COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Hydrogen-containing Synthesis Gas

We, TEXACO DEVELOPMENT CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 100, West 10th
5 Street, Wilmington, Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained
10 in and by the following statement:—

This invention relates to a process for the manufacture of gas containing carbon monoxide and hydrogen suitable for charging to a synthesis reaction zone for
15 the production of hydrocarbons, oxygen-containing compounds and the like.

In accordance with the invention there is provided a process for the production of gas consisting essentially of carbon
20 monoxide and hydrogen without substantial carbon formation by reaction of carbonaceous material with oxygen in a reaction zone autogenously maintained at a substantially uniform temperature of at
25 least 2000°F. without external heating, characterized by employing a substantially completely closed unobstructed and unpacked reaction zone, the inverse ratio of whose internal surface to the surface of
30 a sphere of the same internal value is at least 0.65.

The invention also includes a continuous process for producing synthesis gas containing carbon monoxide and
35 hydrogen from a hydrocarbon and oxygen in the absence of external heating and without substantial carbon formation, which comprises establishing a reaction zone formed as a substantially unob-
40 structed and generally cylindrical space having a length to radius ratio of 0.67 to 10, maintaining a high temperature and superatmospheric pressure in said space, continuously introducing hydrocarbon
45 and oxygen into said space to mix and exothermically react therein in a pre-determined area, continuing the reaction

[Price 2s.]

of the products of the exothermic reaction in an endothermic reaction in the space around the area of the exothermic reaction 50 to utilize heat from the exothermic reaction, and continuously removing from said reaction zone an effluent stream of reaction products containing essentially carbon monoxide and hydrogen. 55

In the accompanying drawings, Figure 1 is a section taken along the horizontal axis of a gas generator, shown somewhat diagrammatically.

Figure 2 is a longitudinal section of a 60 preferred form of gas feeder.

Figure 3 is a graph representing the relation of the surface ratios of generators of different shapes as compared to the surfaces of spheres of corresponding 65 volumes.

In one embodiment of this invention a hydrocarbon consisting essentially of methane is reacted with oxygen, in the absence of added steam and in the absence 70 of a catalyst, at a temperature in the range of 2000—2600° F. and in a reaction zone in which the ratio of interior surface area to interior volume is relatively small, as later explained. The 75 hydrocarbon gas separately preheated to at least 800° F., if preheated, and preferably about 1200° F., preferably with no cracking, is charged at a rate of 1000—3000 cu. ft./hr./cu. ft. of reaction 80 space. The oxygen is, if preheated, separately preheated to at least 600° F. and preferably 800° F. or higher and charged to the reaction zone in an amount such that combustion or what can be 85 termed a primary reaction occurs with a substantially non-luminous flame within the reaction zone, except in the relatively small region adjacent the point of initial contact between entering gas and oxygen 90 streams, this primary reaction being substantially exothermic. If preheating is omitted, the reaction may be initiated by ignition of the mixture. Some of the

products of the primary reaction and excess hydrocarbon then enter into a secondary reaction or reactions which are substantially endothermic. The final products of reaction are continuously removed from the reaction zone as an effluent stream consisting essentially of carbon monoxide and hydrogen and containing approximately 5 mol per cent. water or less and substantially less than 2 mol per cent. of carbon dioxide. The effluent stream is substantially free from suspended carbon in that it contains less than 1 gram/1000 cu. ft. of product gas measured under standard conditions. The residual methane content of the product gas does not exceed 4 or 5 mol per cent. It contains carbon monoxide and hydrogen in the proportion of about 1 mol carbon monoxide to 2 mols of hydrogen. The molecular proportions depend, however, upon other factors, such as the composition of the feed hydrocarbon, and these factors may be taken advantage of in producing gas containing carbon monoxide and hydrogen in the desired proportions.

The temperature of the effluent stream leaving the reaction zone is quickly reduced by quenching or cooling. It is desirable to reduce the temperature, for example, from about 2600° F. to 1000—1500° F. in not more than 1 second, so as to avoid undesired secondary reactions, some of which lead to carbon formation at this stage.

Oxygen of relatively high purity, at least 80 per cent. and preferably at least 95 per cent., is used, thereby eliminating a large amount of nitrogen from the reactant feed to the gas generator. This materially reduces the heat requirements and also results in a synthesis gas more suitable for the synthesis operation.

The proportion of oxygen charged to the gas generator relative to the hydrocarbon feed appears critical from the standpoint of avoiding free carbon production and excessive carbon dioxide and water formation. Suitable conditions of operation are realized at the preferred minimum of 2000° F. by initially regulating the oxygen charged to the generator, or, as it can be otherwise stated, the O/C ratio (atomic ratio of total oxygen to total carbon in the feed) within the relatively broad limits of approximately 1.0 to 1.2, and adjusting the O/C ratio within these limits, so that the residual methane content of the effluent gas from the generator is in the range of 0.5 to 5 mol per cent. and preferably 2 to 3 mol per cent. This principle applies whether the oxygen be from substantially pure oxygen, an oxygen enriched gas or air and the carbon be from a solid hydrocarbon as coal, a liquid hydrocarbon as fuel oil or a gaseous hydrocarbon as natural gas.

When the residual methane content of the effluent gas from the generator exceeds about 5 mol per cent. under the aforesaid conditions, free carbon is produced in at least appreciable amount, as evidenced by noticeable discolouration of water used in quenching the effluent stream. There appears to be no discolouration of the quench water when the residual methane content amounts to 5 mol per cent. or less. It is thus desirable to maintain the residual methane content of the effluent gas in the range 0.5 to 5 mol per cent., this being accomplished by maintaining the O/C ratio between 1.0 and 1.2 and adjusting it within this range. If sufficient oxygen is charged so that methane is absent from the effluent gas, then a relatively large proportion of the oxygen disappears in the form of carbon dioxide and water. In addition, the reaction temperatures tend to be excessive.

From the standpoint of realizing maximum conversion of carbon in the feed gas into synthesis gas (carbon monoxide and hydrogen) and the formation of little or no free carbon, maintaining the methane content of the generator effluent in the range of 0.5 to 2 mol per cent. is advantageous. Below the lower figure, there appears to be an excess production of carbon dioxide and water. On the other hand, maximum conversion of oxygen to synthesis gas appears to be realized when the methane content is maintained around 2 to 3 mol per cent., the yield declining outside this range.

Under the conditions of temperature and pressure contemplated and with a feed hydrocarbon consisting essentially of methane, for example, the oxygen usually amounts to about 5 to 15 mol per cent. in excess of that stoichiometrically required to convert all of the carbon in the hydrocarbon gas to carbon monoxide with the formation of no other oxygenated compounds. The concentration of oxygen is such that under the conditions of temperature and pressure contemplated in the generator and with the aforesaid preheating of the reactants, the reaction is effected without necessity for external heating of the reaction zone. By separately preheating the reactant gases and effecting mixing of the preheated gases entirely within the reaction zone, backfiring in the feed lines and the preheaters is prevented.

Mixing of the reactant gases is accomplished entirely within the reaction zone

by introducing the separate streams of hydrocarbon and oxygen so that they impinge upon each other within the reaction zone while flowing at high velocity, i.e., 100 feet per second or in the range of 30 to 200 feet per second.

A portion of the total oxygen charged may be premixed with the hydrocarbon gas, providing the resulting mixture is incombustible under the prevailing conditions of preheating. For instance, the oxygen or oxygen-enriched gas may be divided into major and minor streams, the major stream containing 55 to 85 per cent. of the total oxygen supplied, while the minor stream contains from 15 to 45 per cent. of the total oxygen. Preferably, the division is effected so that the major stream constitutes 60 to 75 per cent. of the total oxygen and the minor stream 25 to 40 per cent. The major stream of oxygen is combined with the hydrocarbon such as methane and preheated to a temperature of 1000—1200° F., this temperature being practicable because of the proportions of the mix. Adequate mixing is secured by forming the preheater in a manner to effect turbulence of the two reactants.

The minor stream of oxygen or oxygen-enriched gas is heated in a separate preheater, the limit of preheat being governed by the material of which the preheater and conducting pipes are formed. Ordinary carbon steel permits heating of the oxygen to only about 800° F., whereas with a high temperature alloy such as that at present sold under the Registered Trade Mark " Hastelloy ", the oxygen may be preheated to about 1500° F., provided there is only a small pressure differential between the interior and exterior of the tube or pipe in which the oxygen is preheated. ·

Mixing of the two streams is accomplished in the reaction zone by introducing them in a manner to impinge upon one another while flowing at high velocity as already described.

Another important feature is the employment of an unpacked reaction zone with unobstructed flow of radiant energy between the adjacent walls, all wall surfaces being within easy reach of the source or sources of such radiant energy as is evolved by that portion of the reactants undergoing exothermic reaction, i.e., in the primary reaction. With methane as the hydrocarbon, as much as 25 per cent. thereof may undergo combustion forming carbon dioxide and water vapour, which products, in turn, react endothermically with additional methane in the reaction zone to form carbon monoxide and hydrogen. This primary exothermic combustion, which supplies energy required for the secondary endothermic reactions, appears to be effected mainly in the small region of initial contact between entering gas and oxygen.

It has been found that as regards the most efficient utilization of the energy from the primary or exothermic reaction in the secondary or endothermic reactions, the generator, in addition to being devoid of packing, should be of a shape such that the internal surface area is small relative to the internal volume as in the case of a sphere. However, because of other design requirements, a sphere is not always a practical shape, a shape such as a cylinder with a concave or convex end or ends being usually preferred.

The surface-volume ratio of such a generator can best be defined with reference to its relation to a sphere of the corresponding volume, it being readily apparent that the surface-volume ratio of the generator will approach but never quite reach the surface-volume ratio of a sphere of equal volume. This degree of approach to the surface-volume ratio of a sphere can be expressed by a constant K in terms of the ratio of the overall length to the radius of any generally cylindrical generator regardless of whether one or both ends be flat, concave or conical. The constant K can be defined as the ratio of the surface of a sphere to the surface of a generator, the two being of equal volume.

The value of the constant K as related to the ratio of the overall length and the radius of a pure cylindrical generator, and considering the feed and product ports as a continuous part of the surface in which they are located, can be determined as follows :

$$\text{Surface of the generator } (S_z) = 2\pi R^2 + 2\pi RL$$
$$\text{Volume of the generator } (V_z) = \pi R^2 L$$

where R is the radius of the generator and L is the overall length.

The surface and volume of a sphere of equal volume can be determined as follows :

$$\text{Surface of the sphere } (S_s) = 4\pi R_1^2$$

$$\text{Volume of the sphere } (V_s) = \frac{4}{3}\pi R_1^3$$

where R_1 is the radius of the sphere but $V_z = V_s$, so

$$\pi R^2 L = \frac{4}{3}\pi R_1^3$$

$$R_1^3 = \frac{3}{4}R^2L$$

$$R_1 = \left(\frac{3}{4}R^2L\right)^{\frac{1}{3}}$$

Since the volumes of the sphere and the generator are assumed equal, K is determined as follows, i.e.:

$$K = \frac{\text{Surface of the sphere}}{\text{Surface of the generator}} = \frac{S_s}{S_g}$$

or

$$K = \frac{4\pi R_1^2}{2\pi(R^2 + RL)} = \frac{2R_1^2}{R^2 + RL}$$

Substituting the value of R_1,

$$K = \frac{2\left(\frac{3}{4}R^2L\right)^{\frac{2}{3}}}{R^2 + RL}$$

The following table illustrates the value of K for cylindrical generators of selected ratios of overall length to radius:

R	L	Overall L/R	K
1	0.01	0.01	0.0759
1	0.1	0.1	0.3234
1	0.2	0.2	0.4706
1	0.5	0.5	0.6934
1	1	1	0.8254
1	2	2	0.8736
1	5	5	0.8046
1	10	10	0.6966
1	20	20	0.5793
1	50	50	0.4394
1	100	100	0.3522

The aforesaid values of K and L/R are plotted as the solid line in Figure 3 on a logarithmic scale. It will be noted therefrom that in varying the ratio of L/R, K for the cylinder with flat ends approaches and then recedes from a value of 1, the S/V ratio of the sphere never being attained.

The remaining curves in Figure 3 represent the K versus L/R ratios for cylinders of the end shapes indicated and a generator of square cross-section, the radius of an inscribed circle in the latter being taken as R. For cylinders of other than flat ends, R is taken as the radius of the cylindrical section. In the case of the conical ends, the included angle has been taken as 60°. Such curves can readily be determined in the case of each

cylinder by the following formulas.

For a cylindrical generator having one hemispherical end,

$$K = \frac{4(0.5R^3 + 0.75\ R^2L)^{\frac{2}{3}}}{3R^2 + 2RL}$$

where L is the length of the pure cylindrical section.

For a cylindrical generator with two hemispherical ends,

$$K = \frac{2(R^3 + 0.75\ R^2L)^{\frac{2}{3}}}{2R^2 + 2RL}$$

where L is the length of the pure cylindrical section.

For a cylindrical generator with one 60° conical end,

$$K = \frac{4[R^2(0.75L + 0.4330127R)]^{\frac{2}{3}}}{R(3R + 2L)}$$

where L is the length of the pure cylindrical section.

For a cylindrical generator with two 60° conical ends,

$$K = \frac{2[R^2(0.75L + 0.8660254R)]^{\frac{2}{3}}}{R(L + 2R)}$$

where L is the length of the pure cylindrical section.

For a rectangular parallelopiped of square cross-section of a side dimension w.

$$K = \frac{2.417988\ (Lw^2)^{\frac{2}{3}}}{2Lw + w^2}$$

In the case of the cylindrical generator with one hemispherical end, the L of the L/R ratio is taken as the overall length of the generator, i.e., L + R, the corresponding curve in Figure 3 being derived from the following data:

R	L of the formula	Overall L / R	K
1	0	1	0.8399
1	0.01	1.01	0.8427
1	0.1	1.1	0.8643
1	0.2	1.2	0.8828
1	0.5	1.5	0.9148
1	1	2	0.9283
1	2	3	0.9071
1	5	6	0.8073
1	10	11	0.6957
1	20	21	0.5783
1	50	51	0.4389
1	100	101	0.3520

In the case of the cylindrical generator with two hemispherical ends, the L of the L/R ratio is taken as the overall length of the generator, i.e., L+2R, the corresponding curve on Figure 3 being derived from the following data :

R	L of the formula	Overall L / R	K
10	0 (a sphere)	2	1.000
1	0.01	2.01	0.999
1	0.1	2.1	0.9994
1	0.2	2.2	0.9979
1	0.5	2.5	0.9892
15 1	1	3	0.9681
1	2	4	0.9210
1	5	7	0.8073
1	10	12	0.6942
1	20	22	0.5722
20 1	50	52	0.4385
1	100	102	0.3513

In the case of the cylindrical generator with one 60° conical end, L of the L/R ratio is taken as L+1.73205R, the corresponding curve on Figure 3 being derived from the following data :

R	L of the formula	Overall L / R	K
30 1	0	1.73205	0.7631
1	0.01	1.74205	0.7668
1	0.1	1.83205	0.7958
1	0.2	1.93205	0.8210
1	0.5	2.23205	0.8675
35 1	1	2.73205	0.8948
1	2	3.73205	0.8867
1	5	6.73205	0.7988
1	10	11.73205	0.6918
1	20	21.73205	0.5766
40 1	50	51.73205	0.4384
1	100	101.73205	0.3516

For a cylindrical generator with two 60° conical ends, L of the L/R ratio is taken as L+3.46410R, the corresponding curve on Figure 3 being derived from data such as the following :

R	L of the formula	Overall L / R	K
1	0	3.4641	0.9085
1	0.01	3.4741	0.9092
1	0.1	3.5641	0.9145
1	0.2	3.6641	0.9188
1	0.5	3.9641	0.9239
1	1	4.4641	0.9181
1	2	5.4641	0.8878
1	5	8.4641	0.7921
1	10	13.4641	0.6868
1	20	23.4641	0.5740
1	50	53.4641	0.4375
1	100	103.4641	0.3514

For a rectangular parallelopiped of square cross-section, w has been taken as the diameter of an inscribed circle, w being also the width of any one side. In calculating the following data for the curve of Figure 3, 0.5 w has been taken as the radius.

w	L of the formula	Overall L / 0.5w	K
2	0.01	0.01	0.07000
2	0.1	0.1	0.2983
2	0.2	0.2	0.4641
2	0.5	0.5	0.6397
2	1	1	0.7616
2	2	2	0.8060
2	5	5	0.7423
2	10	10	0.6427
2	20	20	0.5344
2	50	50	0.4054
2	100	100	0.3249

With the thus derived curves of Figure 3, it is apparent that the value of K can be determined for any of the reactors of different shapes, providing the ratio of L/R is known, the actual dimensions of the reactor are immaterial.

For example, if it is desired to use a generator formed as a cylinder with one flat end and one hemispherical end, one of the most practical shapes, reference can be made to the curve for such a shape

whereupon it will be found that the closest approach to the surface to volume ratio of the sphere of corresponding volume is found where K is about 0.93. The corresponding L/R ratio is about 2.0. Thus if the selected reactor is to be 10 feet long overall, the radius should be 5 feet.

For the purpose of this invention, a range of L/R from 0.67 to 10 is desirable, the preferred ratio being in the range of 1 to 4.

In any case, it is desirable for the open reaction zone to be sufficiently compact so that the temperature is uniform throughout the entire reaction zone.

Avoidance of external firing of the reaction zone and the absence of refractory packing material from the interior thereof overcomes serious apparatus, construction and operating limitations that have existed heretofore. Absence of packing not only avoids a substantial pressure drop through the reaction zone, but also materially reduces the tendency toward carbon formation and deposition since it appears that large surface area increases free carbon formation. Deposition of carbon also increases the pressure differential through the reaction zone.

A further advantage of the absence of packing and the surface-volume or length to radius ratio already described is found in the fact that the clear unobstructed space so formed, with its large volume relative to its internal surface, enables a substantially complete transfer of the energy from the primary exothermic reaction to the secondary endothermic reactions by radiation. Whatever energy may be radiated from the exothermic reaction onto the surrounding walls of the reactor is immediately re-radiated back into the reaction zone, very little energy being lost, the wall surfaces being preferably of a character to insure maximum re-radiation. Moreover, all the products of the primary reaction, whether they be in the form of radicals or activated molecules, are free to proceed to the secondary reaction in a highly mixed and energized state without interference by a physical body such as packing. The absence of packing insures a free path of travel for both the radiant energy from the primary reaction and the radiant energy re-radiated from the walls to the zone of secondary reaction, thereby causing the secondary reaction or reactions to proceed faster and at a higher and more uniform temperature or energy level at which a better product composition is attained.

This action is in decided contrast to the action in a packed reactor, wherein (1) the products of the exothermic reaction come into physical contact with packing almost immediately upon formation, causing them to react to form more stable molecules, deposit carbon on the packing surfaces, and to deactivate the active molecules, so losing energy that would otherwise be available to the secondary reaction, (2) the products entering into the secondary reaction are shielded to a material extent from the radiant heat of the exothermic reaction and any re-radiation from the walls, and (3) the products of the exothermic reaction tend to pocket in the interstices of the packing with consequent carbon deposition and loss of final product.

In Figure 1, the numeral 1 designates a cylindrical vessel lined with refractory material 2. A baffle formed of walls 3a and 3b is provided within the vessel to divide it into two sections, one section being the reaction zone 5 which, for example, is about 8 feet in length along its horizontal axis, while the other section 6 is used for cooling the resulting product gases. With a radius of 2.5 feet, the L/R ratio is about 3.2 which is well within the preferred range. Walls 3a and 3b are designed to permit flow of reaction gases therethrough with no substantial drop in pressure while protecting the interior of the cooling section from direct radiation from the reaction section and insuring re-radiation back to the reaction zone, this being accomplished by the staggering arrangement of the openings 3c.

A cooling coil 7 is embedded in the refractory lining of the reaction section and adapted for the circulation therethrough of water, or any other fluid heat carrier, the purpose being to prevent overheating of the metal shell. The heat, so absorbed, may be used for preheat purposes and for steam or power generation for use elsewhere in the process.

The reactant gases are introduced to the reaction zone through a plurality of gas feeders 8 which are described in more detail in connection with Figure 2.

The reaction products are discharged from the generator through passages 3c into cooling section 6 where they are reduced to a temperature suitable for introduction to an intermediate storage facility or to the synthesis reactor by a water spray 9. The quench water passes out through opening 6a with the synthesis gas. With a synthesis catalyst of the iron type, these gases are reduced in temperature by the quench water and while still under pressure of 200—250 pounds, pass in contact with the synthesis catalyst at that temperature so as to effect conversion

of carbon monoxide and hydrogen into hydrocarbons, oxygen-containing compounds and the like.

The gas feeders 8, as indicated in Figure 2, comprise essentially two concentric tubes 11 and 12 terminating in a water cooled tip 13. Thus, the tip 13 is of hollow construction having a water space 14 to which water is introduced through a tube 15 and removed through a tube 16.

One of the reactant gases flows through the annular space between the tubes 11 and 12, while the other reactant flows through the interior of the inner tube 12. Thus methane may flow through the annular space, while oxygen flows through the inner passage, or vice versa. Thus, the methane and oxygen streams impinge upon each other at the point of discharge from the tip 13 which is just inside the reaction zone. As indicated in Figure 1, the feeder tips may be substantially flush with the interior surface of the refractory lining of the vessel 1.

In operation there is a small zone of blue flame, glow or radiation immediately adjacent the tip while in the rest of the reaction zone there is no visible flame. It is in this small region where blue flame exists, and where as much as 25 per cent. of the entering methane may undergo relatively complete combustion, forming carbon dioxide and water vapour which products subsequently react with additional methane in the reaction zone to form carbon monoxide and hydrogen.

There may be a plurality of the feeders 8. For example, there may be several uniformly disposed in the end of the vessel 1.

By way of example, a feed gas consisting essentially of methane is preheated to a temperature of about 930° F., and a stream of substantially pure oxygen is separately heated to a temperature of about 800° F., the preheated gas streams are passed into an unpacked reaction zone, having a L/R ratio of about 2.7 which is within the aforesaid preferred range of 1 to 4, operating under a pressure of about 250 pounds per square inch gauge and subjected to combustion therein at a temperature of about 2000° F. in the absence of a catalyst. The hydrocarbon or feed gas is charged at the rate of about 2000 cubic feet (S.C.) per hour per cubic foot of total reaction zone volume. The quantity of oxygen charged to the reactor is maintained at about 39.3 mol per cent. of the total gas charged, i.e., both oxygen and feed gas. The product gas amounts to about 3.2 mols of total gas per mol of hydrocarbon feed gas. The compositions of the hydrocarbon feed gas and of the product gas are:

Mol %	Feed Gas	Product Gas	
CH_4	83.6	2.8	
C_2H_6	10.2	—	70
C_3H_8	4.5	—	
C_4H_{10}	0.1	—	
CO_2	1.0	1.4	
Air	0.6	—	
CO	—	32.9	75
H_2	—	56.9	
N_2	—	0.9	
H_2O	—	5.1	
	100.0	100.0	

Under such conditions, more than 80 per cent. of the oxygen charged is converted to carbon monoxide and the quench water used for cooling the hot product gas is substantially free from solid carbon.

By contrast, when operating the reactor under substantially the same conditions of temperature and pressure but regulating the oxygen content so that it amounts to about 35 mol per cent. of the total gas charged, the methane content of the product gas is at least 10 mol per cent. and production of solid carbon is excessive as evidenced by the fact that the quench water is distinctly black in colour due to its large content of free carbon.

On the other hand when operating the reactor so that the oxygen charge amounts to 42.2 mol per cent. of the total gas charged, in which case the product gas contains only a trace of methane, substantially less than 80 per cent. of the oxygen is converted to carbon monoxide, the carbon dioxide and water being increased.

The following example shows the relationship between methane content of the effluent gas from the generator and the yield of carbon monoxide and hydrogen when charging hydrocarbon gas of the same composition as that previously set forth to the generator operating under a pressure of about 250 pounds and at a temperature of about 2000° F. The hydrocarbon gas was preheated to about 830° F., while the oxygen was separately preheated to about 600° F. The oxygen charge rate was in the proportion of 53 to 62 volumes per 85 volumes of hydrocarbon gas:

Mol % CH_4 in Effluent Gas	Yield of $CO + H_2$ as Mol % of Theoretical Max. Yield	
6.0	71.9	
3.2	75.6	
0.4	70.9	125
0.1	69.0	

From the foregoing data it is seen that a yield of 75.6 per cent. of the maximum theoretical yield is obtained when conditions are maintained so that the effluent gas contains 3.2 per cent. methane. When the methane content of the effluent gas is either substantially below 3 mol per cent. or substantially above it, the yield of synthesis gas is less. The yield of 75.6 per cent. corresponds to about 80.5 per cent. conversion of oxygen to carbon monoxide.

While mention has been made of quenching the product gas with water, other methods of cooling involving steam generation may be used.

Mention has been made of charging methane or a gas consisting essentially of methane to the generator. It is contemplated, however, that the hydrocarbon charge to the generator may comprise higher molecular weight hydrocarbons either normally gaseous or normally liquid. The hydrocarbon charge may consist essentially of liquid hydrocarbons or it may comprise a combination of gaseous and liquid hydrocarbons. For the purposes of this invention, liquid hydrocarbons may embrace not only relatively high boiling hydrocarbon mixtures boiling in the range of fuel oil, but also asphalt and other solid hydrocarbons which melt and flow when heated. Coal and lignite are examples of solid carbonaceous materials that may be reacted with oxygen to form synthesis gas in a reaction zone such as described. Such material may be introduced to the generator in the form of finely divided particles suspended in steam or other gas, steam being preferably added to supplement the oxygen, and supply the needed oxygen where a hydrogen-carbon monoxide mixture is desired. Obviously such a generator must be mechanically designed for proper feed of solid material such as coal and the discharge of slag therefrom.

Liquid hydrocarbons when charged to the reactor undergo some decomposition into light hydrocarbons including methane. Furthermore, the gases in the reactor tend to produce some methane in accordance with the reaction:

$$CO + 3H_2 = CH_4 + H_2O$$
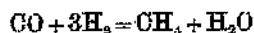
Therefore, when charging liquid hydrocarbons, it also appears that regulation of the oxygen charge so that the product gas contains nothing in excess of the aforementioned small amount of methane avoids formation of free carbon.

As previously mentioned, it is contemplated employing no preheating, preheating of only the hydrocarbon, or separate preheating of the hydrocarbon and oxygen streams. These streams may be preheated to temperatures as high as conveniently possible having regard to the inherent limitations in existing materials of construction. The preheating of an oxygen stream to relatively high temperatures requires employment of preheating apparatus constructed of material resistant to oxygen at such temperatures. It is advisable to preheat separately the oxygen stream to as high as 600 to 800° F. and higher if possible and the hydrocarbon stream to as high as 800 to 1200° F. Higher preheats cause the attainment of higher effective reaction temperatures which are desirable in that higher overall yields are obtained, the production of undesirable carbon dioxide and methane is reduced, and there are reduced tendencies toward carbon formation at low O/C ratios.

If necessary the hydrocarbon feed may be treated to remove sulphur compounds prior to introduction to the generator. This is desirable in order to produce a synthesis feed gas free from or substantially free from sulphur compounds.

Obviously, many modifications of the invention as above set forth may be made without departing from the scope thereof.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of gas consisting essentially of carbon monoxide and hydrogen without substantial carbon formation by reaction of carbonaceous material with oxygen in a reaction zone autogenously maintained at a substantially uniform temperature of at least 2000° F. without external heating, characterized by employing a substantially completely closed unobstructed and unpacked reaction zone, the inverse ratio of whose internal surface to the surface of a sphere of the same internal volume is at least 0.65.

2. A continuous process for producing synthesis gas containing carbon monoxide and hydrogen from a hydrocarbon and oxygen in the absence of external heating and without substantial carbon formation which comprises establishing a reaction zone formed as a substantially unobstructed and generally cylindrical space having a length to radius ratio of 0.67 to 10, maintaining a high temperature and superatmospheric pressure in said space, continuously introducing hydrocarbon and oxygen into said space to mix and exothermically react therein in a predetermined area, continuing the

reaction of the products of the exothermic reaction in an endothermic reaction in the space around the area of the exothermic reaction to utilize heat from the exothermic reaction, and continuously removing from said reaction zone an effluent stream of reaction products containing essentially carbon monoxide and hydrogen.

3. A process according to either of claims 1 or 2 for the production of carbon monoxide and hydrogen by partial combustion of a carbonaceous fuel with oxygen wherein a portion of the fuel is reacted exothermically with oxygen with the production of some carbon dioxide and water vapour and said last mentioned reaction products are reacted endothermically with a further portion of the reactant materials to form carbon monoxide and hydrogen, characterized by the fact that said reaction zone has radiation boundary surfaces substantially uniformly maintained at a temperature approaching the reaction temperature so that, by reason of the shape of said surface, said endothermic reaction is effected in close proximity to the exothermic reaction and heat is passed to said endothermic reaction by radiation, said oxygen being supplied to the reaction zone in a quantity such that both said exothermic and endothermic reactions are effected within the reaction zone while autogenously maintaining said zone uniformly throughout at said uniform temperature of at least 2000° F., and an effluent stream of reaction products comprising carbon monoxide and hydrogen substantially free from carbon is continuously removed from said reaction zone.

4. A process according to any one of the preceding claims, in which the reaction products contain a small amount not in excess of 4 mol per cent. of methane.

5. A process as defined in any one of claims 1 to 4, in which the reaction products contain from 0.1 to 4 mol per cent. of methane.

6. A process according to any one of the preceding claims, wherein said reaction zone is maintained under a pressure of 200—300 pounds per square inch gauge, and the proportion of oxygen relative to hydrocarbons passing to the reaction zone is regulated so that said reaction is effected with a substantially non-luminous flame.

7. A process according to any one of the preceding claims, in which the oxygen is preheated to an elevated temperature of at least 600° F. and the hydrocarbon is preheated to an elevated temperature of at least 800° F.

8. A process according to any one of the preceding claims, wherein said hydrocarbon gas consists mainly of methane.

9. A continuous process for producing synthesis gas containing carbon monoxide and hydrogen involving reaction of a carbonaceous material with oxygen, comprising passing said material and oxygen to a non-catalytic unpacked reaction zone of generally cylindrical shape in which the ratio of internal diameter to internal radius is within the range 0.67 to 10, effecting non-catalytic conversion of carbon in said carbonaceous material to carbon monoxide without external heating of said reaction zone at a temperature of at least 2000° F. and under superatmospheric pressure, and continuously removing from the reaction zone an effluent stream of products of reaction consisting essentially of synthesis gas.

10. A process according to either of claim 1 or 2, wherein the oxygen to carbon ratio of the feed to the reaction zone is varied in the range of 1.0 to 1.2 to maintain a methane content in the effluent of from 0.5 to 5 mol per cent.

11. A process according to any one of the preceding claims, wherein a stream of oxygen is divided into major and minor streams, and the major stream is combined with the hydrocarbon gas, and said mixture is raised to an elevated temperature, said minor stream of oxygen also being raised to an elevated temperature and said preheated reactants being separately introduced into the reaction zone.

12. The process for producing synthesis gas substantially as hereinbefore described.

13. Synthesis gas whenever obtained by the process according to any of the preceding claims.

Fig.1.

Fig.2.

Fig.3.

Fig.1.

Fig.2.

Fig.3.