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PROCESS FOR THE GENERATION OF CARBON MONOXIDE AND HYDROGEN

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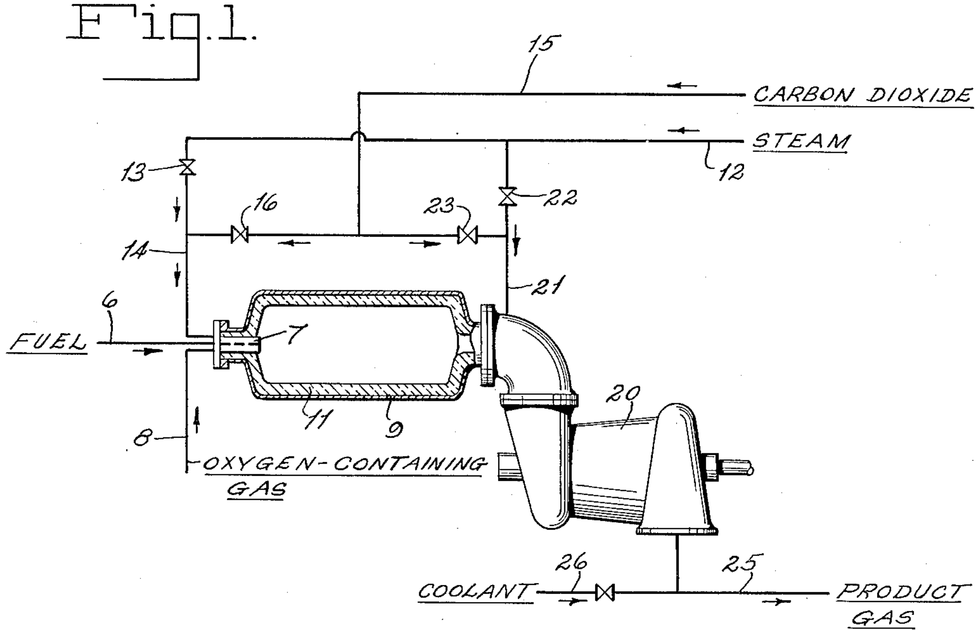
Fig. 1.



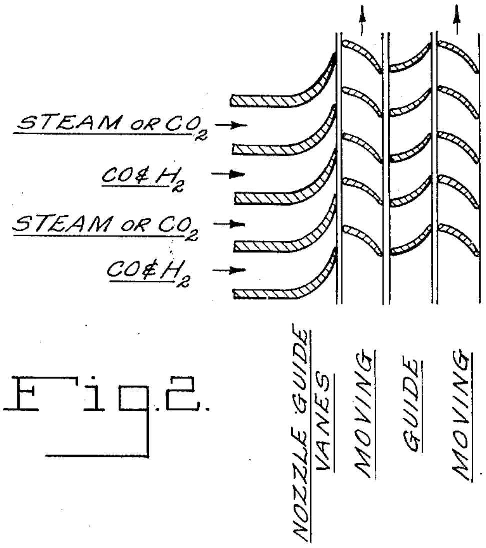


Fig. 2.

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PROCESS FOR THE GENERATION OF CARBON MONOXIDE AND HYDROGEN

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3 Claims. (Cl. 48—196)

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This invention relates to a process for the preparation of carbon monoxide and hydrogen by the partial combustion of a carbonaceous fluid fuel. In one of its more specific aspects, the invention comprises subjecting a gaseous hydrocarbon to partial combustion to form carbon monoxide and hydrogen substantially free from residual methane and free carbon. The process is applicable to liquid or gaseous carbonaceous fuels, particularly hydrocarbon gases and oils.

This application is a continuation-in-part of my copending application, Serial No. 605,090, filed July 14, 1945, now abandoned.

In accordance with my invention, carbon monoxide and hydrogen are prepared by controlled oxidation of the fuel with an oxygen-rich gas in a combustion gas turbine. The gases are generated at a temperature within the range of from about 2,000 to 3,000° F. The heat content of these generated gases, which is at a high level due to the exothermic nature of the oxidation reaction, is partially converted to mechanical energy by means of a gas turbine in which the gases are subjected to expansion and cooling. The carbon monoxide and hydrogen are produced in the combustion section of the turbine and immediately subjected to cooling and pressure reduction by expansion in the blading of the turbine. The sudden reduction in temperature and pressure is effective for suppressing carbon formation in the effluent stream. Power thereby generated may be used advantageously in compressing reactant gases used in the process, e. g., in supplying power to an oxygen plant.

In commercial processes for the generation of carbon monoxide and hydrogen, it is highly desirable to generate the gases at elevated pressure and to recover heat energy from the product gases. This is usually accomplished by indirect heat exchange between the gases and water in a boiler to produce steam. The temperature reduction is relatively slow and, for efficiency, must be carried out at the elevated pressure at which the gases are generated.

It is important in the production of carbon monoxide and hydrogen to rapidly cool the products of reaction from the reaction temperature, for example, 2,000 to 3,000° F., to a temperature on the order of 500 to 600° F. to prevent undesirable side reactions. The interval during which the temperature of the gas is reduced through the temperature range of from about 1,600 to about 600° F. appears very important from the standpoint of carbon formation, carbon formation being minimized by extremely rapid cooling

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through this temperature range. Reduction of the pressure of the synthesis gas from superatmospheric pressure to a lower pressure also minimizes the formation of carbon during the temperature reduction.

Accordingly, it has been found that an internal combustion turbine is a very effective means of generating carbon monoxide and hydrogen, utilizing the heat energy contained in the product gas, and at the same time substantially preventing any carbon formation during the cooling period. As indicated above, it is important that the product gases from the combustion section of the turbine pass directly into the blading section for immediate quenching of the reaction by temperature and pressure reduction.

The present invention may be used for the generation of synthesis feed gas for the production of hydrocarbons, oxygenated hydrocarbons and the like. Carbon dioxide, formed in the catalytic conversion of carbon monoxide and hydrogen into the desired products may be recycled to the gas turbine. The carbon dioxide may be recycled in whole or in part to the combustion section of the turbine wherein it serves a twofold function. First, it aids in controlling the temperature in the combustion chamber wherein there is a tendency to attain a higher temperature than desired because of the highly exothermic nature of the oxidation reaction, particularly with a liquid hydrocarbon as fuel. Carbon dioxide serves this purpose because it acts as a diluent, absorbing heat as sensible heat and exerting a moderating effect on hydrocarbon oxidation. Moreover, carbon dioxide reacts endothermically with the hydrocarbon to yield carbon monoxide and hydrogen, thereby avoiding the dilution effect of an ordinary diluent. Alternatively, the carbon dioxide may be admixed with the product gases from the combustion section of the turbine prior to introduction to the turbine blades.

The second function served by the carbon dioxide is that it affords a means of varying the ratio of carbon monoxide to hydrogen in the product gases. The reaction of methane, for example, with oxygen, tends to give a mixture of carbon monoxide and hydrogen substantially in the ratio of 1:2, whereas the reaction between methane and carbon dioxide gives substantially an equi-molecular mixture of carbon monoxide and hydrogen. It is possible, therefore, to vary the molecular ratio of carbon monoxide and hydrogen by varying the quantity of carbon dioxide supplied to the combustion gas turbine.

It is further contemplated that steam, prepared, for example, by heat exchange with the exhaust gas from the turbine, may be supplied to the combustion gas turbine. The steam may be introduced into the combustion section of the turbine or, alternatively, admixed with the product gas from the combustion section prior to the introduction of the gas to the turbine blades. Steam may be introduced into the combustion zone wherein it would serve the same dual function as carbon dioxide, as explained hereinabove. It would serve as a diluent and since steam also reacts endothermically with a gaseous hydrocarbon like methane, it would play the role of a temperature control agent just as carbon dioxide does. Steam reacts with methane, for example, to produce a mixture of carbon monoxide and hydrogen in the molecular ratio of 1:3. Therefore, by the introduction of varying quantities of steam into the combustion zone, it is possible to alter the molecular ratio of the carbon monoxide and hydrogen in the gases issuing therefrom.

Steam, carbon dioxide, or a mixture of steam and carbon dioxide may be admitted to the turbine blades separately from the carbon monoxide and hydrogen, thereby serving to prevent overheating of the turbine blades and, at the same time, aid in rapidly cooling the product gas.

The mixture of carbon monoxide and hydrogen produced by the partial combustion of a hydrocarbon may be used advantageously as a source of hydrogen, carbon monoxide, or both, for other chemical processes, for example, hydrogenation, reduction of ores, synthesis of ammonia, etc. The water gas shift reaction may be employed to produce hydrogen at the expense of carbon monoxide or to produce carbon monoxide at the expense of hydrogen, as desired.

Since different catalysts used for the catalytic conversion of carbon monoxide and hydrogen into hydrocarbons, oxygenated hydrocarbons, etc., are most effective with different molecular ratios of carbon monoxide to hydrogen, it is most important to be able to vary the ratio of carbon monoxide to hydrogen in the synthesis of gas. Iron catalysts operate best using a molecular ratio of carbon monoxide to hydrogen of about 1:1, whereas cobalt and nickel catalysts operate most effectively with a synthesis gas containing carbon monoxide and hydrogen in the ratio of 1:2. Therefore, the ability to vary the molecular ratio of carbon monoxide to hydrogen in the synthesis gas, afforded by the recycling of carbon dioxide or the introduction of steam into the combustion zone, is very advantageous.

Where the carbon monoxide and hydrogen produced by the process of this invention is used for the synthesis of hydrocarbons, carbon dioxide may be obtained as a by-product of the synthesis reaction. The reaction between carbon monoxide and hydrogen, using an iron catalyst for example, gives considerable quantities of carbon dioxide. This carbon dioxide may be recycled in whole or in part to the combustion zone after it has been stripped from the other constituents of the effluent gas from the hydrocarbon synthesis reaction, such as unreacted carbon monoxide and hydrogen, diluent nitrogen and light hydrocarbon gases. Cobalt or nickel catalysts may also be used in the hydrocarbon synthesis reaction; appreciable quantities of carbon dioxide are formed even when they are used as a catalyst. However, when cobalt and nickel are used, there is not available such a wide latitude in selecting the quantity of carbon dioxide to be recycled. In this instance, the alternative use of steam in the combustion zone, as suggested above, may be advantageous.

The oxygen-rich gas which is used in the combustion zone to oxidize the hydrocarbon gas, preferably contains at least 40% free oxygen. Often substantially pure oxygen is advantageous, as where the gas is used in hydrocarbon synthesis, otherwise provision must be made for removing diluent or inert material, such as nitrogen, before the gas is introduced into the synthesis converter. If the hydrocarbon synthesis feed gas contains too great a percentage of diluent, a large portion of the active area of the converter apparatus is not being effectively used, and since the synthesis converter is a costly piece of apparatus, such operation may not be practical.

An advantage of this invention is that power is generated in the preparation of carbon monoxide and hydrogen rather than being absorbed as is the case with the more usual methods of synthesis gas preparation. The available power may advantageously be used in the compression and liquefaction of air to yield the oxygen used in the process. A further advantage resides in the continuous method of flow employed therein.

Another advantage is the simplicity of the construction which results from the temperature control available in the combustion gas turbine resulting from the introduction of steam or carbon dioxide thereto.

The invention will be more readily understood by reference to the accompanying drawings. Fig. 1 illustrates diagrammatically a system suitable for carrying out the process for the production of carbon monoxide and hydrogen according to this invention. Fig. 2 illustrates diagrammatically an alternative method for the operation of the blading section of the combustion gas turbine.

In describing the process of the invention, natural gas will be taken as an illustrative example of a fluid hydrocarbon, and commercially pure oxygen, as the oxygen-containing gas.

A stream of natural gas is introduced through pipe 6 into a mixer 7 in the combustion section of a combustion gas turbine wherein it is admixed with oxygen from line 8. The combustion section comprises a pressure vessel 9 provided on its inner surface with a layer of insulation 11 to define a compact combustion zone free from packing and catalyst. The premixed reactants are converted to carbon monoxide and hydrogen in the combustion section of the turbine.

The combustion section is so proportioned that the ratio of the internal surface of the combustion zone to a surface of a sphere of equal volume is not greater than about 1.5. In this type combustion zone, carbon monoxide and hydrogen, substantially free from methane and free carbon may be produced at pressures ranging from atmospheric to 600 pounds per square inch gauge or higher. The temperatures in the combustion zone may be within the range of from about 2,000 to about 3,000° F.; preferably the temperature is within the range of from about 2,200 to about 2,600° F. Temperature control may be effected by supplying carbon dioxide, steam or a mixture of carbon dioxide and steam to the combustion section of the turbine into admixture with the reactants. The fuel preferably is preheated; a preheat temperature on the order of 400 to 1,200° F., depending upon the thermal stability of the fuel, is preferred. The oxygen may or may not be preheated; it is generally not desirable to preheat oxygen to a temperature in excess of about 400 to 600° F.

Steam from line 12 may be admitted through valve 13 and pipe 14 into the mixer 7. Alternatively, carbon dioxide from line 15 may be admitted through pipe 14 to the burner 9 as controlled by valve 16.

The hot gases from the combustion section of the turbine are passed directly into the blading section 20 of the turbine wherein the gases are rapidly expanded and cooled. The hot product gases from the combustion section of the turbine may be admixed with steam from line 12 prior to its introduction to the blading of the turbine. This is accomplished by means of pipe 21 which admits the steam from line 12 as controlled by line 22. Similarly, carbon dioxide from line 15 may be admitted to pipe 21 as controlled by valve 23. The product gases are discharged from the turbine through line 25. If desired, a suitable coolant, for example carbon dioxide, steam or water, may be admitted through line 26 into admixture with the product gas for further cooling.

As illustrated in Fig. 1 the steam or carbon dioxide is admixed with the carbon monoxide and hydrogen from the combustion section of the turbine and the mixture passed into the blading of the turbine. An alternative arrangement is illustrated diagrammatically in Fig. 2. In this arrangement, steam, carbon dioxide, or a mixture of steam and carbon dioxide is admitted to the turbine blades separately from the carbon monoxide and hydrogen. In the illustrated arrangement, which is self-explanatory, the gas streams enter through alternate nozzles. Immediately following contact between the turbine blades and the hot carbon monoxide and hydrogen from the combustion section of the turbine, the blades are brought into contact with a cooler stream of gas, suitably steam. This prevents overheating of the turbine blades.

Combustion gas turbines of the type described herein are old and well known. It is to be understood that no novelty is claimed either for the combustion gas turbine, per se, or the method of cooling the turbine blades.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In the production of gas consisting mainly of hydrogen and carbon monoxide by the partial combustion of a fluid hydrocarbon with oxygen in a combustion gas turbine having a combustion section and an expansion section, the steps which comprise introducing a fluid hydrocarbon and an oxygen-rich gas containing at least 40% molecular oxygen into the combustion section of a combustion gas turbine at a pressure substantially above atmospheric pressure, effecting reaction of said hydrocarbon and oxygen in said combustion section at a substantial superatmospheric pressure under exothermic combustion conditions effective to maintain the temperature of said reaction zone in the range of 2,000° F. and above, and in relative proportions yielding a product gas stream consisting mainly of hydrogen and carbon monoxide at said elevated reaction temperature, and immediately thereafter reducing the temperature and pressure of said high temperature product gas stream through the range of from about 1600° F. to about 600° F. by expansion and cooling of said gas stream in said gas turbine.

2. The method according to claim 1 wherein the product gas from the combustion section of said turbine is admixed with a gasiform fluid selected from a group consisting of carbon dioxide and steam prior to said reduction in pressure.

3. A process as defined in claim 1 wherein the temperature in said combustion section is regulated by supplementing the oxygen feed with an oxidizing agent selected from the group consisting of carbon dioxide and steam.

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