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## Canadian Patents Database

12/19/2001 - 08:25:07

(11) CA 309664

(12) Patent:

(54) PROCESS AND APPARATUS FOR OBTAINING GASEOUS MIXTURES OF CARBON MONOXIDE AND HYDROGEN

(54) PROCÉDE ET APPAREIL A PRODUCTION DE MELANGE GAZEUX DE MONOXYDE DE CARBONE ET D'HYDROGENE

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(45) Date of issue:	Mar. 24, 1931
(22) Filing date:	
(43) Publication date:	
(52) International Class:	48/4
(51) IPC Class:	N/A
(30) Priority:	No
(30) Priority:	None
(30) Priority:	N/A
(30) Priority:	Unknown

\*\*\* Note: Data on abstracts and claims is shown in the official language in which it was submitted.

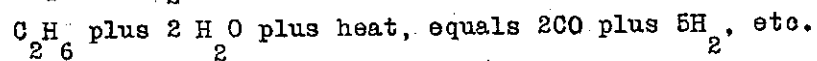
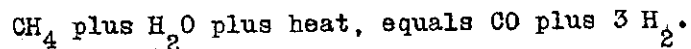
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It has been known for many years that hydrocarbon gases and vapors may be cracked by exposure to a high temperature. Many processes exist and have been the subject of patent, in which hydrocarbons are made to yield carbon and hydrogen, according to the equation (assuming methane to be the hydrocarbon employed),  $\text{CH}_4$  plus heat equals C plus  $2 \text{H}_2$ . A practice somewhat earlier in point of time, used when candle power was the chief desideratum in gas, and before the advent of the Welsbach mantle, was the conversion of natural gas to a product resembling water gas obtained from coke as a preliminary to carburetting it with oil by passing natural gas with steam through a body of carbon brought to incandescence by precedent blasting, according to the equation,  $\text{CH}_4$  plus  $\text{H}_2\text{O}$  equals  $\text{CO}$  plus  $3 \text{H}_2$ . A study of these processes and of such patents as were issued thereon, will reveal the fact that under the conditions created, dissociation was not complete. While adequate temperatures may have been stated in some patents, means of maintenance of the temperatures are not shown. A substantial fraction of undecomposed hydrocarbons remained in the product. This, however, was not a seriously objectionable matter, and no efforts appear to have been made to effect a complete dissociation, or if made were not successful.

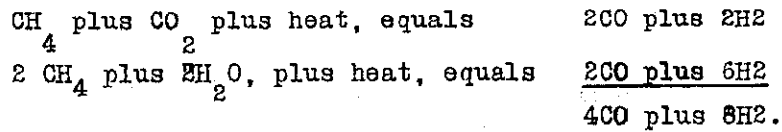
More recently a use for mixtures of carbon monoxide and hydrogen in the catalytic synthesis of alcohols and liquid hydrocarbons has come into existence, of which the more important is for the synthesis of methanol, according to

the equation CO plus 2 H<sub>2</sub> plus heat and pressure, equals CH<sub>3</sub>OH. Here a complete dissociation is very important. My process embodies procedure by which natural gas, still gases, by-product coke oven gas, etc., composed largely of gaseous hydrocarbons, may be made to yield mixtures of carbon monoxide and hydrogen in controlled proportions, but more generally in the volumetric rate of one and two for the synthesis of methanol. Where the carbon is oxidized with steam, according to equations:



There is a preponderance of hydrogen above this ratio.

A pure oxygen may be used. Using oxygen with methane, CH<sub>4</sub> plus O equals CO plus 2H<sub>2</sub>, giving the one to two ratio, but when gases richer in carbon relative to hydrogen forms part of the mixture processed, there is an excess of carbon monoxide relative to hydrogen in the product. This may be prevented by using oxygen and steam in determined proportions. But oxygen obtained in the most economic way by the liquefaction and fractioning of air is rather high in cost relative to the cost of the other gases used, and can only with extreme difficulty be obtained free from any substantial percentage of nitrogen. I prefer for this reason to use as a source of oxygen along with steam, carbon dioxide gas (CO<sub>2</sub>). Assuming again for simplicity of illustration, that the hydrocarbon gas treated is a pure methane, a mixture of one volume of carbon monoxide to two of hydrogen may readily be obtained according to the equations:



If a large proportion of carbon monoxide be desired to secure the synthesis of higher alcohols or liquid hydrocarbons containing a greater proportion of carbon, this may readily be brought about by using a larger proportion of CO<sub>2</sub> relative to steam. While the use of CO<sub>2</sub> rather than oxygen in my process is new and not shown or employed in recent patents directed toward the preparation of gaseous mixtures suitable for synthesis, there are other features in my procedure which are new and which may be employed in connection with the use of oxygen derived from the air as a means of converting the carbon of the hydrocarbons to monoxide.

At 1100° C., the equilibrium between hydrocarbons and hydrogen has proceeded in the direction of increased hydrogen to the point where the hydrocarbons are practically eliminated. But even where a catalyst is employed to accelerate dissociation, the rate at which it proceeds, especially in the case of methane, the more stable of the hydrocarbons, is quite slow. I have found that to bring dissociation by heat to completion within a practicable time-space interval, it is necessary to employ higher temperatures than have been suggested or employed by others in the past. I operate within a range of 2100° F. to 3,000° F., employing in practice a maximum determined by the resistance to heat of the refractories obtainable for use in the con-

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struction of the apparatus. The manner in which I proceed and the means by which the high temperatures required are created and maintained may be better understood by reference to the accompanying drawings in which

Figure 1 shows a vertical cross-section cut along the center line of the conversion chamber from end to end, and

Figure 2 a vertical cross-section taken on line II-II of Figure 1.

A and B are sections of the conversion chamber or conduit, filled for the most part with refractory heat-absorbing surfaces, either checker brick or preferably a multiplicity of small flues having enclosing walls of refractory material. These sections are separated at an intermediate interval by an open space C. 5-5 indicate brick flues. At the outer extremity of B is an air inlet 1; a steam inlet 2, and a gas outlet 3, closeable by damper 4. There is a fuel gas inlet 6 into C, the gas being distributed through 7a, 7b, 7c, etc. At the outer extremity of A, are inlets for oxygen or CO<sub>2</sub>, 9; for steam, 10; for hydrocarbon gases, 11; through main pipe, 8; and gas outlet 12, closeable by damper 13.

In operation, outlet 12 being open, outlet 3 closed, air is admitted through 1, and a combustible fuel gas through 6. This mixture is ignited and an active combustion maintained in the flues 5 between space C and outlet 12. The hot combustion gases passing out through 12 will preferably be passed

into a waste heat boiler for the production of steam. Combustion is continued until a high temperature well in excess of 2100<sup>o</sup> F. has been created in the flue walls.

The air and gas are not shut off, and sufficient steam admitted through 2 to purge the air and combustion products from A-B. Outlet 12 is now closed. Outlet 3 opened. Hydrocarbon gases, steam, and oxygen or CO<sub>2</sub> are admitted in controlled proportions through 11, 10, and 9, under sufficient pressure to cause their passage through the highly heated flues of A. It is apparent that the higher temperature in the flues is at the extremity adjacent to C where active combustion took place. The counter current flow of the gaseous mixture is an important factor in securing the greatest efficiency in the absorption of the heat from the flue surfaces. The gaseous mixture is brought in contact with increasingly hot surfaces, and when passing into C, is at a temperature not much below the maximum temperature attained in the flues during the preceding cycle of operation. As these hot gases pass through the flues in B toward outlet 3, much of their sensible heat is imparted to the walls of these flues. They are brought to a high temperature. Since all of the reactions where CO<sub>2</sub> and steam are used are endothermic, to say nothing of the heat losses through the escape of sensible heat in the exit gases, the temperature of the flues in A will shortly be lowered to a level at which the desired reactions are not completed. 9 and 11 are closed, 12 kept open until sufficient steam has been introduced to drive the conserved gases from A-B. Outlet 3 is closed.

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Outlet 12 is opened. Air is admitted through 1; fuel gas through 6, and the conduit reheated. Since in the preceding cycle the flues in B were brought to a high temperature, the air entering C will now be highly preheated, and the flame temperature resulting from combustion greatly increased, so that the high temperature desired in the flues of A will be much more quickly attained. The CO<sub>2</sub> preferably employed may be most readily secured by washing the combustion gases passing from 12 with water under pressure, or with an alkaline solution, methods of CO<sub>2</sub> recovery well-known in the art. Calculations of the volume of combustion gas relative to the volume of conserved gases indicate an adequate supply of CO<sub>2</sub> from this source. While the use of catalysts does not change equilibrium relations or reduce materially the maximum temperature necessary to secure complete dissociation, they are effective in speeding up the change toward equilibrium. The refractory surfaces with which the gaseous mixture is contacted, exercise a catalytic effect, but nickel, of a considerable group of catalysts, has been found most efficient as a catalyst in the dissociation of hydrocarbons.

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## WHAT I CLAIM IS:-

1. The improvement in the process of obtaining a mixture of carbon monoxide and hydrogen in controlled proportions by the dissociation of hydrocarbon gases and vapors, which comprises heating a conduit, the interior of which is filled with a multiplicity of refractory heat-absorbing surfaces, to a temperature substantially in excess of  $2100^{\circ}\text{F}$ . by maintaining an active combustion therein, then passing through the conduit a mixture of hydrocarbon gases and vapors with oxidizing gases, so proportioned that the carbon and oxygen atoms in the mixture are substantially equal and the carbon and hydrogen atoms in such proportion as desired.

2. The improvement in the process of obtaining a mixture of carbon monoxide and hydrogen in controlled proportions by the dissociation of hydrocarbon gases and vapors, which comprises heating a conduit, the interior of which is filled with a multiplicity of refractory heat-absorbing surfaces, to a temperature substantially in excess of  $2100^{\circ}\text{F}$ . by maintaining an active combustion therein; then passing through the conduit, in a direction contrary to the travel of the combustion gases, a mixture of hydrocarbon gases and vapors with oxidizing gases, so proportioned that the carbon and oxygen atoms in the mixture are substantially equal, and the carbon and hydrogen atoms in such proportion as desired.



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A

3. The improvement in the process of obtaining a mixture of carbon monoxide and hydrogen in controlled proportions by the dissociation of hydrocarbon gases and vapors, which comprises heating a conduit, the interior of which is filled with a multiplicity of refractory heat-absorbing surfaces, to a temperature substantially in excess of 2100<sup>0</sup>F. by maintaining an active combustion therein, using highly preheated air to support the combustion; then passing through the conduit a mixture of hydrocarbon gases and vapors with oxidizing gases, so proportioned that the carbon and oxygen atoms in the mixture are substantially equal, and the carbon and hydrogen atoms in such proportions as desired.

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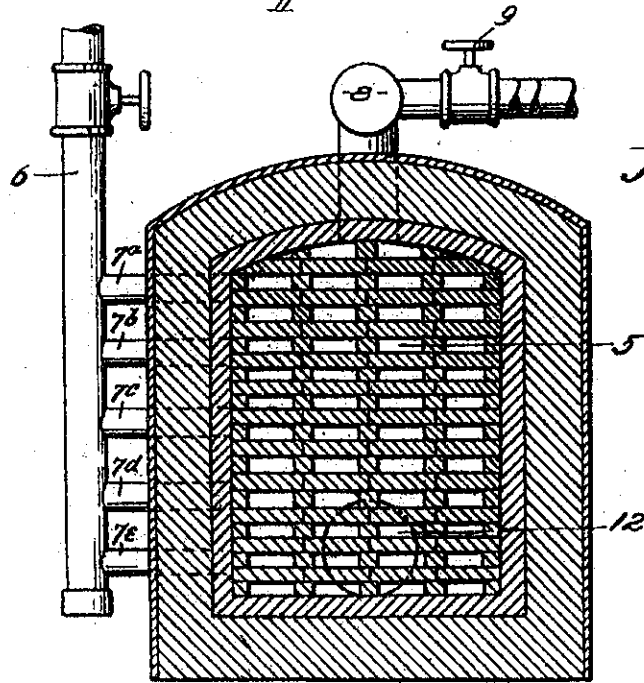
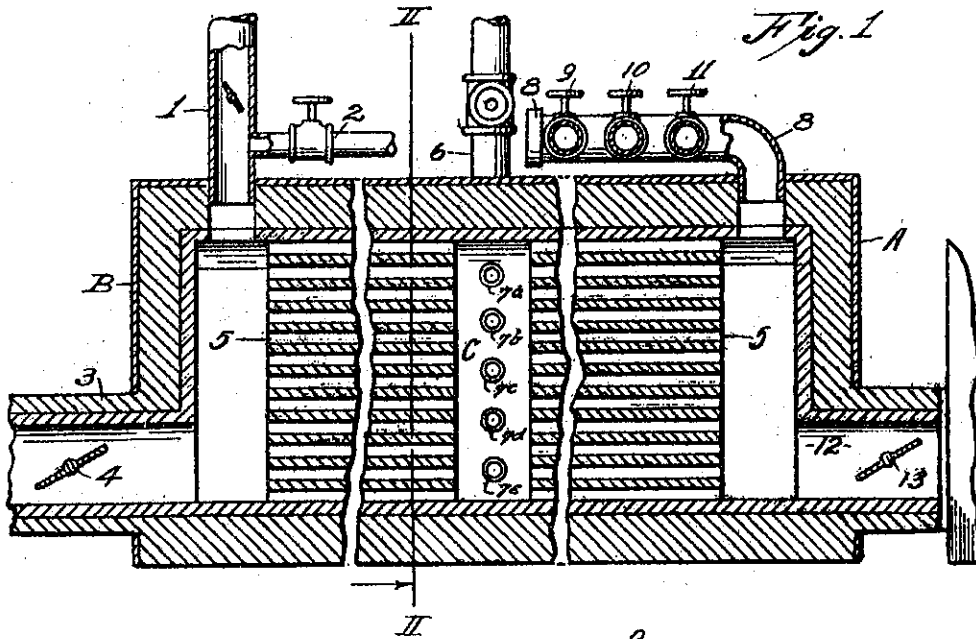
4. In apparatus for the thermal dissociation of hydrocarbon gases and vapors, the combination of a conduit, a multiplicity of refractory heat-absorbing surfaces within the interior of the conduit; means for introducing air and fuel gas into the conduit; means for withdrawing the products of combustion from the conduit; means for passing hydrocarbon gases and vapors through the conduit; means for adding oxidizing gases to the hydrocarbon gas; means for withdrawing the resultant products.

5. In apparatus for the thermal dissociation of hydrocarbon gases and vapors, the combination of a conduit, a multiplicity of refractory heat-absorbing surfaces within the interior of the conduit; means for introducing air and fuel gas into the conduit; means for preheating the air within the conduit; means for withdrawing the products of combustion from the conduit; means for passing hydrocarbon gases and vapors through the conduit; means for adding oxidizing gases to the hydrocarbon gases; means for withdrawing the resultant products.

6. In apparatus for the thermal dissociation of hydrocarbon gases and vapors, the combination of a conduit, a multiplicity of refractory heat-absorbing surfaces within the interior of the conduit; means for introducing air and fuel gas into the conduit; means for withdrawing the products of combustion from the conduit; means for passing hydrocarbon gases and vapors through the conduit, in a direction counter-current to the passage of the combustion gases through the conduit; means for adding oxidizing gases to the hydrocarbon gases; means for withdrawing the resultant products.

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 Process of and Apparatus for Obtaining  
 a Gaseous Mixture of Carbon Monoxide and  
 Hydrogen in Controlled Proportions by the  
 Dissociation of Hydrocarbon Gases and Vapors.

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CERTIFIED TO BE THE DRAWINGS  
 REFERRED TO IN THE SPECIFICATION  
 HEREUNTO ANNEXED.

INVENTOR

*W. D. Wiley*  
*Marks & Clerk*  
 ATTORNEYS

OTTAWA

*Jan. 24. 1930.*

BY