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PROCESS AND ARRANGEMENT OF APPARATUS FOR PRODUCTION OF MIXTURES OF CARBON OXIDES AND HYDROGEN

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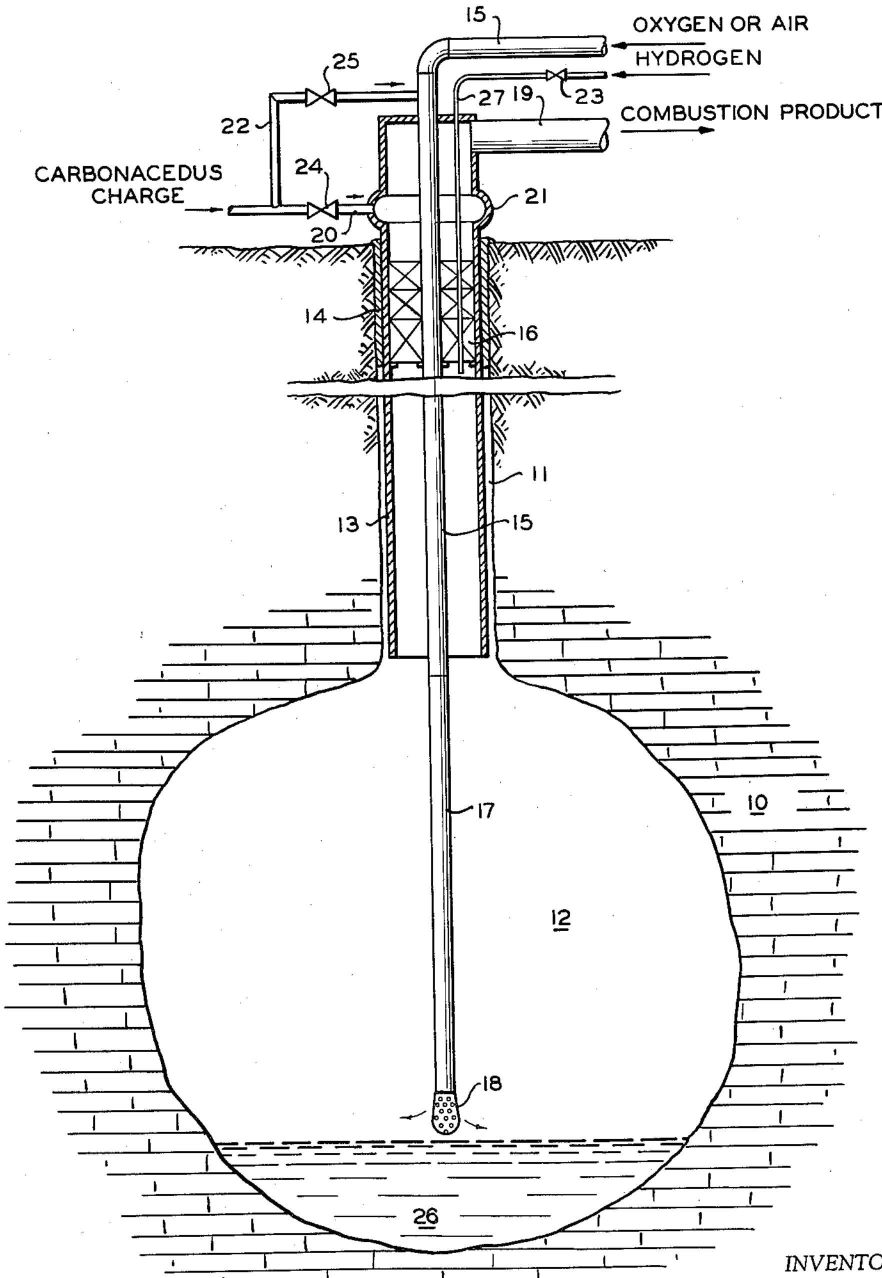

INVENTOR.
FORREST E. GILMORE
BY Hudson & Young
ATTORNEYS

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PROCESS AND ARRANGEMENT OF APPARATUS FOR PRODUCTION OF MIXTURES OF CARBON OXIDES AND HYDROGEN

Forrest E. Gilmore, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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This invention relates to a process and arrangement of apparatus for production of mixtures of carbon oxides and hydrogen. In one aspect, the invention relates to a method and apparatus for controlled combustion of carbonaceous fuels in an underground cavity to produce mixtures of carbon oxides and hydrogen.

It is an object of the invention to provide process and arrangement of apparatus for making mixtures of carbon oxides and hydrogen which provide increased operational efficiency, lower initial investment costs, and minimum maintenance. Another object of the invention is to provide a process and apparatus for the controlled combustion of carbonaceous materials whereby increased operational safety is realized.

According to the invention, synthesis gas or other mixtures of carbon oxides and hydrogen are produced in a process utilizing a natural cavity, or a cavity preformed, in an underground location in a suitably impervious formation, such as a clay or shale formation, in which process a carbonaceous fuel is injected down into the cavity, and a combustion supporting gas such as elemental oxygen or air is also injected downwardly into the cavity in which incomplete combustion is effected, combustion products are withdrawn from the cavity in indirect heat exchange relationship with the supplied combustion supporting gas, thus preheating the gas and performing necessary cooling of the combustion products. Preferably, the carbonaceous feed material is a normally liquid or solid material and is injected into the cavity in direct heat exchange relationship with the combustion products being withdrawn. However, the carbonaceous feed can be injected into the cavity in admixture with the combustion supporting gas. Usually, also, there is injected into the cavity an amount of moisture or steam, as will be understood by those skilled in the art, for instance, in the production of synthesis gas mixtures. The feed carbonaceous material, as well as the combustion supporting gas, is usually preheated to some extent before the underground injection.

One advantage of the direct heat exchange between the carbonaceous feed and the combustion products leaving the cavity is that it is more efficient than indirect heat exchange. Another very important advantage is that any carbon dioxide present in the combustion product gases from the partial combustion in the cavity are substantially converted to carbon monoxide when direct contact of carbonaceous feed and combustion products is made, thus assuring the carbon monoxide product in the gaseous mixture with hydrogen.

Economics largely influence the choice between the use of compressed oxygen or compressed air as the combustion supporting gas. Compressed oxygen is technically preferred in order that the product be substantially free of nitrogen, while compressed air is, of course, the cheaper material. Mixtures of oxygen and air can be employed, also.

It is usually advantageous to employ superatmospheric pressures, although atmospheric pressures can be employed. Pressures as high as 1000 p.s.i.a. or higher are applicable, although maximum pressures of less than 300 p.s.i.a. are usual.

A particular advantage of the invention is that the formation surrounding the cavity can withstand the high temperatures encountered in the combustion process, and can retain sufficient heat for the chemical reaction taking place. The formation can also furnish a high pressure reaction zone, and at low cost.

An apparatus and process of an embodiment of my invention is illustrated in the accompanying diagrammatic drawing.

Referring to the drawing, in a relatively impervious natural or man-made formation, such as a clay or shale formation 10, a shaft hole 11 is sunk to the desired depth at or near the top of a cavity 12 in formation 10. An outer conduit or casing 13 is cemented at 14 to the shaft hole 11 by conventional operations. Mounted substantially concentrically in casing 13 is tubing 15. At the open lower or outlet end of tube 15 there is preferably mounted a fluid distributor device 18, such as a perforate end portion of an otherwise blanked off tube. At the upper end of annular casing 13 is fluid outlet 19. Conduit 20 communicating with casing 13 is provided for the introduction of carbonaceous charge material through valve means 24 located therein. Conduit 22 is provided for the alternate introduction of carbonaceous material through valve 25 into inner tubing 15 with the combustion supporting gas, although this is less preferred. It is preferred that valve 25 be closed and valve 24 be open so that there will be direct heat exchange between the gaseous products and the incoming carbonaceous charge in casing 13.

In one embodiment of the apparatus, catalyst cases in the form of donut rings are provided in the upper portion of casing 13, filled with a suitable synthesis catalyst such as sintered iron or reduced iron oxide, and there is provided, extending down through the catalyst cases, conduit 27 containing valve 23, for the introduction of hydrogen to a point in casing 13 below cases 16.

In operation of the apparatus, with valve 23 closed and catalyst cases empty or removed, a hydrocarbon feed is introduced either through conduit 22 or conduit 20, but preferably through conduit 20. Examples of carbonaceous feed materials include coal, coke, petroleum asphalt, pitch, and natural asphalts, such as gilsonite, etc. The combustion supporting material such as oxygen or air, or oxygen-enriched air, is introduced into 15 and flows out through 18. The combustion supporting gas as well as the carbonaceous feed are preferably preheated. The carbonaceous fuel collects at 26 in the bottom of the cavity and undergoes partial combustion with the combustion supporting gas, the gaseous combustion products flowing upwardly in the cavity and out through casing 13, in direct heat exchange with the downfalling carbonaceous charge, and in indirect heat exchange with the combustion supporting gas in tube 15.

When operating with catalyst in cases 16, the hydrocarbon feed is introduced through conduit 22 with the combustion supporting gas, valve 23 is open and there is introduced through 27 enough hydrogen to provide the desired ratio of hydrogen to CO, usually about 2 moles hydrogen for each mole of CO. The mixed gases are thus converted to hydrocarbons and oxygenated compounds, such as alcohols, ketones, esters, etc., in the well known manner.

In a specific operation of the invention according to the figure wherein valves 25 and 23 are closed and valve 24 is open and the catalyst cases are removed, thus introducing the feed into the annulus formed by 13 and 15, the charge is a petroleum pitch of the following characteristics:

Density, gm./cc.	1.0010
Ring and ball softening point, ° F.	180
Penetration, 100 gms., 5 sec., 77° F.	0

Composition, wt. percent:

Carbon	91
Hydrogen	9

This pitch is produced from vacuum distillation of topped crude. The combustion supporting gas is compressed air containing steam. In starting up the operation excess air over that amount shown in the operating conditions given in the table below is used to produce carbon dioxide for greater evolution of heat to bring the chamber up to the desired operating temperature. A liquid pool of pitch forms at **26** and is contacted by the compressed air containing steam, and the partial combustion reaction is effected. The cavity employed in this example is in clay formation **10** and is about 20 feet in diameter and about 50 feet long vertically, while casing **13** is about 200 feet long. The tubing with the distributor **18** is located in the cavity so that distributor **18** is in close proximity to the surface of the liquefied pitch. It is noted that it is also possible to operate the apparatus of the drawing with **18** located below the surface of the carbonaceous material. The conditions of operation and the composition of the gaseous effluent in this example are shown in the table.

Combustion zone:	
Temperature, ° F.	2532
Pressure, p.s.i.g.	25
Ratio # steam/# feed	0.2
Ratio # air/# feed	5.63

The system produces 92.5 standard cubic feet of gas per pound of feed, the product gas having the following composition, volume percents:

Carbon monoxide	25.7
Carbon dioxide	6.1
Hydrogen	7.5
Nitrogen	60.6
Other	0.1
	100.0

In the process of my invention, as stated, water or steam can be injected in addition to the combustion supporting gas. The endothermic reaction resulting from forming hydrogen from the water is one method to aid in control of the total reaction temperature; other controls being, of course, the temperature at which the reactants enter the cavity.

The casing **13** and the upper portions of tubing **15** can be made of conventionally available high temperature metals or alloys, such as a nickel-chromium stainless steel. The lower portion **17**, from about the top of the cavity to the bottom of the tubing is preferably of ceramic material able to withstand high temperatures, or of titanium metal. Examples of suitable ceramic materials are zirconium oxide or Carbofrax manufactured by the Carborundum Company. This latter material is silicon carbide.

In the process of the invention, the amount of oxygen employed in the combustion supporting gas is in the range of from 80 to 110% of that theoretically required to convert all of the carbonaceous fuel to carbon dioxide and water. When producing synthesis gas, such as for use in a Fischer-Tropsch process, this range is preferably from 95 to 100% of theory. The amount of water employed is in the range of from 1/6 to 1.0 mole per mole of oxygen.

One economic advantage of the invention is illustrated by the fact that an above ground installation for effecting the process described with respect to the specific example would cost about $500,000.00, while the apparatus of drawing as described with respect to the example costs less than $75,000.

As will be evident to those skilled in the art, various modifications of this invention can be made or followed in the light of the foregoing disclosure and discussion without departing from the spirit or scope of the disclosure or from the scope of the claims.

I claim:

1. A method for producing a mixture of carbon oxides and hydrogen which comprises introducing a carbonaceous material and a combustion supporting gas into an underground earth cavity from above ground level maintaining a body of said carbonaceous material in the lower portion of said cavity, burning said body of carbonaceous material by partial combustion with said combustion supporting gas in said cavity and thereby forming a mixture of carbon oxides and hydrogen and thereby storing heat in the earth formation around said cavity, withdrawing said gaseous mixture in indirect heat exchange flow relationship with said combustion supporting gas being introduced into said cavity, thereby cooling said mixture and preheating said combustion supporting gas, the said carbonaceous material being introduced in direct countercurrent flow heat exchange relationship with said gaseous mixture being withdrawn from said cavity, said countercurrent flow being effected before said carbonaceous material enters said cavity, said carbonaceous material falling downwardly through said upwardly rising gas.

2. A method of claim 1 wherein said combustion supporting gas is selected from the group consisting of oxygen, air, and oxygen enriched air.

3. A method for producing a mixture of carbon oxides and hydrogen which comprises introducing a carbonaceous material and a combustion supporting gas into an underground cavity in an earth formation from above ground level maintaining a body of said carbonaceous material in the lower portion of said cavity, burning said body of carbonaceous material by partial combustion with said combustion supporting gas in said cavity and thereby forming a mixture of carbon oxides and hydrogen and thereby storing heat in the earth formation around said cavity, withdrawing said gaseous mixture in indirect heat exchange flow relationship with said combustion supporting gas being introduced into said cavity, thereby cooling said mixture and preheating said combustion supporting gas.

4. A method of claim 3 wherein said combustion supporting gas is selected from the group consisting of oxygen, air, and oxygen enriched air.

5. A method according to claim 1 wherein steam is also introduced into said cavity.

6. A method according to claim 3 wherein steam is also introduced into said cavity.

7. A method according to claim 3 wherein said carbonaceous material is introduced into said cavity in admixture with said combustion supporting gas.

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