United States Patent

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[72] Inventors **Paul E. Fischer**
Lafayette;
Melvin M. Holm, Alameda, both of Calif.

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[73] Assignee **Chevron Research Company**
San Francisco, Calif.

[54] **HYDROGEN PRODUCTION BY REACTION OF CARBON WITH STEAM OR STEAM AND OXYGEN**
8 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** **48/204,**
23/19 V, 23/140, 23/183, 23/212, 48/202, 48/206
[51] **Int. Cl.** **C10j 3/16**
[50] **Field of Search** 48/204,
206, 202, 197; 252/373; 23/212, 212 A, 212 B

[56] **References Cited**

UNITED STATES PATENTS

1,505,065	8/1924	West et al.	48/204
1,926,587	9/1933	Hansgirg	23/212
3,004,839	10/1961	Tornquist	48/197

Primary Examiner—Joseph Scovronek
Attorneys—A. L. Snow, F. E. Johnston, C. J. Tonkin and T. G. De Jonghe

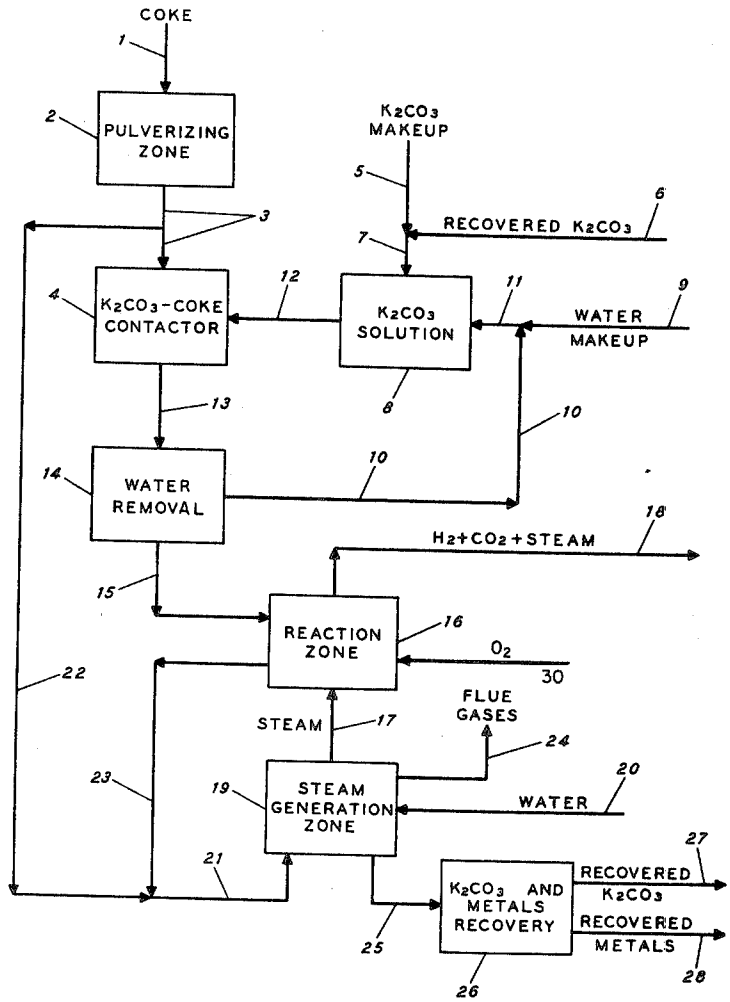
ABSTRACT: Process for producing a hydrogen-rich gas mixture which is lean in CO and CH_4 relative to CO_2 by:

a. contacting subdivided carbonaceous matter with steam and oxygen in a reaction zone at temperatures between about 800° and 1,350° F. to form H_2 and CO_2,

b. feeding sufficient steam to the reaction zone so that the hydrogen-rich gas mixture which is withdrawn from the reaction zone contains at least 60 volume percent steam, and

c. withdrawing the hydrogen-rich gas mixture from the reaction zone at a temperature between 800° and 1,250° F.

The ratio of CO_2 to CO and CO_2 to CH_4 in the hydrogen-rich gas withdrawn from the reaction zone is maintained above 2.5. According to a preferred embodiment only steam is used as an oxidizing source in the reaction zone.



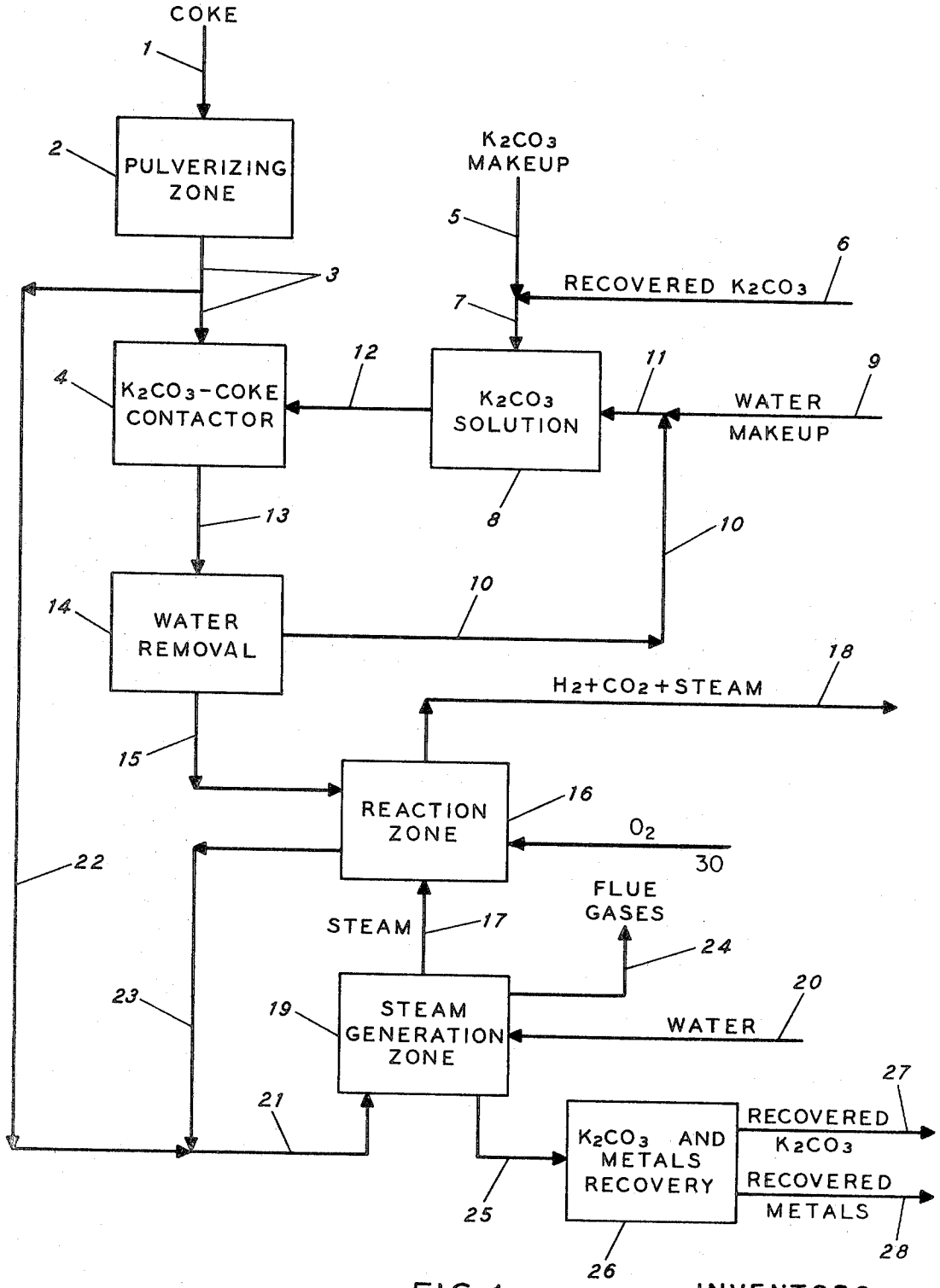


FIG. 1

INVENTORS
PAUL E. FISCHER
MELVIN M. HOLM
BY J. D. DeJongh
C. J. Tonkin
ATTORNEYS

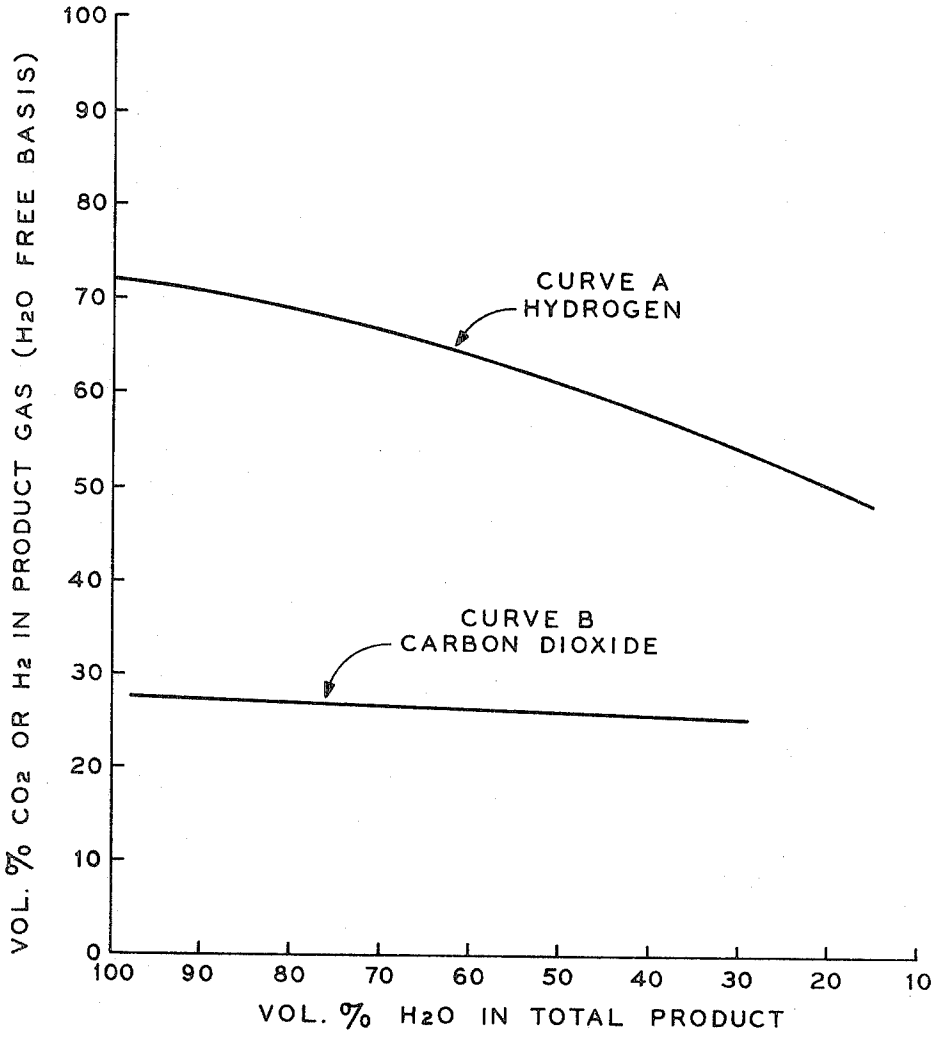


FIG. 2

INVENTORS
PAUL E. FISCHER
MELVIN M. HOLM
BY J. A. De Jonghe
C. J. Tonkin
ATTORNEYS

HYDROGEN PRODUCTION BY REACTION OF CARBON WITH STEAM OR STEAM AND OXYGEN

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the production of a hydrogen-rich gas; more particularly, the present invention relates to the production of an H_2–CO_2gas mixture in a process wherein steam is reacted with carbonaceous matter. Our application Ser. No. 830,468, titled "Hydrogen Production by Reaction of Carbon with Steam an Oxygen" filed on June 4, 1969, relates to a hydrogen production process somewhat similar to the process of the present patent application, and the disclosure of the aforesaid patent application is hereby incorporated by reference to the present patent application.

DESCRIPTION OF THE PRIOR ART

Various methods have been suggested for the production of hydrogen-rich gas mixtures. Among these methods are steam-hydrocarbon reforming, partial oxidation of hydrocarbons, Lurgi heavy hydrocarbons gasification, the traditional steam, red-hot coke reaction, and modified methods of reacting carbonaceous matter with steam and oxygen, such as described in U.S. Pat. No. 1,505,065.

The two leading processes, that is the two processes which are most frequently used to generate hydrogen, are steam-hydrocarbon reforming and partial oxidation of hydrocarbons.

In typical steam reforming processes, hydrocarbon feed is pretreated to remove sulfur compounds which are poisons to the reforming catalyst. The desulfurized feed is mixed with steam and then is passed through tubes containing a nickel catalyst. While passing through the catalyst-filled tubes most of the hydrocarbons react with steam to form hydrogen and carbon oxides. The tubes containing the catalyst are located in a reforming furnace, which furnace heats the reactants in the tubes to temperatures of 1,200°–1,700° F. Pressures maintained in the reforming furnace tubes range from atmospheric to 450 p.s.i.g. If a secondary reforming furnace or reactor is employed, pressures used for reforming may be as high as 450 p.s.i.g. to 700 p.s.i.g. In secondary reformer reactors, part of the hydrocarbons in the effluent from the primary reformer is burned with oxygen. Because of the added expense, secondary reformers are generally not used in hydrogen manufacture but are used where it is desirable to obtain a mixture of H_2 and N_2,as in ammonia manufacture. The basic reactions in the steam reforming process are:

$$C_nH_{2n+2}+nH_2O \rightleftarrows nCo+(2n+1)H_2$$
$$C_nH_{2n+2}+2nH_2O \rightleftarrows nCO_2+(3n+1)H_2$$

e.g., methane-steam:

$$CH_4+H_2O \rightleftarrows cO+3H_2; \text{ and}$$
$$CH_4+2H_2O \rightleftarrows CO_2+4H_2$$

Because the hydrogen product is used in high-pressure processes, it is advantageous to operate at high pressure to avoid high compression requirements. However, high pressures are adverse to the equilibrium; and higher temperatures must be employed. Consistent with hydrogen purity requirements of about 95 to 97 volume percent H_2in the final H_2product, and consistent with present metallurgical limitations, generally single stage reforming is limited commercially to about 1,550° F. and 300 p.s.i.g.

In typical partial oxidation processes, a hydrocarbon is reacted with oxygen to yield hydrogen and CO. Insufficient

oxygen for complete combustion is used. The reaction may be carried out with gaseous hydrocarbons or liquid or solid hydrocarbons, for example, with methane, the reaction is:

$$CH_4+1/2O_2 \rightleftarrows 2H_2+CO$$

With heavier hydrocarbons, the reaction may be represented as follows:

$$C_7H_{12}+2.8O_2+2.1H_2O \rightleftarrows 6.3CO+0.7\,CO_2+8.1\,H_2$$

Both catalytic and noncatalytic partial oxidation processes are in use. Suitable operating conditions include temperatures from 2,000° F. up to about 3,200° F. and pressures up to about 1,200 p.s.i.g., but generally pressures between 100 and 600 p.s.i.g. are used. Various specific partial oxidation processes are commercially available, such as the Shell Gasification Process, Fauser-Montecatini Process, and the Texaco Partial Oxidation Process.

There is substantial CO in the hydrogen-rich gas generated by either reforming or partial oxidation. To convert the CO to H_2 and CO_2, one or more CO shift conversion stages are typically employed. The CO shift conversion reaction is:

$$CO+H_2o \longrightarrow H_2+CO_2$$

This reaction is typically effected by passing the CO and H_2O over a catalyst such as iron oxide activated with chromium.

Typical analyses for hydrogen-rich gas mixtures produced by steam reforming, partial oxidation and the other hydrogen production processes previously referred to are given in table 1, page 5.

In all processes represented in table 1 it can be seen that considerable CO is produced relative to CO_2. It can be seen from table 1 that none of the processes has a ratio of CO_2 to CO greater than 2 in the raw hydrogen-rich gas mixture produced. The CO which is present in the raw hydrogen-rich gas typically is shift converted to obtain additional H_2 and CO_2, as mentioned previously in the discussion of the steam reforming partial oxidation processes. CO_2 is more easily removed from hydrogen than is CO. Also, it can be readily seen from the reactions

$$C+2H_2O \longrightarrow CO_2+2H_2$$
$$C+H_2O \longrightarrow CO+H_2$$

that more hydrogen is produced when carbon is oxidized fully to obtain CO_2, rather than partially to obtain CO. Similarly, more hydrogen is produced when hydrocarbons are oxidized completely to form CO_2 and H_2 rather than partially to form CO and H_2.

As indicated by table 1,U.S. Pat. No. 1,505,065 relates to a process wherein steam and oxygen are reacted in a reaction apparatus with carbonaceous matter to obtain a hydrogen-rich gas mixture. It is stated in that patent that a low temperature favors the production of carbon dioxide, but yet that the temperature must be sufficiently high to enable the reaction to proceed at the desired rate. The hydrogen-rich gas mixture which is obtained according to the processes disclosed in U.S. Pat. No. 1,505,065 has a CO_2 to CO ratio of 1.5.

U.S. Pat No. 1,505,065 also states that the production of carbon dioxide at a given temperature, pursuant to the reaction

$$CO+H_2O \longrightarrow H_2+CO_2,$$

is favored by the presence of an excess of steam above the amount of steam which actually reacts with the carbonaceous matter. The amount of steam used according to the process disclosed in U.S. Pat. No. 1,505,065 is about 3 to pounds per pound of carbon gasified. On a nitrogen-free basis, the upper

TABLE 1.—HYDROGEN PRODUCTION PROCESSES

	Steam-hydrocarbon reforming	Partial oxidation	Lurgi heavy hydrocarbon gasification	Steam, red-hot coke	USP 1,505,065
H_2, volume percent	74.2	44.5	39.4	50	47
CO, volume percent	11.5	49	16.4	49	12
CO_2, volume percent	11.7	5.3	32.3	1	18
N_2, volume percent	0.3	0.4	0.4	----------	23
CH_4, volume percent	2.2	0.6	11.3	----------	----------
Volume ratio, CO_2/CO	1	0.1	2	0.02	1.5
Volume ratio, CO_2/CH_4	5.3	9	2.9	----------	----------
Oxidant	Steam	(1)	(1)	Steam	(2)
Hydrogen gas withdrawal temperature, ° F	1,525	2,700	1,800	2,730–3,270	1,112–1,382

[1] Steam plus O_2. [2] Steam plus air.

limit (5 pounds per pound of carbon gasified) of the amount of steam used according to the disclosure of U.S. Pat. No. 1,505,065 would result in about 42 volume percent steam in the hydrogen-rich gas which is produced. Using 23 volume percent nitrogen as the nitrogen content of the hydrogen-rich gas produced according to the process of U.S. Pat. No. 1,505,065, the percent steam in the hydrogen-rich gas produced is about 33 volume percent.

U.S. Pat. No. 1,505,065 does not disclose the use of excess steam to minimize the methane content of the hydrogen-rich gas mixture which is produced.

SUMMARY OF THE INVENTION

According to the present invention, a process is provided for producing a hydrogen-rich gas mixture which is lean in CO and CH_4 relative to CO_2 by:

a. contacting subdivided carbonaceous matter with steam and oxygen in a reaction zone at temperatures between about 800° and 1,350 F. to form H_2 and CO_2,

b. feeding sufficient steam to the reaction zone so that the hydrogen-rich gas mixture which is withdrawn from the reaction zone contains at least 60 volume percent steam, and

c. withdrawing the hydrogen-rich gas mixture from the reaction zone at a temperature between 800° and 1,250° F.

The present invention is based partly on the finding that it is necessary to feed sufficient steam to the carbon-steam reaction zone so that the hydrogen-rich gas mixture which is withdrawn from the reaction zone contains at least about 60 volume percent steam, and preferably about 75 volume percent steam, in order to obtain a hydrogen-rich gas which contains only relatively small amounts of CH_4 and CO relative to CO_2.

Thus, according to the present invention, sufficient steam is fed to the carbon-steam reaction zone, so that the ratio of CO_2 to CH_4 and the ratio of CO_2 to CO are both at least about 2.5 in the hydrogen-rich gas mixture withdrawn from the reaction zone. Preferably, sufficient steam is fed to the reaction zone so that the ratio of CO_2 to CH_4 and the ratio of CO_2 to CO are both at least about 4.0 in the hydrogen-rich gas withdrawn from the reaction zone.

According to the preferred embodiment of the present invention, steam is the only oxidant which is reacted with the subdivided carbonaceous matter in the reaction zone. It is preferred to heat the steam to a high temperature, as for example 1,500° to 1,800° F., and then introduce the steam to the reaction zone for endothermic reaction with the subdivided carbonaceous matter to produce the hydrogen-rich gas mixture. The steam is preferably heated to a sufficient temperature and/or a sufficient amount of steam is used so that after some cooling has occurred due to the endothermic reaction, the hydrogen-rich gas mixture is withdrawn from the reaction zone at a temperature between 800° and 1,250° F., preferably 1,100° to 1,200° F.

It has been found that the reaction rate is much faster for finely subdivided carbonaceous matter than for coarsely divided carbonaceous matter. According to a preferred embodiment of the present invention, the reaction zone is comprised of a fluidized bed of subdivided carbonaceous particles. The bed preferably is fluidized by hot, upwardly flowing steam. Preferably, the carbonaceous matter is subdivided to a Tyler mesh size of 8 to 42, or smaller.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic flow diagram of a preferred embodiment of the process of the present invention to produce a hydrogen-carbon dioxide gas mixture;

FIG. 2 is a graph illustrating the percent hydrogen and the percent CO_2 in the hydrogen-rich gas withdrawn from a carbon-steam reaction zone, as a function of volume percent steam in the hydrogen-rich gas which is withdrawn from the

DETAILED DESCRIPTION

Referring now in more detail to FIG. 1, coke is introduced via line 1 to pulverizing zone 2. Various other feeds may be used instead of coke, such as coal or other solid carbonaceous matter. By carbonaceous matter is meant any substance containing carbon, either in the amorphous or cystalline carbon state and/or as hydrocarbon compounds. Petroleum coke is a particularly preferred feed. The pulverizing zone grinds the solid coke to small particles, preferably 8 to 42 Tyler mesh size; and more preferably 100 to 200 mesh size. The smaller mesh sizes have been found by experimental work to result in a considerably faster reaction rate when steam is contacted with the particles at elevated temperature.

For an example case, about 1,300 tons per day of coke are fed to pulverizing zone 2 and about 820 tons per day of coke are passed to K_2CO_3—coke contacting zone 4. In zone 4 the finely subdivided carbonaceous matter is impregnated with K_2CO_3 added in aqueous solution form to zone 4 via line 12. The aqueous solution of K_2CO_3 is made up in zone 8. Makeup K_2CO_3 via line 5 and recovered K_2CO_3 via line 6 are combined and introduced to zone 8 via line 7. Recycle water via line 10 and water makeup via line 9 are combined and added to zone 8 via line 11.

The finely divided coke particles which have been impregnated with K_2CO_3 are withdrawn from zone 4 via line 13 in an aqueous slurry form. Water is separated from the slurry in water-removal zone 14. The water which is removed is recycled via line 10 to be used again in forming the aqueous solution of K_2CO_3. The finely divided coke particles impregnated with K_2CO_3 are withdrawn via line 15 from water-removal zone 14 substantially free of excess water. The coke particles are fed to reaction zone 16, wherein they are reacted with steam introduced to reaction zone 16 via line 17.

The K_2CO_3 which was previously impregnated into the fine coke particles has a catalytic effect on the reaction

$$C+H_2O \longrightarrow H_2+CO$$

Other alkaline carbonates also have been determined to have a catalytic effect on the above reaction. Alkaline carbonates are frequently present in coal, and coke, and other carbonaceous matter in appreciable concentrations such as 2 to 5 weight percent. Thus, in many instances the process of the present invention can be carried out catalytically, but yet without adding any makeup catalysts.

Oxygen can be added to reaction zone 16 via line 30. Steam is added via line 17.

The hydrogen-rich stream which is produced in reaction zone 16 is withdrawn in line 18 from the reaction, together with a large amount of unreacted steam in accordance with the process of the present invention.

The steam which is fed to reaction zone 16 in large quantities is generated in steam generation zone 19. Steam generation zone 19 operates essentially in accordance with well-known procedures normally used for a boiler plant. Water is added to steam generation zone 19 via line 20 and vaporized to form steam at a temperature of about 1,500° to 1,800° F. The hot steam is withdrawn in line 17.

According to a preferred embodiment of the present invention, heating fuel for the steam generation zone is provided, in part, by using a portion of the coke withdrawn via line 22 from pulverizing zone 2. In some instances it is economically preferable to omit pulverizing the coke which is used as a fuel for steam generation zone 19. However, in the preferred embodiment illustrated by FIG. 1, 48 tons per day of pulverized coke are fed to steam generation zone 19 via lines 3, 22 and 21. This 480 tons per day of coke is augmented by 108tons per day of unreacted carbonaceous matter (together with metallic ash and K_2CO_3) withdrawn from reaction zone 16 via line 23.

After burning, the coke and unreacted carbonaceous matter comprised of K_2CO_3 and metals (or ash) is left. This residue is withdrawn from steam generation zone 19 via line 25 and is passed to K_2CO_3 and metals recovery zone 26. In zone 26 K_2CO_3 is separated and withdrawn via line 27. The K_2CO_3 may then be recycled to zone 8 via line 6.

Metals such as vanadium and nickel are removed in the oxide form from zone 26 via line 28. The stream of recovered metals may be subjected to further processing to obtain satisfactory separation of valuable metals, or metal com-

pounds, from less valuable ash constituents. Because hydrogen is advantageously produced in the process of the present invention from "heavy" carbonaceous matter such as coal, coke or petroleum residue, the overall process of the present invention affords and attractive process to recover metals from various carbonaceous materials. Metals are recovered both from coke fed to the steam generation zone from the pulverizing zone and from unreacted material withdrawn via line 23 from reaction zone 16.

Referring once again to reaction zone 16, example numbers for a preferred embodiment of the present invention include the following: the coke fed to reaction zone 16 preferably contains about 0.2 pounds of the catalytic agent K_2CO_3 per 0.8 pounds of coke. It is preferred to carry out the reaction using a large volume of coke so that large quantities of hydrogen-rich gas can be generated at relatively low temperatures. Thus, on a basis of 820 tons per day of K_2CO_3–free coke, two reactors, each 20 feet in diameter by 64 feet long, are required in this preferred embodiment wherein 100 million s.c.f.d. of hydrogen are produced. The reactors are operated at an internal pressure of approximately 250 p.s.i.g. Heat required per pound of carbon reacted, in accordance with the endothermic steam-carbon reaction employed in the process of the present invention, is about 3,600 b.t.u.'s per pound of carbon reacted. To furnish the required heat, about 740,000 pounds per hour of steam are added to the reactor vessels at a temperature of about 1,680° F. The temperature and the amount of steam are selected so that there will be at least 60 volume percent steam in the hydrogen-rich gas withdrawn from the reactors and so that the temperature at which the hydrogen-rich gas is withdrawn is between 800° and 1,200° F. In this particular instance there is about 67 volume percent steam in the hydrogen-rich gas withdrawn from reaction zone 16, and the temperature of the hydrogen-rich gas which is withdrawn is about 1,200° F.

Referring now in more detail to FIG. 2, the volume percent carbon dioxide and the volume percent hydrogen, respectively, are plotted as the ordinate vs. volume percent steam in the total hydrogen produced as the abscissa. The data for FIG. 2 was obtained by reacting 8 to 42 Tyler mesh pulverized coke with steam at various steam rates through the coke bed. The coke contained a small percentage of hydrocarbons which also reacted with the steam to yield hydrogen and carbon dioxide. The initial charge in the reactor was about 40 grams material, consisting of 33.3 grams coke which had been impregnated with about 6.7 grams of K_2CO_3.

The reaction was carried out at a pressure of about 75 to 90 p.s.i.g. Temperature was maintained at approximately 1000° to 1,200° F. for each of the various runs at different steam rates. The scatter in the data at the various temperature levels and water rates was very small for about any given volume percent steam in total hydrogen product.

Curve A illustrates the percent hydrogen in the hydrogen-rich gas withdrawn from the reaction zone as a function of the volume percent steam in the total hydrogen product withdrawn from the reactor. Similarly, curve B represents the volume percent CO_2 in the hydrogen product withdrawn from the reactor vs. the volume percent steam in the total hydrogen product withdrawn from the reactor.

As can be seen from the curves, when the volume percent steam in the total hydrogen product from the reactor is about 60, the percent hydrogen in the hydrogen product, on a water-free basis, is about 64, and the percent CO_2 on the same basis is about 26.5. Thus, the percent hydrogen plus CO_2 in the hydrogen product, on a steam-free basis, is about 90.5. The remaining 9.5 volume percent of the hydrogen product on a steam-free basis is primarily carbon monoxide and methane. Typically, the 9.5 percent is comprised of about 60 volume percent CH_4. Thus it can be seen that by using a sufficient amount of steam so that the hydrogen withdrawn from the reaction zone will contain at least about 60 volume percent steam, reasonably low carbon monoxide and CH_4 contents in the product hydrogen gas mixture are obtained. Using a lesser amount of steam so that the product hydrogen gas contains, for example, only about 30 volume percent steam, the volume percent hydrogen in the product gas, as can be seen from FIG. 2, is about 54.5 and the CO_2 content is about 25.5. Thus, there is a considerable amount of unconverted carbon monoxide, as well as methane, remaining in the product hydrogen gas when only about 30 volume percent steam is present in the product hydrogen gas. Moving in the other direction on curves A and B, with about 75 volume percent steam in the hydrogen product from the reactor, it is seen that the hydrogen content in the hydrogen product, on a water-free basis, is about 68 volume percent, and the CO_2 content is about 27 volume percent. Thus, using sufficient steam so that the volume percent steam in the total hydrogen product from the reactor is about 75 percent, a hydrogen gas is obtained which is comprised of about 95 percent hydrogen and CO_2 and only about 5 percent carbon monoxide and methane.

Although various specific embodiments of the invention have been described and shown, it is to be understood they are meant to be illustrative only and not limiting. Certain features may be changed without departing from the spirit or essence of the invention. It is apparent that the present invention has broad application to the production of hydrogen-carbon dioxide gas mixtures. Accordingly, the invention is not to be construed as limited to the specific embodiments illustrated but only as defined in the appended claims.

We claim:

1. A process for producing a hydrogen-rich gas mixture which is lean in CH_4 and CO relative to CO_2 and having a ratio of CO_2 to CH_4 in the hydrogen-rich gas mixture of at least 2.5 and a ratio of CO_2 to CO of at least 2.5 which comprises:
   a. contacting subdivided carbonaceous matter with steam and oxygen in a reaction zone maintained at temperatures between about 800° and 1,350° F. to form a hydrogen-rich gas mixture comprising H_2 and CO_2.
   b. feeding sufficient steam to the reaction zone so that the hydrogen-rich gas mixture which is withdrawn from the reaction zone contains at least 60 volume percent steam, and
   c. withdrawing the hydrogen-rich gas mixture from the reaction zone at a temperature between 800° and 1,250° F.

2. A process in accordance with claim 1 wherein the hydrogen-rich gas mixture is withdrawn from the reaction zone at a temperature between 800° and 1,100° F.

3. A process in accordance with claim 1 wherein sufficient steam is fed to the reaction zone so that the hydrogen-rich gas mixture which is withdrawn contains at least 75 volume percent steam.

4. A process in accordance with Claim 1 wherein the amount of steam fed to the reaction zone is sufficient so that the ratio of CO_2 to CH_4 and the ratio of CO_2 to CO in the hydrogen-rich gas mixture withdrawn from the reaction zone are each at least about 4.0.

5. A process in accordance with claim 4 wherein the hydrogen-rich gas mixture is withdrawn from the reaction zone at temperatures of between 800° and 1100° F.

6. A process in accordance with claim 1 wherein the contacting of the subdivided carbonaceous matter with steam and oxygen in the reaction zone is carried out in the presence of potassium carbonate catalyst added to the reaction zone.

7. A process for producing a hydrogen-rich gas mixture which is lean in CH_4 and CO relative to CO_2 and having a ratio of CO_2 to CH_4 in the hydrogen-rich gas mixture of at least 2.5 and a ratio of CO_2 to CO of at least 2.5 which comprises:
   a. contacting subdivided carbonaceous matter with steam as the only oxidant in a reaction zone maintained at temperatures between about 800° and 1,350° F. to form a hydrogen-rich gas mixture comprised of H_2 and CO_2.
   b. feeding sufficient steam to the reaction zone so that the hydrogen-rich gas mixture which is withdrawn from the reaction zone contains at least 60 volume percent steam, and
   c. withdrawing the hydrogen-rich gas mixture from the reaction zone at a temperature between 800° and 1,250° F.

8. A process in accordance with claim 7 wherein the amount of steam fed to the reaction zone is sufficient so that the ratio of CO_2 to CH_4 and the ratio of CO_2 to CO in the hydrogen-rich gas mixture withdrawn from the reaction zone are each at least about 4.0.

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