis gas is generally accomplished by either steam reforming, autothermal reforming, non-catalytic partial oxidation of light hydrocarbons or non-catalytic partial oxidation of any hydrocarbons. Of these methods, steam reforming is generally used to produce a synthesis gas for conversion into methanol. For this purpose, simple steam reforming produces synthesis gas having too high a ratio of hydrogen to carbon monoxide with a high carbon dioxide content, as well as too low a pressure. A high carbon dioxide content in the synthesis gas results in the formation of water which must be subsequently removed from the product, usually by distillation, though some methanol conversion catalysts require a small carbon dioxide concentration for their efficient operation. Modifications of the simple steam reforming process have been proposed in, for example, GB-A-1,569,014 and GB-A-1,550,754.

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 hydrocarbon feed and steam to conditions at which primary reforming occurs by radiant heating and reforming said 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.

In this process, all the reforming is done by steam and the process would appear to be particularly adapted for producing synthesis gas of a composition desirable for subsequent conversion into ammonia and similar processes in which high hydrogen to carbon monoxide ratios are preferred. The synthesis gas production pressure is limited by the mechanical constraint of the differential pressure on the radiant reformer tubes.

GB-A-1,569,014 describes a process for producing, from a desulphurised hydrocarbon containing feedstock, a synthesis gas having essentially the stoichiometric composition required for methanol synthesis, which comprises:

a) dividing said feedstock into two fractions,

b) subjecting the first fraction frofm (a) to a primary steam reforming reaction, by mixing said fraction with steam, and heating the mixture thereof by indirect heat exchange, in the presence of a reforming catalyst, to form a gaseous effluent including hydrogen at a temperature between 650°C and 880°C,

c) preheating the second fraction from (a) to a temperature higher than 350°C,

d) combining effluent gas streams from (b) and (c), thus obtaining a gas mixture containing at least 37 per cent methane equivalent,

e) reacting the gas mixture from (d) with a free-oxygen rich gas in a secondary reforming reactor operating under essentially adiabatic conditions, and containing a bed of reforming catalyst, thus producing a synthesis gas at a minimum temperature of 880°C, and containing less than seven per cent methane on a dry gas basis.

The flexibility of this process is somewhat limited. Again, the synthesis gas production pressure is limited by the mechanical constraint of the differential pressure on the radiant reformer tubes.

The process of the present invention substantially overcomes at least some of the problems associated with prior art processes and can produce substantially carbon dioxide free synthesis gas having a molar ratio of hydrogen to carbon monoxide substantially equal to 2 at higher pressures. Such a feed composition, in combination with a synthesis gas conversion catalyst not requiring carbon dioxide for its efficient operation can result in the elimination of the need to remove water from the methanol product, which is particularly useful for fuel grade methanol production because it eliminates a distillation step.

Accordingly, the present invention provides a process for the production of synthesis gas having a stoichiometric composition desirable for subsequent conversion into methanol or Fischer-Tropsch products from a substantially sulphur-free gaseous hydrocarbon-containing feedstock which process comprises the steps of:

(I) feeding substantially sulphur-free hydrocarbon-containing gas, steam and carbon dioxide to a single primary reforming zone comprised of an exchanger reactor containing a steam reforming catalyst under reforming conditions wherein hydrocarbon gas is partially reformed to produce a primary reformer effluent,

(II) feeding substantially sulphur-free hydrocarbon-containing gas, oxygen-containing gas, steam, carbon dioxide and primary reformer effluent to a secondary reformer containing reforming catalyst under reforming conditions wherein hydrocarbon gas is reformed to produce a secondary reformer effluent,

(III) passing secondary reformer effluent from step (II) to the primary reforming zone as indirect heating medium for the exchanger reactor,

(IV) removing the secondary reforming effluent from the primary reforming zone.

The individual steps in the aforesaid process will now be examined in greater detail. As regards step (I), the hydrocarbon-containing gas may suitably be any hydrocarbon capable of undergoing a steam-reforming reaction, for example at least one hydrocarbon ranging from methane to naphthas having an end point of about 220°C, including natural gas, ethane, propane and LPG. A preferred hydrocarbon-containing gas is natural gas. If necessary, the hydrocarbon-containing gas is first of all desulphurised using technology conventional in the art and pressurised to about 40 to 80 atmospheres. The hydrocarbon-containing gas, steam and carbon dioxide may suitably be preheated to a temperature in the range 400 to about 550°C. Preheating may suitably be accomplished in part by using waste heat from elsewhere in the process and in part by, for example, 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 into the primary reforming zone suitably comprised of a convective heat exchanger reactor containing a steam reforming catalyst under steam reforming conditions. These exchanger reactors are known in the art. One type of exchanger reactor includes a shell having a tube bundle positioned in the shell; the shell directs a heating fluid about the tube bundle; the tube bundle includes a plurality of tubes for passing the process fluid to be both heated and chemically reacted; the plurality of tubes of the tube bundle are packed with a catalyst, for example, for causing the process fluid to chemically react in the tubes. Exchanger reactors are described in, for example, USP-A-3,972,688, USP-A-3,958,951 and GB-A-1,578,270. Whilst steam reforming catalyst may be packed either on the shell side thereof or within the tubes thereof, it is preferably packed in the tubes of the exchanger reactor. Conventional steam reforming catalyst, such as for example, nickel, nickel oxide, chromia, molybdenum, or mixtures thereof, either supported or unsupported may be employed. The primary reformer exit temperature may suitably be in the range from 750 to 950°C, preferably between about 800 to 900°C.

The primary reformer effluent comprising unchanged hydrocarbon, carbon monoxide and hydrogen is fed in step (II) to a secondary reformer containing reforming catalyst which may suitably be a conventional catalyst, for example of the same type as that used in step (I) of the process. Also fed to the secondary reformer is steam, carbon dioxide, oxygen-containing gas and a small proportion of substantially sulphur free hydrogen-containing gas. The hydrocarbon-containing gas feed to the secondary reformer is preferably obtained by dividing the feed to the primary reformer, suitably after the preheating step. Suitably from 5 to 70% by weight of the total hydrocarbon-containing gas is diverted to the secondary reformer. The oxygen-containing gas may suitably be air, oxygen-enriched air of oxygen, preferably oxygen, and preferably preheated to a temperature in the range from 100 to 300°C.

The seconary reformer may suitably take the form of a refractory lined reactor operating under essentially adiabatic conditions. In this reactor, hydrocarbon is both reformed and combusted in order to increase the temperature of the secondary reformer effluent, suitably to a temperature in the range from 850 to 1100°C, for example about 1000°C.

The secondary reformer effluent is then passed to the primary reforming zone as the indirect heat exchange medium for the exchange reactor.

In a preferred embodiment of the invention a steam reforming catalyst is packed within the tubes of the exchanger reactor and a carbon monoxide shift catalyst is provided on the shell side of the exchanger reactor. 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, an extra exotherm is given out as the shift reaction:–

$$CO+H_2 \rightarrow CO_2+H_2$$

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 temperature driving force at the cooler end of the exchanger. This enables operation with a lower steam consumption to the primary and secondary stages 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:–

$$2\ CO \rightarrow CO_2+C$$

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. In this particular embodiment it is not particularly preferred since carbon formation, though thermodynamically possible is kinetically limited. However, it may be more preferable in higher temperature coolers.

The primary and secondary reformers may, if desired, be incorporated in a single vessel.

In step (IV), the secondary reformer effluent is thereafter 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 steps (I) and (II) of the process. After cooling, carbon dioxide is preferably recovered wholly or partially from the effluent. Methods for removing carbon dioxide from such compositions are well known in the art. Any of such methods 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. For certain applications it may not be necessary to remove all the carbon dioxide from the effluent. The synthesis gas remaining after removal of some or all the carbon dioxide is particularly adapted by virtue of its composition for methanol production. Furthermore, it can be produced at higher pressure than in a conventional reforming scheme and can in consequence be fed directly or with a single compression stage to a low-pressure methanol production process.

In a preferred step (V) of the process carbon dioxide recovered in step (IV) is recycled as feed to steps (I) and/or (II) of the process. Preferably sufficient carbon dioxide is available to supply the compositional requirements of both steps (I) and (II) of the process.

An advantage of the process of the present invention is that the decomposition of hydrocarbon in the overall system can be essentially total. Thus, when substantially pure oxygen is fed to the secondary reformer, a synthesis gas substantially free of inerts can be produced. This has economic advantages in the production of methanol since high internal recycle ratios can be used with a small purge and hence a very high overall conversion efficiency to methanol. A further advantage is that good high temperature heat economy can be effected with heat being transferred over small temperature differences. In consequence the exergy or work potential of process streams is not unnecessarily degraded.

Although the process of the present invention has been described with particular reference to the production of a synthesis gas having a composition of the stoichiometric proportions desirable for the production of methanol, it will be appreciated by those skilled in the art that by suitable modification the process may be adapted to produce synthesis gas having higher and lower hydrogen to carbon monoxide ratios or containing carbon dioxide.

The process of the present invention will now be further described in the following Examples with reference to the accompanying Figure which is a flow-diagram illustrating the interconnection of the various pieces of equipment useful in the operation of one embodiment of the invention.

With reference to the Figure, 2 is a preheater, 3 is a fired heater, 6 is a guard bed, 8 is a primary reformer in the form of an exchanger reactor containing in the tube bundle thereof a conventional steam reforming catalyst, 12 is a secondary reactor in the form of a refractory lined reactor operating under essentially adiabatic conditions and containing a conventional reforming catalyst, 18 is a boiler for generating superheated steam and 19 is a carbon dioxide recovery plant.

The Examples are computer derived and are not examples illustrating the actual working of the process of the invention. The calculated compositions of the process streams, their temperatures, pressures etc at various points (i), (ii), (iii), (iv) etc on the flow diagram were calculated and are presented in Tables appropriate to each Example.

Example 1

Desulphurised natural gas was fed at a rate of approximately 100 te/hr (6250 kmol (methane)/hour) through line 1 to the preheater 2 and thereafter through the fired heater 3 in which its temperature was raised to about 550°C. After exiting through line 4, it was passed through the guard bed 6 wherein poisons detrimental to the operation of the reforming catalysts were removed. A lesser part of the natural gas (40 t/h) was then passed through line 7 to the primary reformer 8. Also fed to the primary reformer 8 through line 10 was preheated recycle carbon dioxide. The facility also existed for adding superheated steam via line 9. The carbon dioxide to natural gas molar ratio was about 5.4 and the steam to natural gas molar ratio was substantially zero. A purpose of adding steam could be to prevent the Boudourd reaction ($2CO—CO_2+C$) occuring at the outlet of the primary reformer. The effective major methane decomposition reaction in this stage is believed to be by reaction with CO_2, i.e.

$$CO_2+CH_4-2CO+2H_2$$

The gas at exit from the primary reformer (temperature 850°C) containing a considerable proportion of unconverted methane was passed through line 11 to the secondary reformer 12. Also passed to the secondary reformer was a major proportion of the preheated fresh natural gas (60 te/hr) through line 13, steam through line 14 and preheated oxygen through line 15. The facility also existed for adding carbon dioxide through line 21. The following reactions are believed to occur in the secondary reformer:

$$CH_4+H_2O-CO+3H_2$$
$$CH_4+CO_2-2CO+2H_2$$
$$CH_4+2O_2-CO_2+2H_2O$$
$$CO+H_2-CO_2+H_2$$

The effect of the excess steam is to regenerate the carbon dioxide required for recycle. The added steam to total fresh natural gas (line i) molar ratio was about 2.0 and the CO_2 ratio substantially zero.

The gaseous stream exiting from the secondary reformer through line 16 (exit temperature of about 1045°C) was passed as the indirect heating medium to the shell side of the primary reformer 8 which contained a catalyst to promote the shift reaction. In cooling and reacting it heated the primary reaction gases to their exit temperature of about 850°C.

The secondary reformer effluent stream was then passed out of the primary reformer through line 17 and was cooled in the boilers 18. The steam raised thereby was used in the process. Carbon dioxide was then recovered from the cooled gas stream in the carbon dioxide removal plant 19 using conventional technology. Recovered carbon dioxide was recycled through line 20 to the primary reformer 8 and the secondary reformer 12, optionally via a gas compressor.

The overall reaction in both reformers consumed substantially no net steam and substantially no net carbon dioxide and satisfied the overall equation:

$$CH_4+\tfrac{1}{2}O_2\rightarrow CO+2H_2$$

A gas containing virtually no carbon dioxide and inerts (less than 0.3%) was produced. The calculated data at the points (i), (ii), (iii), (iv) etc in the process is shown in Table 1.

Example 2

Example 1 was repeated except that the primary reforming was effected less by carbon dioxide and more by steam by adjustment of natural gas, steam and carbon dioxide flows. Less total steam (line xii) was required to give a stoichiometric gas (after carbon dioxide removal), i.e. $CO=2H_2$, than in Example 1 and less heat was exchanged in the primary reformer, both factors leading to improved economy. The penalty for this was that unconverted methane in the product gas was much higher, though still lower than in the conventional single stage steam reforming process.

The calculated data at the points (i), (ii), (iii), (iv) etc in the process scheme is shown in Table 2.

Example 3

Example 1 was effectively repeated, except that approximately 4% carbon dioxide was left in the product synthesis gas for the purpose of satisfying the demands of certain types of methanol synthesis catalyst, e.g. those of the Cu/Zn type. To compensate for the extra loss of carbon dioxide in the methanol synthesis reaction, a gas slightly deficient in hydrogen, relative to the stoichiometric composition, was produced.

The calculated data at points (i), (ii), (iii) and (iv) etc in the process scheme is shown in Table 3.

Example 4

Example 2 was repeated except that 4% carbon dioxide was left in the synthesis gas.

The calculated data at points (i), (ii), (iii) and (iv) etc in the process scheme is shown in Table 4.

Examples 5 to 8

The procedure of Example 1 was repeated except that no carbon monoxide shift catalyst was incorporated on the shell side of the primary reformer 8. The effect of this was that higher steam feeds were required, though this could still be internally generated.

The calculated data at the points (i), (ii), (iii), (iv) etc in the process is shown in Tables 5 to 8.

The method of heat exchange is only indicative. In particular, in a commercial plant the duty shown for the fired heater 3 could well be satisfied by heat exchange with high temperature streams such as 17 or those external to the scheme. An overall heat integration would be desirable by means well known to those skilled in the art to arrive at the optimum practical integrated scheme.

TABLE 1 - FLOWS IN KMOL/H

STREAM	H_2	CO	CO_2	N_2	AR	H_2O	CH_4	O_2	TOTAL	P (BAR)	T (°C)
(i)	41.5	0.0	13780.4	0.0	0.0	0.0	0.0	0.0	13821.9	45.00	550.0
(ii)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	45.00	550.0
(iii)	1962.4	7327.3	8774.2	0.0	0.0	2685.3	226.8	0.0	20975.9	45.00	850.0
(iv)	0.0	0.0	0.0	0.0	15.4	0.0	0.0	3068.6	3084.1	45.00	200.0
(v)	8759.0	9937.3	10063.5	0.0	15.4	16634.2	24.4	0.0	45433.8	40.00	1045.0
(vi)	12480.0	6216.3	13784.4	0.0	15.4	52.5	24.4	0.0	32573.0	37.20	30.0
(vii)	41.5	0.0	13780.4	0.0	0.0	0.0	0.0	0.0	13821.9	50.00	10.0
(viii)	0.0	0.0	0.0	0.0	0.0	13000.0	0.0	0.0	13000.0	45.00	250.0
(ix)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	45.00	550.0
(x)	12480.0	6216.3	13784.4	0.0	15.4	12913.2	24.4	0.0	45433.8	38.70	605.0
(xi)	0.0	0.0	0.0	0.0	0.0	13000.0	0.0	0.0	13000.0	45.00	550.0
(xii)	0.0	0.0	0.0	0.0	0.0	13000.0	0.0	0.0	13000.0	45.00	550.0
(xiii)	1962.4	7327.3	8774.2	0.0	0.0	15685.2	226.8	0.0	33975.8	45.00	738.4
(xiv)	12438.5	6216.3	4.1	0.0	15.4	0.1	24.4	0.0	18698.9	36.70	10.0
(xv)	0.0	0.0	0.0	0.0	0.0	0.0	2550.0	0.0	2550.0	45.00	550.0
(xvi)	0.0	0.0	0.0	0.0	0.0	0.0	3700.0	0.0	3700.0	45.00	550.0

TABLE 2 - FLOWS IN KMOL/H

STREAM	H_2	CO	CO_2	N_2	AR	H_2O	CH_4	O_2	TOTAL	P (BAR)	T (°C)
(i)	18.1	0.0	6026.9	0.0	0.0	0.0	0.0	0.0	6045.0	45.00	550.0
(ii)	0.0	0.0	0.0	0.0	0.0	3125.0	0.0	0.0	3125.0	45.00	550.0
(iii)	3099.4	3712.8	4023.7	0.0	0.0	3418.6	1412.7	0.0	15667.2	45.00	815.0
(iv)	0.0	0.0	0.0	0.0	15.2	0.0	0.0	3028.8	3044.0	45.00	200.0
(v)	9318.0	8849.2	7266.5	0.0	15.2	12140.3	173.9	0.0	37763.1	40.00	975.0
(vi)	12105.8	6061.4	10054.3	0.0	15.2	43.8	173.9	0.0	28454.4	37.39	30.0
(vii)	30.2	0.0	10044.8	0.0	0.0	0.0	0.0	0.0	10075.0	50.00	10.0
(viii)	0.0	0.0	0.0	0.0	0.0	9375.0	0.0	0.0	9375.0	45.00	250.0
(ix)	12.1	0.0	4017.9	0.0	0.0	0.0	0.0	0.0	4030.0	45.00	550.0
(x)	12105.8	6061.4	10054.3	0.0	15.2	9352.5	173.9	0.0	37763.1	38.89	615.0
(xi)	0.0	0.0	0.0	0.0	0.0	6250.0	0.0	0.0	6250.0	45.00	550.0
(xii)	12.1	0.0	4017.9	0.0	0.0	6250.0	0.0	0.0	10280.0	45.00	546.4
(xiii)	3111.5	3712.8	8041.6	0.0	0.0	9668.6	1412.7	0.0	25947.2	45.00	706.0
(xiv)	12075.5	6061.4	9.5	0.0	15.2	0.1	173.9	0.0	18335.7	36.89	10.0
(xv)	0.0	0.0	0.0	0.0	0.0	0.0	3125.0	0.0	3125.0	45.00	550.0
(xvi)	0.0	0.0	0.0	0.0	0.0	0.0	3125.0	0.0	3125.0	45.00	550.0

TABLE 3 - FLOWS IN KMOL/H

STREAM	H_2	CO	CO_2	N_2	AR	H_2O	CH_4	O_2	TOTAL	P (BAR)	T (°C)
(i)	30.3	0.0	10081.9	0.0	0.0	0.0	0.0	0.0	10112.2	45.00	550.0
(ii)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	45.00	550.0
(iii)	1781.5	6001.8	6026.1	0.0	0.0	2109.8	239.6	0.0	16158.9	45.00	860.0
(iv)	0.0	0.0	0.0	0.0	15.8	0.0	0.0	3145.8	3161.6	45.00	200.0
(v)	9715.3	8764.9	7524.9	0.0	15.8	15641.4	37.1	0.0	41699.1	40.00	1045.0
(vi)	13072.5	5407.4	10882.2	0.0	15.8	46.0	37.1	0.0	29461.0	37.20	30.0
(vii)	30.3	0.0	10081.9	0.0	0.0	0.0	0.0	0.0	10112.2	50.00	10.0
(viii)	0.0	0.0	0.0	0.0	0.0	13000.0	0.0	0.0	13000.0	45.00	250.0
(ix)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	45.00	550.0
(x)	13072.5	5407.4	10882.2	0.0	15.8	12284.1	37.1	0.0	41699.1	38.70	640.0
(xi)	0.0	0.0	0.0	0.0	0.0	13000.0	0.0	0.0	13000.0	45.00	550.0
(xii)	0.0	0.0	0.0	0.0	0.0	13000.0	0.0	0.0	13000.0	45.00	550.0
(xiii)	1781.5	6001.8	6026.1	0.0	0.0	15109.8	239.6	0.0	29158.8	45.00	724.0
(xiv)	13042.1	5407.4	800.2	0.0	15.8	0.1	37.1	0.0	19302.7	36.70	10.0
(xv)	0.0	0.0	0.0	0.0	0.0	0.0	2187.5	0.0	2187.5	45.00	550.0
(xvi)	0.0	0.0	0.0	0.0	0.0	0.0	4062.5	0.0	4062.5	45.00	550.0

TABLE 4 - FLOWS IN KMOL/H

STREAM	H_2	CO	CO_2	N_2	AR	H_2O	CH_4	O_2	TOTAL	P (BAR)	T (°C)
(i)	12.0	0.0	3991.7	0.0	0.0	0.0	0.0	0.0	4003.7	45.00	550.0
(ii)	0.0	0.0	0.0	0.0	0.0	3125.0	0.0	0.0	3125.0	45.00	550.0
(iii)	3211.6	2946.4	2592.9	0.0	0.0	2976.1	1574.9	0.0	13302.0	45.00	825.0
(iv)	0.0	0.0	0.0	0.0	14.6	0.0	0.0	2901.6	2916.2	45.00	200.0
(v)	10375.9	7602.6	5013.0	0.0	14.6	10855.6	282.2	0.0	34143.9	40.00	975.0
(vi)	12774.8	5203.7	7411.9	0.0	14.6	38.0	282.2	0.0	25725.3	37.39	30.0
(vii)	20.0	0.0	6652.9	0.0	0.0	0.0	0.0	0.0	6672.9	50.00	10.0
(viii)	0.0	0.0	0.0	0.0	0.0	9375.0	0.0	0.0	9375.0	45.00	250.0
(ix)	8.0	0.0	2661.1	0.0	0.0	0.0	0.0	0.0	2669.2	45.00	550.0
(x)	12774.8	5203.7	7411.9	0.0	14.6	8456.7	282.2	0.0	34143.9	38.89	620.0
(xi)	0.0	0.0	0.0	0.0	0.0	6250.0	0.0	0.0	6250.0	45.00	550.0
(xii)	8.0	0.0	2661.1	0.0	0.0	6250.0	0.0	0.0	8919.2	45.00	546.7
(xiii)	3219.6	2946.4	5254.1	0.0	0.0	9226.1	1574.9	0.0	22221.2	45.00	711.7
(xiv)	12754.8	5203.7	758.7	0.0	14.6	0.1	282.2	0.0	19014.2	36.89	10.0
(xv)	0.0	0.0	0.0	0.0	0.0	0.0	3125.0	0.0	3125.0	45.00	550.0
(xvi)	0.0	0.0	0.0	0.0	0.0	0.0	3125.0	0.0	3125.0	45.00	550.0

TABLE 5 - FLOWS IN KMOL/H

STREAM	H_2	CO	CO_2	N_2	AR	H_2O	CH_4	O_2	TOTAL	P (BAR)	T (°C)
(i)	27.9	0.0	9261.9	0.0	0.0	0.0	0.0	0.0	9289.8	50.00	550.0
(ii)	0.0	0.0	0.0	0.0	0.0	4000.0	0.0	0.0	4000.0	50.00	550.0
(iii)	5414.3	6989.0	5384.3	0.0	0.0	4766.2	1884.7	0.0	24438.6	45.00	850.0
(iv)	0.0	0.0	0.0	0.0	15.9	0.0	0.0	3161.1	3177.0	45.00	200.0
(v)	12317.5	6233.6	9265.6	0.0	15.9	34089.0	11.7	0.0	61933.3	40.00	1042.0
(vi)	12317.5	6233.6	9265.6	0.0	15.9	42.4	11.7	0.0	27886.7	37.39	30.0
(vii)	27.9	0.0	9261.9	0.0	0.0	0.0	0.0	0.0	9289.8	50.00	10.0
(viii)	0.0	0.0	0.0	0.0	0.0	34000.0	0.0	0.0	34000.0	50.00	250.0
(ix)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	50.00	550.0
(x)	12317.5	6233.6	9265.6	0.0	15.9	34089.0	11.7	0.0	61933.3	38.50	604.1
(xi)	0.0	0.0	0.0	0.0	0.0	30000.0	0.0	0.0	30000.0	50.00	550.0
(xii)	0.0	0.0	0.0	0.0	0.0	30000.0	0.0	0.0	30000.0	50.00	550.0
(xiii)	5414.3	6989.0	5384.3	0.0	0.0	34766.2	1884.7	0.0	54438.6	45.00	686.0
(xiv)	12289.6	6233.6	3.7	0.0	15.9	0.1	11.7	0.0	18554.6	36.89	10.0
(xv)	0.0	0.0	0.0	0.0	0.0	0.0	5000.0	0.0	5000.0	45.00	550.0
(xvi)	0.0	0.0	0.0	0.0	0.0	0.0	1250.0	0.0	1250.0	45.00	550.0

TABLE 6 - FLOWS IN KMOL/H

STREAM	H_2	CO	CO_2	N_2	AR	H_2O	CH_4	O_2	TOTAL	P (BAR)	T (°C)
(i)	9.9	0.0	3274.9	0.0	0.0	0.0	0.0	0.0	3284.8	50.00	550.0
(ii)	0.0	0.0	0.0	0.0	0.0	8000.0	0.0	0.0	8000.0	50.00	550.0
(iii)	5817.1	2529.3	2847.5	0.0	0.0	6325.5	2894.2	0.0	20413.6	45.00	800.0
(iv)	0.0	0.0	0.0	0.0	15.5	0.0	0.0	3076.5	3092.0	45.00	200.0
(v)	12146.4	6130.7	8191.0	0.0	15.5	24036.7	121.6	0.0	50641.9	40.00	949.2
(vi)	12146.4	6130.7	8191.0	0.0	15.5	39.7	121.6	0.0	26644.9	37.63	30.0
(vii)	24.6	0.0	8187.3	0.0	0.0	0.0	0.0	0.0	8211.9	50.00	10.0
(viii)	0.0	0.0	0.0	0.0	0.0	24000.0	0.0	0.0	24000.0	50.00	250.0
(ix)	14.8	0.0	4912.4	0.0	0.0	0.0	0.0	0.0	4927.1	50.00	550.0
(x)	12146.4	6130.7	8191.0	0.0	15.5	24036.7	121.6	0.0	50541.9	38.50	609.2
(xi)	0.0	0.0	0.0	0.0	0.0	16000.0	0.0	0.0	16000.0	50.00	550.0
(xii)	14.8	0.0	4912.4	0.0	0.0	16000.0	0.0	0.0	20927.2	50.00	547.2
(xiii)	5831.9	2529.3	7759.9	0.0	0.0	22325.5	2894.2	0.0	41340.8	45.00	671.8
(xiv)	12121.8	6130.7	3.7	0.0	15.5	0.1	121.6	0.0	18393.3	37.13	10.0
(xv)	0.0	0.0	0.0	0.0	0.0	0.0	5000.0	0.0	5000.0	45.00	550.0
(xvi)	0.0	0.0	0.0	0.0	0.0	0.0	1250.0	0.0	1250.0	45.00	550.0

TABLE 7 - FLOWS IN KMOL/H

STREAM	H_2	CO	CO_2	N_2	AR	H_2O	CH_4	O_2	TOTAL	P (BAR)	T (°C)
(i)	22.4	0.0	7453.0	0.0	0.0	0.0	0.0	0.0	7475.4	50.00	550.0
(ii)	0.0	0.0	0.0	0.0	0.0	4000.0	0.0	0.0	4000.0	50.00	550.0
(iii)	5361.1	6050.5	4267.4	0.0	0.0	4328.7	2131.1	0.0	22130.9	45.00	850.0
(iv)	0.0	0.0	0.0	0.0	16.4	0.0	0.0	3265.9	3282.3	45.00	200.0
(v)	12677.0	5658.4	8027.7	0.0	16.4	33723.9	11.9	0.0	60115.3	40.00	1045.0
(vi)	12677.0	5658.4	8027.7	0.0	16.4	39.5	11.9	0.0	26430.8	37.38	30.0
(vii)	22.4	0.0	7453.0	0.0	0.0	0.0	0.0	0.0	7475.4	50.00	10.0
(viii)	0.0	0.0	0.0	0.0	0.0	34000.0	0.0	0.0	34000.0	50.00	250.0
(ix)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	50.00	550.0
(x)	12677.0	5658.4	8027.7	0.0	16.4	33723.9	11.9	0.0	60115.3	38.50	637.0
(xi)	0.0	0.0	0.0	0.0	0.0	30000.0	0.0	0.0	30000.0	50.00	550.0
(xii)	0.0	0.0	0.0	0.0	0.0	30000.0	0.0	0.0	30000.0	50.00	550.0
(xiii)	5361.1	6050.5	4267.4	0.0	0.0	34320.7	2131.1	0.0	52130.9	45.00	678.8
(xiv)	12654.5	5658.4	574.7	0.0	16.4	0.1	11.9	0.0	18916.0	36.88	10.0

TABLE 8 - FLOWS IN KMOL/H

STREAM	H_2	CO	CO_2	N_2	AR	H_2O	CH_4	O_2	TOTAL	P (BAR)	T (°C)
(i)	0.0	0.0	2520.0	0.0	0.0	0.0	0.0	0.0	2520.0	50.00	550.0
(ii)	0.0	0.0	0.0	0.0	0.0	8000.0	0.0	0.0	8000.0	50.00	550.0
(iii)	5893.0	2198.1	2362.4	0.0	0.0	6117.1	2955.5	0.0	19526.1	45.00	800.0
(iv)	0.0	0.0	0.0	0.0	15.2	0.0	0.0	3016.1	3031.2	45.00	200.0
(v)	12747.5	5554.4	6851.5	0.0	15.2	23375.2	139.2	0.0	48682.9	40.00	950.0
(vi)	12747.5	5554.4	6851.5	0.0	15.2	36.9	139.2	0.0	25344.6	37.63	30.0
(vii)	0.0	0.0	6300.0	0.0	0.0	0.0	0.0	0.0	6300.0	50.00	30.0
(viii)	0.0	0.0	0.0	0.0	0.0	24000.0	0.0	0.0	24000.0	50.00	250.0
(ix)	0.0	0.0	3780.0	0.0	0.0	0.0	0.0	0.0	3780.0	50.00	550.0
(x)	12747.5	5554.4	6851.5	0.0	15.2	23375.2	139.2	0.0	48682.9	38.50	609.5
(xi)	0.0	0.0	0.0	0.0	0.0	16000.0	0.0	0.0	16000.0	50.00	550.0
(xii)	0.0	0.0	3780.0	0.0	0.0	16000.0	0.0	0.0	19780.0	50.00	547.5
(xiii)	5893.0	2198.1	6142.4	0.0	0.0	22117.1	2955.5	0.0	39306.1	45.00	673.3
(xiv)	12728.6	5554.4	551.5	0.0	15.2	0.1	139.2	0.0	18988.9	37.13	10.0

CLAIMS

1. A process for the production of synthesis gas having a stoichiometric composition desirable for subsequent conversion into methanol or Fischer-Tropsch products from a substantially sulphur-free gaseous hydrocarbon-containing feedstock which process comprises the steps of:

(I) feeding substantially sulphur-free hydrocarbon-containing gas, steam and carbon dioxide to a single primary reforming zone comprised of an exchanger reactor containing a steam reforming catalyst under reforming conditions wherein hydrocarbon gas is partially reformed to produce a primary reformer effluent,

(II) feeding substantially sulphur-free hydrocarbon-containing gas, oxygen-containing gas, steam, carbon dioxide and primary reformer effluent to a secondary reformer containing reforming catalyst under reforming conditions wherein hydrocarbon gas is reformed to produce a secondary reformer effluent,

(III) passing secondary reformer effluent from step (II) to the primary reforming zone as indirect heating medium for the exchanger reactor,

(IV) removing the secondary reforming effluent from the primary reforming zone.

2. A process according to claim 1 wherein the hydrocarbon-containing feedstock is natural gas.

3. A process according to either claim 1 or claim 2 wherein the hydrocarbon-containing gas, steam and carbon dioxide are preheated to a temperature in the range from 400 to about 550°C.

4. A process according to any one of the preceding claims wherein the exchanger reactor includes a shell having a tube bundle positioned in the shell, the shell directs a heating fluid about the tube bundle, the tube bundle includes a plurality of tubes for passing the process fluid to be both heated and chemically reacted, the plurality of tubes of the tube bundle are packed with a stream reforming catalyst, the catalyst being packed within the tubes.

5. A process according to any one of the preceding claims wherein the primary reformer exit temperature is in the range from 750 to 950°C.

6. A process according to any one of the preceding claims wherein the hydrocarbon gas feed to the secondary reformer is obtained by dividing the feed to the primary reformer.

7. A process according claim 6 wherein from 5 to 70% by weight of the gas feed to the primary reformer is fed to the secondary reformer.

8. A process according to any one of the preceding claims wherein the oxygen-containing gas is oxygen.

9. A process according to any one of the preceding claims wherein the oxygen-containing gas is preheated to a temperature in the range from 100 to 300°C.

10. A process according to any one of the preceding claims wherein in the secondary reformer hydrocarbon is both reformed and combusted to increase the temperature of the reformer effluent to a value in the range from 850 to 1100°C.

11. A process according to claim 4 wherein a carbon monoxide shift catalyst is provided on the shell side of the exchanger reactor.

12. A process according to any one of the preceding claims wherein the secondary reformer effluent is removed from the primary reformer zone at a temperature in the range from 450 to 700°C and is cooled to raise some or all the steam required in steps (I) and (II).

13. A process according to any one of the preceding claims wherein the primary and secondary reformers are incorporated in a single vessel.

14. A process according to any one of the preceding claims wherein carbon dioxide is removed wholly or partially from the secondary reforming effluent removed in step (IV) from the primary reforming zone.

15. A process according to any one of the preceding claims wherein in a further step [step (V)] recovered carbon dioxide is recycled as feed to steps (I) and/or (II) of the process.

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