PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Method of Making Fuel Gas from Hydrocarbon Oils and Steam.

We, CARBURETTED GAS, INC., a Corporation organised and existing under and by virtue of the laws of the State of Delaware, United States of America, and having its principal place of business at No. 19—21, Dover Green, City of Dover, County of Kent, State of Delaware, United States of America; do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process for the making of gas, a process especially adapted for using heavy oil, and provides for the making of a hydrogen and carbon-monoxide gas mixture and also a gas of almost any desired heating value—a gas mixture of hydrogen, carbon-monoxide and hydrocarbon permanent gases.

It has been proposed in an apparatus for manufacturing gas from liquid hydrocarbons and steam to employ a fixing chamber within which is placed a mass of fragmentary refractory material in conjunction with a converter or decomposing chamber and a mixing chamber. In this apparatus hydrocarbon, steam and air are injected into the converter and react to produce a gas which if required as fuel gas only is withdrawn from the mixing chamber before reaching the fragmentary mass. If an illuminating gas is required additional hydrocarbon is injected into the mixing chamber and the gas mixture is passed through the heated fragmentary mass, which thus serves to provide the heat for fixing the hydrocarbon enrichment gas.

It has been stated that this apparatus may also be used for making a fixed fuel gas from hydrocarbon and steam only which are admitted to the converter and passed through the mixing chamber and the heated fragmentary mass. In this case it is stated that the carbon of the hydrocarbon and the steam are practically burnt together producing carbonic acid and liberating the hydrogen and that a portion of the oxygen of the carbonic acid absorbs carbon from the hydrocarbon, converting it into carbonic oxide.

[*Price* 1/-]

In the above described process the steam and hydrocarbon are admitted together, whereas in the process of the present invention as hereinafter defined the oil and steam may be admitted either separately or together as the steam reaction takes place primarily with the oil carbon deposited either initially or during the cracking step. Further in the process of the present invention the carbon is not first completely oxidised to CO_2, which is then reduced to CO, but an excess of carbon is always present ensuring a direct reaction to CO without intermediate formation of CO_2.

Further in the description of a known process for making hydrogen or gases containing hydrogen from methane and other hydrocarbon gases by the alternate passage of hydrocarbon gas with or without the addition of steam and air through a bed of highly heated coke or refractory material, it is stated that the coke may be replaced by a bed of inert refractory material when the hydrocarbon gas is substantially pure, but that when steam is added to the hydrocarbon gas coke must be employed to meet the requirements of the water-gas reaction.

The present process is distinguished from the last mentioned process in that it is a process for making a mixture of hydrogen and carbon-monoxide with or without enrichment by permanent hydrocarbon gas from liquid hydrocarbon and steam without air and is not dependent on the use of coke for the water-gas reaction.

According to the present invention, a porous bed of material, preferably non-carbonaceous, is employed and the process comprises a preparatory step of heating the porous bed and depositing oil carbon thereon followed by heating the bed to a temperature above that required for cracking all the oil into its elements carbon and hydrogen, passing steam and oil separately or together through the hot bed to crack the oil and effect reaction of the steam with the carbon to produce hydrogen and carbon-monoxide only, stopping the gas making run before the bed has cooled to a temperature at which a sub-

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stantially diluted gas mixture is formed, repeating the heating of the bed and repeating the gas making cycle of operations.

In order that the value and advantages of the present invention may be appreciated it is to be noted that 1000 cubic feet of water-gas, a carbon-monoxide and hydrogen gas mixture, of approximately 300 B.T.U. per cubic foot heating value, generated by the usual water-gas process requires an average of 40 pounds of coke and 45 pounds of steam (see U.S. Bureau of Mines Bulletin No. 301) or according to Morgan "American Gas Practice" 1931, 35 pounds dry coke and 52 pounds steam.

If 4 gallons of heavy oil, analysing 86% carbon and 12% hydrogen and weighing 8 pounds per gallon, for example, be cracked to its elements it will yield 27.5 pounds carbon and 680 cubic feet of hydrogen.

In the making, therefore, of 1000 cubic feet of gas we have 680 cubic feet of hydrogen available in 4 gallons of oil as just pointed out. The balance of the 1000 cubic feet, i.e. 320 cubic feet can be generated by the carbon from the oil and steam producing hydrogen and carbon monoxide in approximately equal volumes, the chemical ingredients of which require 5.33 lbs. carbon and 8 pounds steam. The total heat (latent and sensible) utilised in generating this 1000 cubic feet of gas (approximately 840 cubic feet of hydrogen and 160 cubic feet of carbon monoxide) between 2500° F. and 1850° F. (say an average of 2250° F.) is the order of the following: (See "Richards Metallurgical Calculations" for heat unit constants).

	Heat Balance
Sensible heat of 1000 cubic feet @ 2250°F.	−46,600 B.T.U.
Latent heat cracking 4 gallons oil (700 B.T.U./lb. heat of formation)	−22,400 B.T.U.
Latent heat dissociating 8 lbs. steam	−46,500 B.T.U.
Heat generated 5.33 lbs. carbon to carbon monoxide	+23,500 B.T.U.
Heat utilised	−92,000 B.T.U.

The carbon available for producing the heat necessary for generating 1000 cubic feet of hydrogen and carbon monoxide from 4 gallons oil equals 27.5 − 5.33 = 22.17 pounds by combustion to carbon dioxide amounts to 322,000 B.T.U. of which 92,000 B.T.U. or 28.5% is utilised for generation of the gas and 71.5% constitutes heat losses carried off with the heating gas also radiated and conducted from the generator.

It is apparent, therefore, without the use of solid fuel such as coke that approximately 4 gallons of oil and 8 pounds of steam will provide the gas making materials and supply the necessary heat required to generate 1000 cubic feet of hydrogen and carbon-monoxide gas mixture having a heating value of approximately 300 B.T.U. per cubic foot.

The present invention provides, therefore, in the making of a hydrogen and carbon-monoxide gas mixture having approximately 300 B.T.U. per cubic foot heating value, for instance, for introducing oil and steam in controlled proportions and quantities into a hot porous bed to crack all the oil and steam into their elements, hydrogen, carbon and oxygen, and on passing through the hot porous bed generating carbon-monoxide which mixes with the hydrogen, using 4 gallons of oil and 8 pounds of steam for generating each 1000 cubic feet of gas.

This enables a non-carbonaceous porous bed of lump material to be employed as distinguishing from solid carbon, such as coke now employed in the generation of water-gas, thus effecting economies in gas making materials and eliminating the labour and expense incident to using solid lump fuel, such as renewing the coke bed periodically, breaking clinkers, removing ashes, etc.

It is to be noted also that the present process generates a hydrogen and carbon-monoxide gas mixture in which the hydrogen predominates, the gas of the present invention containing a much greater percentage of hydrogen than is contained in water-gas.

Owing to this high hydrogen content and consequently low content of carbon-monoxide, the gas of this invention has a lower specific gravity and is less toxic than water-gas, two qualities which are highly desirable when the gas is mixed with hydrocarbon fixed gas to form public utility gas..

As first mentioned above the present process provides for controlling the heating value of the gas generated so that a gas of almost any desired heating value may be produced; in this connection when a gas is desired having a heating value greater than 300 B.T.U. per cubic foot, as will be brought out in detail hereinafter, the gas making run is continued for a longer period than when making a 300 B.T.U. gas. This longer period of gas making reduces the porous bed temperature below where the heat of the bed cracks all of the oil into its elements so

that a part of the oil will pass through the bed cracked to hydrocarbon fixed gases, the gas making run being continued until the generated gas, the fixed heating value of which gradually increases, has the desired maximum hydrocarbon content and the total gas run by diffusion produces practically a uniform gas mixture of the desired average fixed heating value.

The apparatus necessary for the carrying out of the present process may take various forms, but in any event will be of simple design. Inasmuch as the claims of this application are directed to a method as distinct from an apparatus, the accompanying drawing is merely illustrative and schematic.

For converting oil and steam into a hydrogen and carbon-monoxide gas mixture, having a heating value of 300 B.T.U. per cubic foot, is provided a generator 1 which, as shown, may take the form of a vertical cylindrical steel shell having a dome 2 of any practical form, the generator being lined with heat insulation and refractories. The generator chamber 1 will have a valve controlled outlet 3, in this case shown near the bottom.

4 designates a grate or perforated floor for supporting a porous bed 5 of lump material, fire brick, for example, or any other desirable refractory. In the dome 2 are valve controlled inlets for air, steam and oil designated 6, 7 and 8 respectively. In the valve controlled outlet 3 a valve controlled stack 9 is provided for exhausting products of combustion used for heating the generator.

In preparing the generator for operation, air and oil are introduced through inlet nozzles 6 and 8 and burned, the products of combustion passing downwardly through the porous bed 5 and exhausting from the generator through the valve controlled stack 9, the valve for the gas outlet 3 at this time being closed. Oil is then introduced into the hot bed 5 through oil inlet 8 to effect a deposit of carbon on the surface of the hot lumps composing the porous bed.

With the valve for the gas outlet 3 still closed and the valve for the exhaust outlet 9 open, air inlet 6 is opened admitting air for combustion of some of the deposited carbon throughout the bed 5, or when desired, air and oil may be admitted for complete combustion to heat the bed and the interior of the generator, the products of combustion exhausting through outlet 9 as will be understood. When the generator is sufficiently heated for gas generation, say, for example, to 2500° F. steam is introduced through the inlet 7 to purge the generator of inert products of combustion.

The steam is then cut off, the valve for outlet 9 is closed and the valve for gas outlet 3 opened and steam is introduced through the inlet 7 through the bed 5 for reaction with the oil carbon deposit to carbon-monoxide and hydrogen, the gas thus formed flowing through the outlet 3 and then usually through gas cooling, scrubbing and purifying equipment and finally into a gas holder. Oil is then introduced through the line 8 in an atomised or vaporised condition, into the hot porous bed 5. Inasmuch as this bed is at a temperature sufficiently high to crack the oil into its elements, hydrogen will be liberated and carbon deposited on the lumps of the porous bed, the hydrogen flowing through the bed and outlet 3.

The steam supply should be cut off when the temperature of the bed 5 has been lowered to around 1850° F., for example, to prevent detrimental dilution of the gas with carbon dioxide.

It is to be understood that for making a mixture of hydrogen and carbon-monoxide the oil supply through the inlet 8 should be cut off before the bed 5 becomes cooled to a temperature at which hydrocarbon fixed gas passes through the porous bed.

On conclusion of the gas run, the operating cycle has been completed and the bed 5 is reheated as before to around 2500° F. for example, and the other operations of the cycle repeated.

While the steam has been mentioned as introduced separately and ahead of the oil it is to be appreciated, of course, that the steam and oil may be introduced simultaneously or that the oil may be introduced separately and ahead of the steam, in accordance with the quality of the desired gas as will hereinafter be pointed out.

It will be appreciated that after one cycle of operation the introduction of oil through the inlet 8 for the purpose of depositing carbon in the bed 5 will usually be unnecessary inasmuch as there will be sufficient carbon deposit left from the previous gas run for reheating the bed by total combustion with air introduced through the inlet 6. On the other hand, the generator may be partially reheated by combustion of oil and air introduced for that purpose when there is a deficiency of carbon deposit.

The process thus far described, therefore, provides for the generation of a hydrogen and carbon-monoxide gas mixture, by cyclic operation, namely, by heating a bed of porous material containing deposited oil carbon to a

sufficiently high temperature to crack all of the oil into its elements hydrogen and carbon and then passing oil and steam through this hot porous bed to crack the oil into its elements and dissociate the steam, the oxygen combining with the deposited carbon to form carbon-monoxide which mixes with the liberated hydrogen.

As above mentioned this process is a simple economic method for generating a hydrogen and carbon-monoxide gas mixture as compared with present methods employed in the making of water-gas, where steam is employed with a bed of lump coke or anthracite and usually excess steam and with the attendant clinker trouble and labour involved in the use of solid carbon.

As above mentioned the present invention provides for making a gas of almost any desired heating value, a gas mixture of hydrogen, carbon-monoxide and permanent or fixed gas of hydrocarbons. With reference to this phase of the invention the operations may be similar to those described and in this case the gas making run with oil continues to lower temperatures for generating hydrocarbon permanent gases.

It will be seen from the drawing that the apparatus for practicing this phase of the invention includes a gas diffusing and tempering chamber 10 communicating with the valve-controlled gas outlet 3. This diffusing and tempering chamber, though larger in volume, may be of similar construction as chamber 1, and is provided with valve-controlled exhaust outlet 11 and valve-controlled gas outlet 12.

In operation the porous bed 5 is heated up as described in connection with the making of hydrogen and carbon-monoxide gas, the valve in exhaust outlet 9 being closed, the valves in gas outlet 3 and exhaust outlet 11 being open, and the valve in gas outlet 12 being closed, so that the entire apparatus is heated to the desired degree.

After gas making operations are started the chamber 10 maintains its own heat.

On the gas-run making gas of higher heating value than hydrogen or a gas mixture of hydrogen and carbon-monoxide, after the apparatus has been heated up and purged of products of combustion, the valve in outlet 11 is closed and the valve in outlet 12 opened, and with the valve in gas outlet 3 also open steam and oil through the supply lines 7 and 8 are introduced into the heated porous bed 5 to crack the oil to its elements carbon and hydrogen and effect reaction of the steam with the oil carbon, the gas generated flowing continuously into the diffusing and tempering chamber. The injections of steam and of oil supplies are properly regulated and controlled during the gas making run, as will be understood; as the temperature of the porous bed 5 lowers all of the oil will no longer be cracked into its elements carbon and hydrogen but some of the oil will be cracked into hydrocarbon permanent or fixed gases. Consequently the gas passing into the diffusing and tempering chamber will then contain a proportion of these hydrocarbon gases instead of being simply a gas mixture of hydrogen and carbon monoxide, and the fixed heating value of the diffused finished gas of the entire gas run will of course be correspondingly increased. When the gas discharging through the outlet 3 has the desired predetermined maximum hydrocarbon content the gas making run is stopped. The bed 5 is then reheated to its original high temperature, any desired temperature above 1850° F. and within the upper temperature limit of the refractories used, for example, around 2500° F. and the cycle of operations repeated.

By this procedure it will be apparent that a gas is produced having a higher fixed heating value as compared to the heating value of a gas mixture of hydrogen and carbon monoxide and as is apparent from the foregoing a gas having almost any desired predetermined fixed heating value can be produced.

It is to be understood of course that the instant of stopping the gas making, i.e. the temperature to which the bed 5 is lowered, depends upon the initial temperature of the bed and the desired fixed heating value of the diffused finished gas. Obviously the higher the initial temperature of the bed 5 the greater the volume of hydrogen produced by the cracking of all the oil into its elements hydrogen and carbon, and reaction of carbon with steam to hydrogen and carbon-monoxide so that the gas making run will be continued correspondingly longer with a consequent further lowering of the bed temperature in order that there will be produced an increased volume of hydrocarbon fixed gas to yield, by diffusion of all the gas made during the gas run, a finished gas of almost any desired fixed heating value. As for example, to further emphasize this point, in the making of a 540 B.T.U. gas, the Standard Public Utility Gas of New York City, the initial temperature of the bed 5 may be approximately 2150° F. and the temperature at the end of the

run approximately 1450° F.; whereas if the initial temperature were approximately 2500° F. then the gas run must be continued until the bed temperature has been lowered to approximately 1300° F. For the short and long temperature ranges of gas making it will be appreciated that there will be a difference in the volume of gas produced in the order of approximately 650° C.F., to approximately 1050 C.F., respectively, when 10,000 B.T.U. are expended for each 100° F. drop in temperature.

Gas of the desired fixed heating value, for example, in this case 540 B.T.U. per cubic foot may be produced in accordance with the present invention as follows:

The porous bed 5 is first heated as above described by the combustion of oil and air, after which oil is introduced into the bed to effect the deposit of carbon on the lumps of the bed. Then by admitting air for combustion of some of the deposited carbon and when necessary admitting some oil for complete combustion to supply the heat necessary for heating the bed to between approximately 2150° F. and 2500° F. for example, and after purging the apparatus of inert products of combustion steam is introduced to generate hydrogen and carbon monoxide only, this procedure lowering the temperature of the bed 5 as will be understood.

When the bed temperature has been lowered to approximately 1850° F., oil is injected, the steam supply being practically cut off; all the oil now will not be cracked into its elements, but some of the oil will be cracked to hydrocarbon fixed gas. The run is continued until the gas coming from the generator has the desired maximum fixed heating value, which occurs in this case when the bed temperature, assuming the initial bed temperature to be approximately 2150° F., is lowered to approximately 1450° F., a minimum temperature range of approximately 700°; and when the initial bed temperature is approximately 2500° F. the bed temperature is lowered to approximately 1300° F., a maximum temperature range of 1200°.

It will be understood that the temperature range of the gas making run is so regulated that the hydrogen, carbon-monoxide gas run followed by the gas run generating hydrogen and fixed or permanent hydrocarbon gas are so proportioned that the total gas made during the gas making run, through diffusion, yields approximately uniform quality gas of approximately the desired predetermined fixed heating value.

It will be seen from the foregoing that a low gravity gas of approximately almost any desired fixed heating value may be generated by properly regulating the temperature range of the gas making cycle and controlling the supplies of steam and of oil throughout the operations of the present method for generating from heavy oil and steam gas of almost any desired heating value.

From the foregoing it will be evident that the present invention provides a simple process for the making of gas, wherein, as distinguished from water-gas and carburetted water-gas practice, a hydrogen and carbon-monoxide gas mixture and a gas mixture of hydrogen, carbon-monoxide and hydrocarbon fixed gas may be made without the employment of coke or other solid carbon material, the heating value of the gas produced by the present method being readily regulated so as to produce a gas of almost any desired heating value.

It is to be noted that when oil alone is supplied to the generator that a small amount of steam is usually supplied with the oil as it has been found that the presence of a small amount of steam facilitates the reactions when cracking oil to form hydrocarbon permanent gases.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The process of making a hydrogen and carbon-monoxide gas mixture from steam and oil employing a porous bed of material, preferably non-carbonaceos, said process comprising a preparatory step of heating the porous bed and depositing oil carbon thereon followed by heating the bed to a temperature above that required for cracking all the oil into its elements carbon and hydrogen, passing steam and oil separately or together through the hot bed to crack the oil and effect reaction of the steam with the carbon to produce hydrogen and carbon-monoxide only, stopping the gas making run before the bed has cooled to a temperature at which a substantially diluted gas mixture is formed, repeating the heating of the bed and repeating the gas making cycle of operations.

2. The process according to Claim 1 characterised in that the porous bed is first heated to above 2000° F.

3. The process according to Claim 1 characterised in that in the finished gas the hydrogen content is substantially greater than that of ordinary water gas.

4. The process according to Claim 1 characterised in that reheating the porous bed is accomplished by combustion of

carbon deposited throughout the bed.

5. The process according to Claim 1 characterised in that the gas-making run is continued until the resulting gas contains a predetermined content of hydrocarbon permanent gas.

6. The process according to Claim 1 characterised in that the porous bed is first heated to between 2150° F. and 2500° F. and when the temperature of the bed has lowered to between 2150° F. and 1850° F. oil is introduced for cracking to hydrocarbon fixed gas.

Dated this 17th day of October, 1933.

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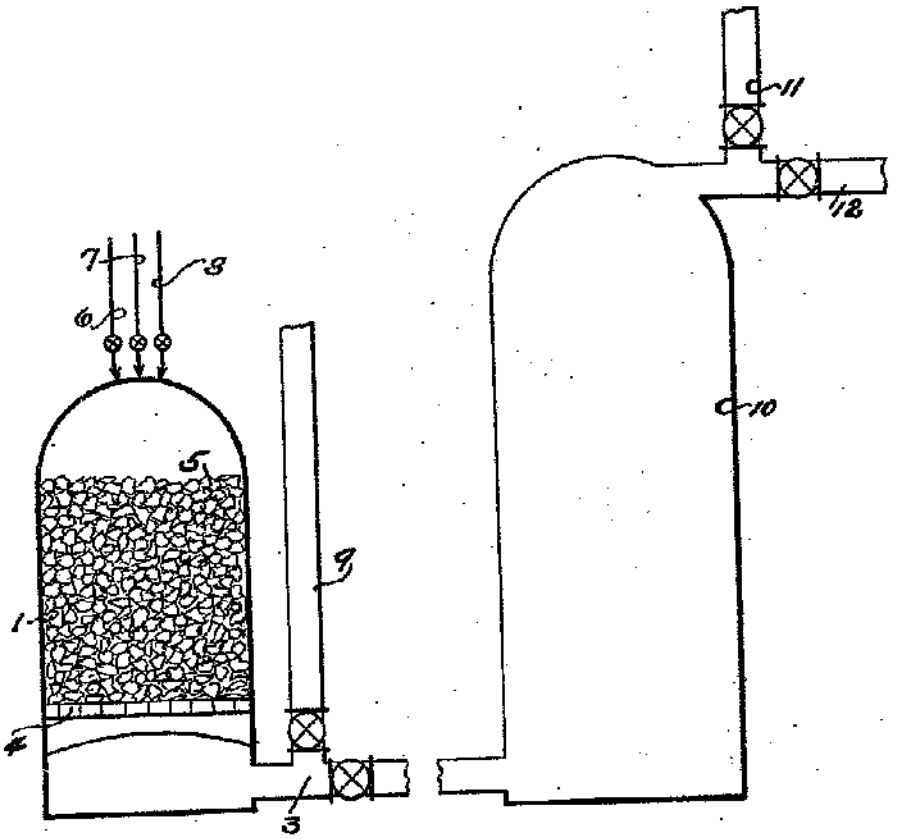

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