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(12) **Patent:** (11) **CA 264324**

(54) HYDROCARBON COMPOUND

(54) COMPOSE D'HYDROCARBURES

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ABSTRACT:

CLAIMS: Show all claims

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

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SPECIFICATION

TO ALL WHOM IT MAY CONCERN:

Be it known that I, ELLWOOD BARKER SPEAR, Chemist, a citizen of the United States of America, residing at Pittsburgh, in the County of Allegheny and State of Pennsylvania, United States of America, have invented a new and useful improvement in the PRODUCTION OF SYNTHETIC COMPOUNDS FROM HYDROCARBONS, of which the following is a full, clear and exact description, reference being had to the accompanying drawings forming part of this specification.

The present invention relates to the production of synthetic compounds from hydrocarbons, and more particularly to the decomposition of hydrocarbons, such as methane, etc., into gaseous products having compositions and proportions suitable for synthesis into methanol, motor fuels, ammonia, fertilizers and other valuable products.

The process is particularly applicable to the treatment of natural gas which usually consists of about 95% methane, but may be employed for the treatment of other gases, such as still gas from the cracking of petroleum, which usually consists of methane together with gaseous homologues and other hydrocarbon gases, such as ethylene. The invention will be described with particular reference to the cracking of natural gas, but it is to be understood that it may be used for the treatment of other hydrocarbons.

In the preferred procedure, a portion of the natural gas is heated to a decomposition temperature, together with steam, whereby a mixture of carbon monoxide and hydrogen is formed. This mixture contains one volume of carbon monoxide gas and three volumes of hydrogen gas. Another portion of the natural gas is cracked to yield hydrogen gas and solid carbon. The hydrogen gas may be used for the manufacture of ammonia, fertilizers, etc. The solid carbon is heated with steam to form a mixture of carbon monoxide and hydrogen containing equal volumes of carbon monoxide gas and hydrogen gas. This mixture of carbon monoxide and hydrogen is mixed with an approximately equal volume of the first mixture which contains one volume of carbon monoxide and three volumes of hydrogen to produce a resultant mixture, which contains approximately one volume of carbon monoxide gas to two volumes of hydrogen gas. This is the theoretically correct mixture to be used for the synthesis of methanol and similar compounds.

While it is preferred to use carbon monoxide for the production of methanol and similar compounds in accordance with the usual methanol-making processes, other processes for making methanol and similar compounds have been developed in which carbon dioxide is used. In case the methanol is made by such processes, carbon dioxide and hydrogen may be produced by my process.

The process will now be described in greater detail, together with the preferred form of apparatus for carrying it out.

In the drawings:

Figure 1 is a vertical section through a retort and carbon-collecting apparatus suitable for use in carrying out the process; and

Figure 2 is a diagrammatic flow sheet.

Any suitable form of retort may be used in which the conditions for carrying out the reactions may be obtained.

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A suitable form of retort, and the one which is preferred, is of the type shown in the Brownlee and Uhlinger patent, No. 1,520,115, of December 23, 1924. A retort of this type, together with the carbon-collecting apparatus, is shown in Figure 1. The retort consists of an outer supporting shell 1 having a heat-insulating lining 2, and containing refractory brick checkerwork 3. The checkerwork 3 is heated by means of a fuel mixture of gas and air introduced at the bottom of the retort by means of the gas pipe 4 and air pipe 5. The heating blast is applied to bring the checkerwork up to a temperature of about 1200° to 1400° C. The products of combustion escape through the discharge opening 6 at the top of the retort, which may be closed when the retort is not under blast, by means of the valve 7. After the checkerwork has been brought up to heat, the gas or mixture of gases to be treated is introduced into the top of the retort through the pipes 8 and passes down through the checkerwork 3 and is discharged through the outlet 9. This type of retort may be used both for the cracking of the natural gas to yield hydrogen and solid carbon particles, and also for the decomposition of the natural gas with steam to yield a wholly gaseous product consisting of carbon monoxide and hydrogen. When the retort is used to produce the gaseous mixture of carbon monoxide and hydrogen, this mixture is taken off directly through the discharge pipe 9 and passes to the methanol plant through pipe 10. If the retort is to be used for cracking the natural gas into hydrogen and solid carbon, the mixture of hydrogen and entrained carbon passes from the discharge pipe 9 into a carbon-separating and col-

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lecting apparatus shown at the right of the retort in Figure 1. The mixture of hydrogen and carbon passes into a spray chamber 11, where it is cooled by means of water sprays 12. It then passes downwardly through a mixing tower 13 and into a collecting chamber 14 containing a number of fabric bags 15, through which the hydrogen passes to the outlet 16. The bags 15 are periodically shaken to dislodge the carbon collected thereon. This carbon which is known as carbon black, is a well known article of commerce and consists of finely divided carbon. The carbon which gathers in the cooling chamber 11, the mixing chamber 13 and the collecting chamber 14 falls to a conveyor 17.

In cracking natural gas in the type of retort illustrated about two-thirds of the available carbon is deposited on the checkerwork and about one-third is collected as carbon black in the collection apparatus.

In the preferred embodiment of the process, two retorts which we may designate as retorts A and B (see flow sheet illustrated in Figure 2) are employed. The retort A is used for the cracking of the gas to produce hydrogen and carbon and for the production of the carbon monoxide and hydrogen mixture containing equal volumes of carbon monoxide and hydrogen. The retort is heated to the desired temperature by means of the blast of fuel gas and air admitted through the pipes 4 and 5 and the products of combustion escape through the top opening 6, the valve 7 being open during the heating blast. During this heating, the supply of gas through the pipes 8 is shut off, as is also the outlet 9. After the checkerwork 3 is heated to the desired point, the heating blast is cut off and the valve 7 is closed. Then the hydrocarbon gas, such as natural gas, and commonly referred to in the plants as the "run gas", is admitted through the pipes 8 at the top of the retort and passes downwardly through the highly heated checkerwork 3. The gas is decomposed into the hydrogen and carbon. The decomposition reaction of the methane, which constitutes the greatest part of the gas, is $CH_4 \rightarrow C + 2H_2$. Any of the higher methane homologues which may be present are decomposed according to a similar reaction. As above noted, about two-thirds of the carbon is deposited on the checkerwork. The hydrogen, in which the remaining one-third of the carbon is entrained as carbon black passes through the carbon-collecting apparatus. The hydrogen passes out through the discharge pipe 16 and to the plant in which the hydrogen is to be utilized. This hydrogen may be used for any purpose for which hydrogen is desired, such as the manufacture of ammonia and fertilizers. The carbon is collected by the conveyor 17.

The above reaction is indicated at the top of the flow sheet as taking place in the retort marked A.

While the checkerwork still remains hot enough for the carbon monoxide producing reaction, the run gas is cut off from the inlet pipes 8 and steam is introduced, either with or without the carbon black produced and collected on the previous gas-cracking operation. An excess of steam is preferably used. If the sale price of the carbon black collected is sufficiently high it is bagged and sold and the carbon which is encrusted on the checkerwork is utilized for the production of the carbon monoxide. However, if it is desired to use the collected carbon black it may be introduced into the retort along with the steam. The steam, on passing through the highly heated checkerwork, is decomposed and combines with the carbon encrusted on the checkerwork and with the carbon black introduced with the steam to form a gaseous mixture having substantially equal volumes of carbon monoxide and hydrogen. This reaction is indicated as taking place in the retort marked A' in Figure 2. The retort A' is the same retort as the retort A, but the legend A' is used to indicate the retort when the carbon monoxide producing reaction is taking place. The gaseous mixture of carbon monoxide and hydrogen is taken off through the branch discharge pipe 10 and is taken to the methanol plant to be mixed with the carbon monoxide and hydrogen mixture produced from the retort B.

The retort B is similar to retort A, but without the carbon-collecting apparatus. Retort B is heated by a blast of fuel gas and air in the same manner as retort A. After its checkerwork has been brought to the desired temperature, the heating blast is shut off and a mixture of the run gas and steam is passed in through the inlet pipes 8 at the top of the retort. The mixture passes down through the heated checkerwork and the methane is decomposed to yield carbon monoxide and hydrogen in accordance with the following equation: $CH_4 + H_2O \rightarrow CO + 3H_2$. Any higher methane homologues or other hydrocarbons which may be present in natural gas are decomposed according to a similar reaction. This reaction is indicated at the bottom of the flow sheet (Figure 2) as taking place in the retort marked B.

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It will be noted that the mixture of carbon monoxide and hydrogen obtained from the retort A (as indicated at A' in Figure 2) consists of equal volumes of carbon monoxide and hydrogen and the mixture of carbon monoxide and hydrogen obtained from the retort B consists of one volume of carbon monoxide to three volumes of hydrogen gas. The carbon monoxide and hydrogen mixtures obtained from the retorts A and B, respectively, are mixed as indicated in the flow sheets of Figure 2 and yield a resultant mixture containing one volume of carbon monoxide to two volumes of hydrogen gas. This is the theoretically correct proportion for the production of methanol or similar products. This mixture goes to the methanol plant where it is synthesized into methanol (CH_4O) by the usual methanol making processes in which carbon monoxide and hydrogen are passed through catalysts under pressure, the reaction being $CO + 2H_2 \rightarrow CH_4O$. The mixture of carbon monoxide and hydrogen may also be used for producing products similar to methanol, such for example, as the new motor fuels ordinarily called synthol.

As will be apparent from the flow sheet indicated in Figure 2, when all of the carbon is utilized in the production of the carbon monoxide, the theoretically correct mixture for making methanol and similar products may be produced by dividing the natural gas into two substantially equal portions, one of which is cracked to yield hydrogen and carbon, the carbon of which is combined with steam to form a mixture of carbon monoxide and hydrogen relatively poor in hydrogen, while the other portion is mixed with steam and decomposed to form a carbon monoxide and hydrogen mixture relatively rich

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in hydrogen, which two mixtures, when added to each other, give the correct mixture for methanol synthesis.

In some processes for making methanol, water fuels, or the like, such as synthol, a mixture of hydrogen with carbon dioxide or with carbon dioxide and carbon monoxide may be employed. In case carbon dioxide or a mixture of carbon dioxide and carbon monoxide is desired instead of carbon monoxide alone, the process may be modified to produce carbon dioxide. When steam is combined with carbon at high temperatures, carbon monoxide is the principal product. When, however, the temperature is lower, there is a tendency to the production of carbon dioxide. By operating the retort A at a lower temperature when steam is injected, the carbon may be converted principally into the dioxide form according to the equation: $C + 2H_2O \rightarrow CO_2 + 2H_2$. It will be noted that in this case, the volume of hydrogen produced from the same amount of carbon is double that produced when carbon monoxide is produced. However, since the carbon dioxide requires a greater amount of hydrogen in making methanol than does carbon monoxide, the mixture of carbon dioxide and hydrogen formed from the carbon produced by cracking one portion of the natural gas in the retort A may be combined with the carbon monoxide and hydrogen mixture formed by treating an approximately equal proportion of natural gas in the retort B. It may be noted that in the synthesis of methanol from carbon dioxide and hydrogen, or a mixture of carbon dioxide, carbon monoxide and hydrogen, the hydrogen and oxygen in excess of that required for the methanol form water. While the source of the carbon dioxide has been described as the carbon treated

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with steam in the retort A, the carbon dioxide content of the gaseous mixture from the retort B may apparently be similarly increased by suitable temperature control.

A modification of the process may be carried out using the retort A only. In this case, instead of using a retort B to produce a mixture or carbon monoxide and hydrogen which is relatively rich in hydrogen, hydrogen produced by the cracking of the methane into carbon and hydrogen in the retort A may be added to the mixture of carbon monoxide and hydrogen produced in the retort A, in order to bring up its hydrogen content to that required for methanol synthesis. This modification of the process may be carried out with advantage in the cracking of the gas for the production of carbon black. In this case, the carbon black is one of the products to be saved, and the carbon black from the carbon-collection apparatus is not blown into the retort with the steam, but the carbon which is encrusted on the checkerwork is utilized by blowing in steam, while the checkerwork is still hot enough to cause the combination of the encrusted carbon with the steam into carbon monoxide. The mixture of carbon monoxide and hydrogen thus produced may be mixed in suitable proportions, with the hydrogen produced during the cracking of the gas, to get any desired carbon monoxide and hydrogen mixture. This is an improvement over the present operation of the retorts operating for producing carbon black in which the carbon encrusted on the checkerwork is burned during the heating blast. It may, however, be employed in other processes.

Natural gas, which is the preferred gas used in our

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process, is, at present, very cheap in the gas fields which are far removed from cities or other centers of consumption. Natural gas, when treated according to our process, probably furnishes the cheapest mixture of hydrogen and carbon monoxide or dioxide at present available, as well as furnishing gases which are substantially uncontaminated with sulphur or other impurities which have proven to be very troublesome because of their poisoning of the catalysts used in synthesizing the mixtures of hydrogen and carbon monoxide or dioxide.

While the present process has been described specifically as applied to methane or natural gas, the process may be employed in the treatment of other hydrocarbons, such as the petroleum hydrocarbons, whether in the form of fixed gases or vaporized liquids. The reactions in converting such hydrocarbons into mixtures of hydrogen and carbon monoxide or dioxide are similar to those described in connection with the decomposition of methane, as will be readily understood by those skilled in this art. While the synthetic products formed are preferably methanol or methanol-containing fluids, such as synthol and motor fuels, other synthetic compounds may be produced. Also while the hydrogen has been spoken of as being preferably used for the synthesizing of ammonia and fertilizers, the hydrogen may be used for other purposes, such as the hydrogenation of oils, or for any other purpose for which hydrogen is suitable.

The present invention is not limited to its applications or to the details of procedure set forth specifically above, but may be modified or otherwise embodied within the scope of the following claims.

I claim:

1. Those steps of the herein described process, which consist in cracking a hydrocarbon to yield carbon and hydrogen, combining the carbon with steam to yield a mixture containing an oxide of carbon and hydrogen, enriching this mixture with hydrogen, and synthesizing it.

2. Those steps of the herein described process, which consist in cracking a hydrocarbon to yield carbon and hydrogen, combining the carbon with steam to yield a mixture containing carbon monoxide and hydrogen, enriching this mixture with hydrogen, and synthesizing it.

3. Those steps of the herein described process, which consist in cracking methane to yield carbon and hydrogen, combining the carbon with steam to yield a mixture containing an oxide of carbon and hydrogen, enriching this mixture with hydrogen, and synthesizing it.

4. Those steps of the herein described process, which consist in cracking methane to yield carbon and hydrogen, combining the carbon with steam to yield a mixture containing carbon monoxide and hydrogen, enriching this mixture with hydrogen so that it contains approximately one volume of carbon monoxide gas to two volumes of hydrogen gas, and synthesizing the carbon monoxide and hydrogen.

5. Those steps of the herein described process, which consist in cracking methane to yield carbon and hydrogen, combining the carbon with steam to yield a mixture containing approximately equal volumes of carbon monoxide and hydrogen gas, decomposing a further quantity of methane with steam to yield a second mixture containing approximately one volume of carbon monoxide and three volumes of hydrogen gas,

enriching the first mixture with hydrogen by adding to it such proportion of the second mixture as to produce a resultant mixture containing approximately one volume of carbon monoxide gas and two volumes of hydrogen gas, and synthesizing the carbon monoxide and hydrogen.

6. Those steps of the herein described process, which consist in passing a hydrocarbon through a heated retort to yield hydrogen and carbon, a part at least of which is deposited in the retort, passing steam through the retort while heated so as to combine with the carbon and yield a mixture containing an oxide of carbon and hydrogen, passing a further quantity of the hydrocarbon through a heated retort together with steam so as to produce a mixture containing an oxide of carbon and hydrogen and richer in hydrogen than the first mixture, mixing the two mixtures in suitable proportions, and synthesizing the resultant mixture.

7. Those steps of the herein described process, which consist in passing a hydrocarbon through a heated retort to yield hydrogen and carbon, a part at least of which is deposited in the retort, passing steam through the retort while heated so as to combine with the carbon and yield a mixture containing carbon monoxide and hydrogen, passing a further quantity of the hydrocarbon through a heated retort together with steam so as to produce a mixture containing carbon monoxide and hydrogen richer in hydrogen than the first mixture, mixing the two mixtures in suitable proportions, and synthesizing the carbon monoxide and hydrogen.

8. Those steps of the herein described process, which consist in passing methane through a heated retort to yield hydrogen and carbon, a part at least of which is de-

posited in the retort, passing steam through the retort while heated so as to combine with the carbon and yield a mixture containing carbon monoxide and hydrogen, passing a further quantity of methane through a heated retort together with steam so as to produce a mixture containing carbon monoxide and hydrogen richer in hydrogen than the first mixture, mixing the two mixtures in suitable proportions, and synthesizing the carbon monoxide and hydrogen.

9. Those steps of the herein described process, which consist in passing methane through a heated retort to yield hydrogen and carbon, a part at least of which is deposited in the retort, and thereafter passing steam through the retort while heated to combine with the carbon and yield a mixture containing carbon monoxide and hydrogen.

10. Those steps of the herein described process, which consist in passing a hydrocarbon through a heated retort to yield hydrogen and carbon, a part at least of which is deposited in the retort, and thereafter passing steam through the retort while heated so as to combine with the carbon and yield a mixture containing an oxide of carbon and hydrogen.

11. Those steps of the herein described process, which consist in passing methane through a heated retort to yield hydrogen and carbon, a part at least of which is deposited in the retort, thereafter passing steam through the retort while heated to combine with the carbon and yield a mixture containing carbon monoxide and hydrogen, enriching this mixture with hydrogen and synthesizing the carbon monoxide and hydrogen.

12. Those steps of the herein described process, which consist in passing a hydrocarbon through a heated retort to yield hydrogen and carbon, a part at least of which is deposited in the retort, thereafter passing steam through the retort while heated to combine with the carbon and yield a mixture containing an oxide of carbon and hydrogen, enriching this mixture with hydrogen, and synthesizing it.

13. Those steps of the herein described process, which consist in heating a checkerwork-containing retort to a temperature above the decomposition point of methane, passing methane through the heated retort to crack it and yield hydrogen and carbon, a part at least of which is deposited in the checkerwork, and thereafter while the checkerwork still remains heated passing steam through the retort to combine with the carbon and yield a mixture containing carbon monoxide and hydrogen.

14. Those steps of the herein described process, which consist in heating a checkerwork-containing retort to a temperature above the decomposition point of the hydrocarbon, passing the hydrocarbon through the heated retort to crack it and yield hydrogen and carbon, a part at least of which is deposited on the checkerwork, thereafter while the checkerwork still remains heated passing steam through the retort to combine with the carbon and yield a mixture containing an oxide of carbon and hydrogen.

15. Those steps of the herein described process, which consist in passing methane through a heated retort to crack it and yield hydrogen and finely divided carbon, separating entrained carbon from the hydrogen and returning it together with steam to the heated retort to produce a mixture containing approximately equal volumes of carbon monoxide and

hydrogen, passing a further quantity of methane through a heated retort to produce a mixture containing approximately one volume of carbon monoxide and three volumes of hydrogen gas, mixing the two mixtures in proportions to yield a resultant mixture containing approximately one volume of carbon monoxide and two volumes of hydrogen gas, and synthesizing the carbon monoxide and hydrogen.

16. Those steps of the herein described process, which consist in cracking methane to yield hydrogen and carbon, heating the carbon together with steam so as to yield a mixture containing oxide of carbon and hydrogen, heating a further quantity of methane with steam so as to yield a mixture containing an oxide of carbon and hydrogen but richer in hydrogen than the first mixture, mixing the two mixtures, and synthesizing the resultant mixture.

17. Those steps of the herein described process which consist in cracking a hydrocarbon to yield hydrogen and carbon, heating the carbon together with steam so as to yield a mixture containing an oxide of carbon and hydrogen, heating a further quantity of the hydrocarbon with steam so as to yield a mixture containing an oxide of carbon and hydrogen but richer in hydrogen than the first mixture, mixing the two mixtures, and synthesizing the resultant mixture.

18. Those steps of the herein described process, which consist in cracking methane to yield hydrogen and carbon, heating the carbon together with steam so as to yield a mixture containing carbon monoxide and hydrogen, heating a further quantity of methane and steam so as to yield a mixture containing carbon monoxide and hydrogen but richer in hydrogen than the first mixture, mixing the two mixtures, and synthesizing the resultant mixture.

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19. Those steps of the herein described process, which consist in cracking a volume of methane to yield hydrogen and carbon, heating the carbon with steam to yield a mixture containing approximately equal volumes of carbon monoxide and hydrogen, heating a second and substantially equal volume of methane with steam to yield a mixture containing approximately one volume of carbon monoxide and three volumes of hydrogen, mixing the two mixtures, and synthesizing the resultant mixture.

IN TESTIMONY WHEREOF I have hereunto set my hand this 7th day of November, 1925, at Pittsburgh, Pennsylvania, United States of America.

Ellwood Barker Spear

In the presence of:

Edwin J. Kelly

Geo. B. Blenning

uction of Synthetic 264324
ompounds from Hydrocarbons

Fig. 1.

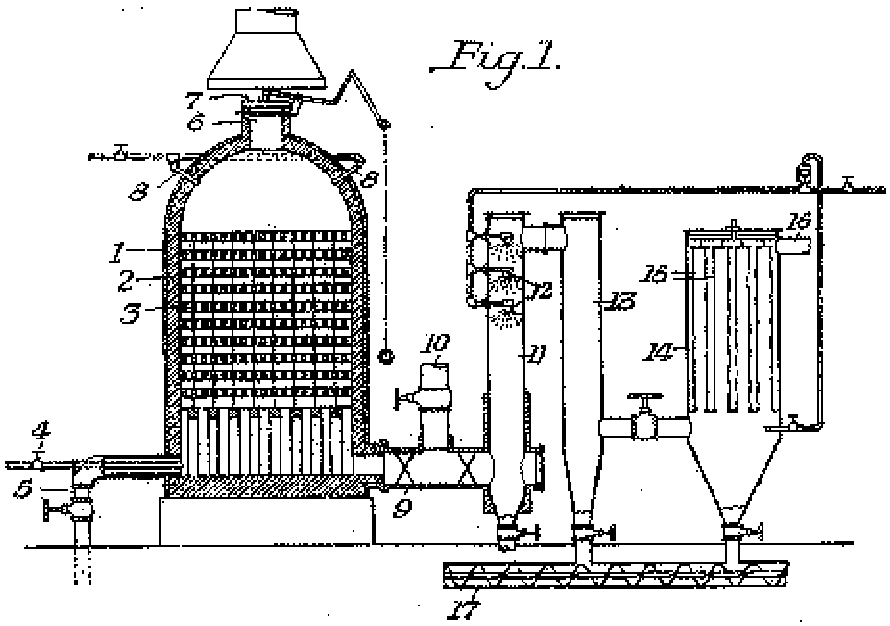
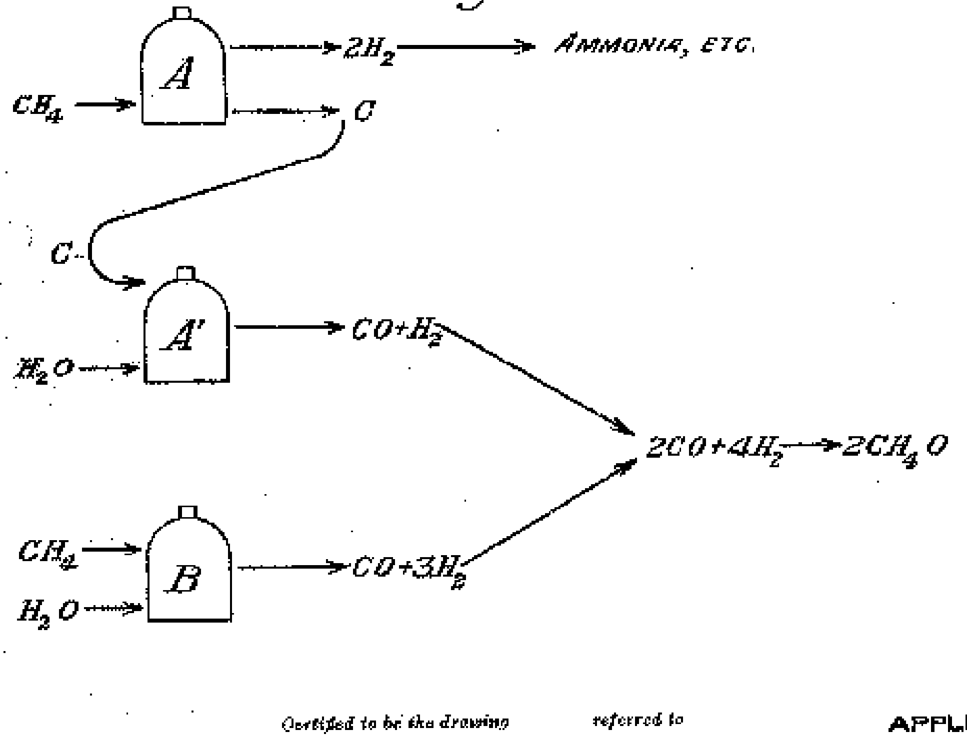


Fig. 2.



Certified to be the drawing referred to in the specification hereunto annexed.

Pittsburgh, Pa., Nov. 7 1925

APPLICANT

Ellwood Burdsall Spear
by
Byrnes, Townsend & Brickenstein

ATTORNEYS