

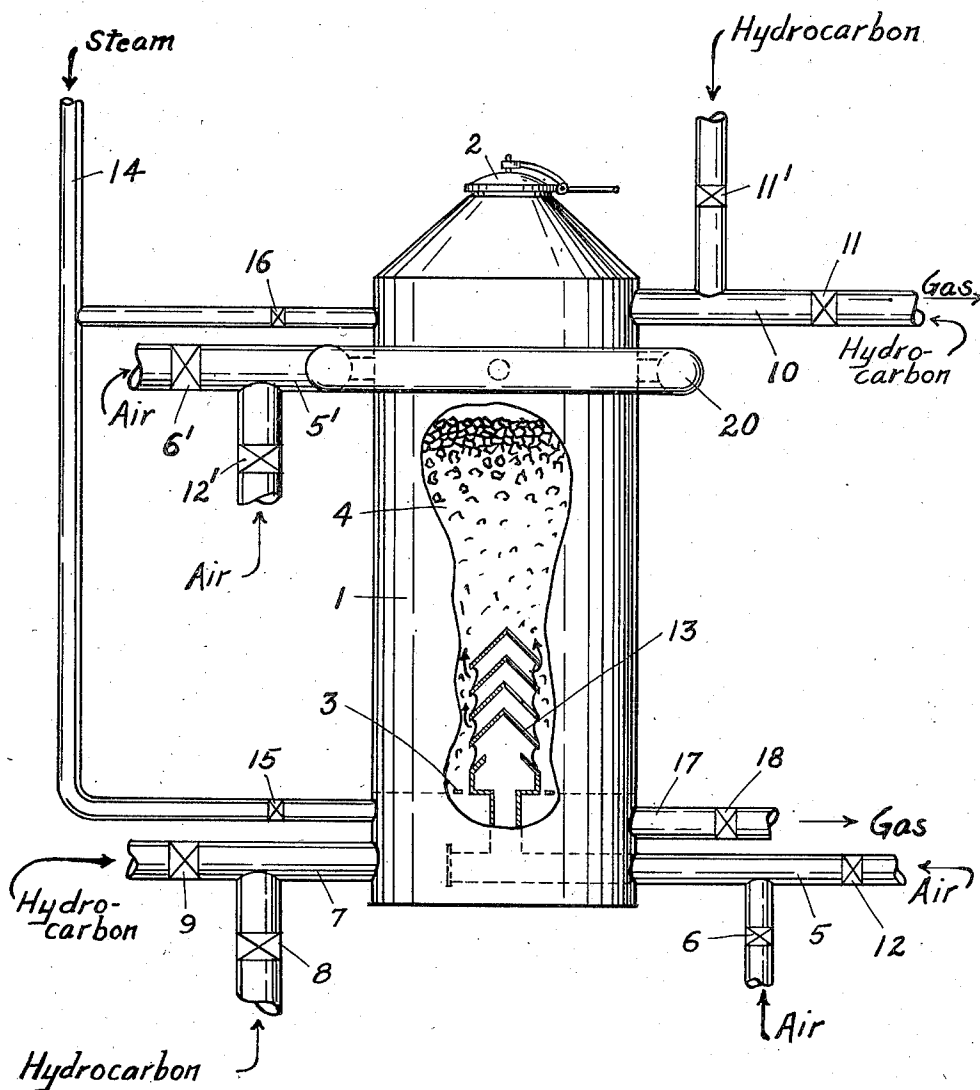
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PROCESS OF MAKING COMBUSTIBLE GAS

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UNITED STATES PATENT OFFICE

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PROCESS OF MAKING COMBUSTIBLE GAS

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16 Claims. (Cl. 48—196)

My invention relates to the re-forming of hydrocarbons, particularly gaseous hydrocarbons, in contact with a heated solid surface such as is afforded by a mass of incandescent solid fuel (a bed of fuel) confined in a generator, using an oxidizing agent of which air is an example, simultaneous with the introduction of a hydrocarbon into said fuel bed, producing gas substantially continuously by reactions, which in the aggregate are normally exothermic.

My invention also relates to the re-forming of hydrocarbon compounds, particularly gaseous hydrocarbons, which are inclusive of natural gas, natural gasoline, petroleum still gases and products therefrom as well as other hydrocarbon compounds. Atomized hydrocarbons may be used in my process with some success, but gases or products completely gasifiable are preferred because they are more completely miscible with other gaseous fluids used in processing. In particular my process has to do with the re-forming of gases by introducing them, along with air or other oxidizing agent, with or without a predetermined and definite relatively small amount of steam into an incandescent mass of solid contact material such as coke, refractory, catalytic material or the equivalent. Coke and carbon are the preferred contact materials under ordinary conditions and are catalytic to the reactions that occur. My process may be conducted in a water-gas generator which may or may not be connected with carbureting chambers. Because it is advantageous to use preheated air, superheated steam and preheated hydrocarbon gas, certain economies are obtainable by the use of a carbureted-water-gas set.

Briefly, my process comprises simultaneously introducing both air and hydrocarbon such as ethylene, propylene, propane, butane, ethane or other gaseous hydrocarbon with or without a small relative amount of steam, into an incandescent bed of solid fuel, the amounts of the gas making fluids being so proportioned that the desired gas-making temperature is maintained in the fuel bed and the operation is substantially continuous.

The objects of this invention include the following:

- (1) Increase the gas-making capacity of a combustible-gas generating-unit.
- (2) Utilize heat liberated in gas-making processes that is frequently wasted.
- (3) Control composition and density of the finished gas.
- (4) To utilize heavy oils or other hydrocar-

bons that are normally used only with difficulty in generating combustible gas.

(5) To use hydrocarbon compounds efficiently even though the ratio of C to H₂ therein is high.

(6) Increase the volume output and control the gas density in making re-formed or enriched re-formed gas.

(7) Make a re-formed gas having a H₂ to CO ratio under control over an appreciable range.

(8) Make gas substantially continuously in a gas generator, the gas made having a calorific value greater than that of producer gas.

(9) Make a gas utilizing a hydrocarbon for stabilizing the calorific value of natural gas.

(10) Make combustible gas in a bed of solid fuel from hydrocarbons without using an appreciable amount of said solid fuel per 1000 cubic feet of gas made.

Other objects will become evident by the following disclosure and claims:

In the dilution of natural gas, natural gas products or other hydrocarbon compound for use in gas-distributing systems, several pertinent factors arise for consideration. The generating equipment for producing the lean or diluent gas should be adaptable for generating other gas such as water gas for example, when the hydrocarbons are not available; the composition of the re-formed gas should approximate that of the lean gas that can readily be made when particular hydrocarbons are not available, particularly with respect to the combustible constituents; the ratio of the per cent of hydrogen in the generated gas to that of the slower-burning gases such as CO and CH₄ should be controlled; and the highest possible generating capacity—output—maintained.

I find that I can control the gas composition, utilize various hydrocarbon compounds and obtain a high generator throughput operating by my process which is or may be substantially continuous. With continuous operation there normally is an appreciable amount of nitrogen in the make gas. However, as a diluent for a large volume of richer gas the nitrogen content is of lesser consequence than otherwise.

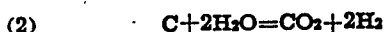
Figure 1 is a diagrammatic front elevation of a generator in which my invention may be practiced. A portion of the generator is cut away in this figure to show the interior in section.

In Figure 1, the generator shell is shown at 1, with a charging door 2 for introducing solid fuel such as coke, carbon or other solid catalyst. Grates for supporting the coke 4 are shown at 3. Supply line for introducing up-run air shown at 55

5 has control valves 6 and 12. The down run air supply line and control valves are shown at 5', 6' and 12'. Intake 7, for introducing up-run hydrocarbon gas has control valves 8 and 9. The down-run hydrocarbon inlet is through the gas offtake and valve 11, or through valve 11' a tuyère is shown at 13 which provides means for bringing air into intimate contact with the hydrocarbon gas in the fuel bed or in the ash beneath the fuel bed. A tuyère is not necessary, but is preferred as a safety measure to avoid the spontaneous ignition of hot gas and air. The steam line 14, has control valves at 15 and 16. An outlet for down-run gas is shown at 17 with control valve 18. Preheated air is introduced through valves 12 and 12' and preheated hydrocarbon gas through valves 8 and 11.

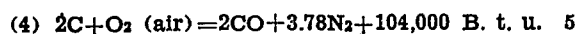
My process comprises the simultaneous injection of a gaseous hydrocarbon steam and air or other oxidizing agent, in substantially definite proportions into an incandescent fuel bed, thereby producing a gas hereinafter referred to as re-formed gas. Before describing the process in more detail, I prefer to show its relation to other processes in common use.

In making ordinary water gas by the typical reaction shown in Equation 1, some of the reaction shown by Equation 2 occurs. The resulting

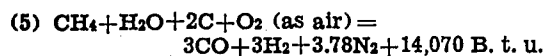


gas has a ratio H_2 to CO of about 1.1. However, in common practice air blast gas is sometimes incorporated in the finished gas resulting in a lowering of the ratio H_2 to CO to 1.0 or even less than 1.0, simultaneously raising the nitrogen content of the generator gas (mixed blue and air-blast gas) to 15 to 32 per cent or more according to conditions. The specific gravity of such mixed gas is appreciably greater than that of ordinary water-gas being commonly within the range 0.60 to 0.70. When this gas is enriched to usual city standards with natural gas or oil gas the resultant gas has a specific gravity not appreciably different from the unenriched gas. In making a re-formed gas as a substitute for, or to be used interchangeably with the described mixed gas in a distributing system it is desirable and in fact essential that the re-formed gas have a composition and density comparable with the substitute gas. Upon enriching the re-formed gas the product obtained will then be substantially the same as the similarly enriched mixed gas (water gas and air blast gas). It is, therefore, one of the objects of this invention to produce re-formed gas having characteristics and properties substantially the same as the water gas containing some blast gas. I not only am able to accomplish this result but have discovered that because of the lesser amount of heat of reaction absorbed in the re-forming process I am able to operate continuously or substantially so. In other words, I find that the amount of air required to make the preferred quality of re-formed gas is sufficient to make the process continuous or substantially so according to the composition of the base gas desired. The proportional amounts of steam, air and hydrocarbon used in the making of the re-formed gas are therefore quite definite, and in using these definite amounts a new result is obtained so far as I am aware. This relation becomes more apparent

by a study of reaction shown in Equations 3, 4 and 5.



By adding (3) and (4) we have:

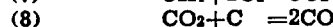
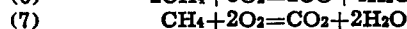
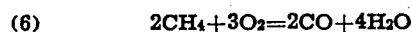


The composition of this theoretical gas is:

	Percent
CO -----	30.7
H ₂ -----	30.7
N ₂ -----	38.6
	100.0

In actual operation there are small amounts of illuminants and methane in the gas, the nitrogen content is somewhat lower and the ratio of H_2 to CO is somewhat higher than shown by the above composition.

The amount of heat liberated in Equation (4) is greater than that absorbed in the reaction shown by Equation (3). By the proper regeneration or by sufficiently superheating the steam and preheating the gas and air the reactions as typified by Equation (5) can be conducted without appreciable loss of heat in the generator during processing. However, under other conditions it is possible to generate gas of an equally low content of nitrogen by making very long runs, only occasionally making straight air-blasts. I find that, when using a moderately fine size fuel such as coke, the pieces of which average 1.5 to 2.0 inches or less in diameter, an amount of hydrocarbon can be used in moderate excess of that shown in Equations (3) and (5), without carrying appreciable amounts of suspended carbon out of the generator entrained in the gas. The benefit derived from this procedure is an increase in the ratio of H_2 to CO in the finished gas accompanied by a decrease in the N_2 content. Simultaneously the generator fuel used per 1000 cubic feet of re-formed gas made is lowered because the carbon that is now evolved by cracking of the hydrocarbon is available as generator fuel. It appears that, when the hydrocarbon and air are admitted in the manner described in the foregoing, reactions such as are indicated by Equations (6), (7) and (8) occur to a certain extent.



Furthermore, when an excess of hydrocarbon is used as referred to above, a further typical reaction is as shown in Equation (9):



The net result of the last four reactions in my process is that appreciably less of the heat required in processing is supplied by burning generator fuel and that a gas having a lower nitrogen content than indicated by the above analysis can be generated without containing appreciable amounts of entrained carbon resulting from pyrolysis of the hydrocarbon. A gas having a nitrogen content approximating 30 to 33 per cent can readily be made. Of course, when the operation is intermittent the relative amount of air used during the gas-making period can be materially reduced, thus reducing the amount of nitrogen

in the make gas. However, since it is preferable to make the operation continuous or substantially so, it is interesting to note that a nitrogen content of about 30.0 to 35 per cent is not appreciably higher than the commonly produced water gas containing air-blast gas.

In the foregoing examples methane has been used as the hydrocarbon; it is to be understood that other hydrocarbons may be similarly used and that similar equations can be written for their reactions with steam and oxygen. Of particular interest is the fact that certain hydrocarbons have negative heat of formation and therefore, behave differently in the process than the paraffin hydrocarbons. The heat of formation of certain hydrocarbons are compared for the purpose of clearness, as follows:

Heat of formation at constant pressure in British thermal units

		Per cu. foot	Per pound
Methane.....	(CH ₄)	+103.1	+2435.6
Ethane.....	(C ₂ H ₆)	+136.0	+1713.6
Propane.....	(C ₃ H ₈)	+167.2	+1436.3
Butane.....	(C ₄ H ₁₀)	+202.2	+1317.3
Ethylene.....	(C ₂ H ₄)	-12.9	-174.2
Propylene.....	(C ₃ H ₆)	+15.3	+138.0
Benzole.....	(C ₆ H ₆)	-47.3	-226.3

The table shows that the heat of reaction in the dissociation of ethylene and benzene is positive, that is, heat is produced during the reaction and that of propylene is negative, but low, whereas the other hydrocarbons shown have a much higher negative heat of dissociation. When using an excess of hydrocarbon in processing as referred to above, it is advantageous to use ethylene, propylene, benzole or similar hydrocarbons for the following reasons:

1. They have lower ignition temperatures than methane, the chief component of natural gas.
2. They crack (dissociate) readily upon being heated and differing from methane do not require contact with heated surfaces for dissociation.
3. They yield a larger quantity of carbon per unit volume of hydrocarbon than methane, and this carbon, up to a certain limit, can be used in the process.
4. Much more reaction and dissociation can be caused to occur before the fuel bed is contacted using these hydrocarbons than when using methane, and lower reaction temperatures are required.

A petroleum refinery gas containing CH₄, with appreciable amounts of C₂H₄ and C₃H₆ are highly satisfactory for use in my process, or ethylene with or without associated gases may be used advantageously.

The mixing of air, oxygen or other oxidizing agent, with hydrocarbon gases is more or less hazardous, even though steam may be present, unless care is used to maintain uniform proportioning. I, therefore, prefer to inject the air with the steam by means that will assure proper proportioning and mixing. The air and steam are preferably heated to a temperature above 1200° F. and approaching 2000° F. and the hydrocarbon may be introduced therein prior to contacting the fuel bed. Under some conditions it is preferable to first mix the steam and gas, heat the mixture to as high a temperature as practicable and then introduce the hydrocarbon into a stream

of the heated mixture prior to contacting the incandescent fuel bed.

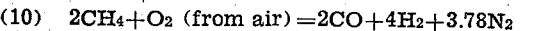
Referring to Equation (5) the relative volumes of methane, air and steam used are approximately and respectively 1.0, 4.8 and 1.0. This means that the mixture at ordinary temperature is too rich in methane to propagate flame. However, when the mixture is heated to 1125° to 1200° F. combustion can occur simultaneously throughout the mixture. In order to avoid a sudden heating of the gaseous mixture due to sudden spontaneous combustion in the generator void space external to the fuel bed, it is desirable to maintain the mixture at a temperature appreciably above 1125° (ignition temperature), or appreciably below it.

When equations are written for butane, for example, similar to (3), (4) and (5) for methane, it is evident that more steam and air are required per volume of butane used, the volume of gas generated being greater, but the nitrogen content of the generated gas is not higher than for methane. The approximate proportions are: butane 1.0 volume, steam 4 volumes, air 14.4 volumes. The proportions of air and butane are similarly outside of the range in which flame propagates through the gas-air mixture at ordinary temperatures. The approximate theoretical gas composition is:

	Per cent
CO.....	32.8
H ₂	30.0
N ₂	37.2
	100.0

In actual operation I find that the nitrogen content is somewhat lower and that some methane and smaller amounts of carbon dioxide and illuminants are present. The proportions of air and butane in the mixture are close to those of the upper-limit mixture which is inflammable. Therefore, this is approximately the minimum amount of butane that should be used, and can be used with safety in ordinary water-gas sets, particularly when supplied beneath the grates and when the temperature may border on the ignition temperature. The optimum relative amount of butane normally used with air is greater than the upper inflammability limit and less than that where it becomes necessary to operate intermittently with short cycles as in ordinary water-gas practice. The optimum amount of steam used is the least that can be used without the generator becoming too hot and without the H₂ to CO ratio becoming too high. Thus with butane, the butane air ratio is preferably greater than 1.0 to 14.4 and not appreciably more than 1.0 to 9.0. The butane : steam ratio usually preferred is within the range 1.0 to 4.0, to 1.0 to 0.0.

Considering the introduction of a mixture of hydrocarbon and air into an incandescent fuel bed or other contact material. The equation typical of the reaction is:



In this reaction heat is evolved (produced) to the extent of approximately 35,000 B. t. u. per 1000 cubic feet of methane processed. When the methane and air are not preheated the heat evolved is represented largely in the sensible heat of the exit gas and steam need not be used. The

composition of this gas, according to Equation (10) is:

CO=20.4 per cent
H₂=40.9 per cent
N₂=38.7 per cent

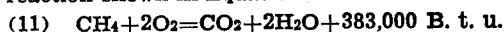
100.0 per cent

In practice the gas usually contains some methane and very small amounts of carbon dioxide and illuminants. The composition is affected by the velocity of flow of the gas-making fluids, the temperature maintained in the generator, kind and size of contact material in generator, etc. It will be noted that solid fuel is not consumed by the reaction shown in Equation (10), and that the methane : air ratio is 2 to 4.78 or 1 to 2.39. The calorific value of the gas thus made, according to the equation is 200 B. t. u. but in actual operation it is somewhat higher than 200 because of the methane present.

The reaction indicated by Equation (10) is exothermic and, therefore, it is obvious that in operation, a state of equilibrium is reached in which substantially all of the heat of reaction appears as sensible heat of the make gas. Using the molecular proportions shown in Equation (10) and without preheating the hydrocarbon and air, the equilibrium temperature will not be high enough to cause the usually desired completion of reaction. It is, therefore, substantially necessary, without regeneration to either add an amount of air in excess of that shown in the equation or to preheat the air and hydrocarbon gas. The temperature of the theoretical gas resulting from Equation (10) as shown, and which has a specific gravity of .60, and a specific heat of about .0180 per cubic foot at 400° F., can be computed from the following equation: Cu. ft. of make gas × specific heat per cu. ft. × temperature rise = B. t. u. By substituting known values in this equation, we have:

$$\frac{9.78}{2} \times .018 \times X = 35 \text{ and therefore } X = 400^\circ \text{ F.}$$

I find that even when starting with a fuel bed heated to a temperature at which the reaction of the equation occurs there is a noticeable drop in the temperature in the fuel bed, some methane passes through the fuel bed without entering into reaction and some carbon dioxide is formed by reaction shown in Equation (11).



When methane and air are mixed in proportions as indicated in Equation (10), at ordinary atmospheric temperature and the mixture is introduced into a hot fuel bed, an equilibrium condition is soon reached, whereby some of both reactions (10) and (11) occur and the temperature is considerably higher than 400° F. In order to reduce the amount of reaction 11 to a minimum and, therefore, reduce the nitrogen content of the gas and simultaneously raise its calorific value, it is desirable to separately preheat the gas and air or to preheat at least one of the two. When the air is preheated to 1200° F. and higher the reaction that occurs is chiefly as indicated by Equation 10, and only a small amount according to Equation 11. In other words at high temperatures the reactions occur whereby CO₂ and H₂O are converted largely into CO and H₂, and an approach to chemical equilibrium results which does not favor Equation 11, particularly when conducted within a fuel bed.

When air and hydrocarbon gas are mixed at a temperature somewhat above ignition tempera-

ture, oxidation of the hydrocarbon occurs with the formation of CO₂, H₂O and some CO; also there is an accompanying cracking reaction (with higher hydrocarbons than methane) whereby hydrogen and carbon are formed. Contact with solid surfaces at high temperature is required for causing appreciable cracking of methane. When the gaseous product containing the CO₂, CO, H₂, C, and more or less hydrocarbon are caused to contact solid surfaces at high temperature equilibrium is rapidly reached whereby the carbon is substantially completely gasified, the CO₂ largely being converted into CO. The reactions involved are as shown in Equations (1), (8) and (3) or the equivalent depending on the hydrocarbon used. These reactions occur particularly well when the contact surface comprises an incandescent fuel bed. For complete re-forming of methane, a temperature approximating 2000° F. or higher is preferred. However, when it is desired to generate a gas containing some hydrocarbons and having a calorific value intermediate those of methane and hydrogen, a lower average temperature may be used.

Because of the narrow limits within which flame will propagate through different cold mixtures of air and hydrocarbon, and the possible danger of preheating such a mixture, under certain conditions, it is sometimes preferable to operate by introducing at least an appreciable part of the air or hydrocarbon into the hydrocarbon gas or its equivalent in the generator directly into or adjacent the highly heated contact mass. Under these conditions if the air and hydrocarbon are not preheated the best results are obtained by operating somewhat intermittently; that is, by alternately making long gas-making runs and relatively short heating runs, herein referred to as air-blasting periods, during which the fuel bed or contact mass is heated. The amount of straight air-blasting employed is much less per 1000 cubic feet of gas made than in the water-gas process even without preheating the air or hydrocarbon used, because the reaction is exothermic, differing from the water-gas reaction which is endothermic.

When air and natural gas comprising largely methane are introduced together at about 70° F. into a bed of incandescent fuel such as coke or carbon, a condition of equilibrium may be obtained in which the temperature approximates 1800° F. and the amounts of reactions (10) and (11) occurring are approximately and respectively, 80 to 85 per cent and 20 to 15 per cent; that is, for every volume of methane reaction according to Equation (11) about four volumes react according to Equation (10). The equilibrium temperature and gas composition vary somewhat according to the initial temperature of the air and natural gas, the size of the particles of solid fuel, condition of the fuel bed, moisture content of the air and gas used and other variables. However, using a clean fuel bed comprised of coke being rather uniformly sized, the average size of the pieces being about 2 inches or less, the composition of gas obtained at said equilibrium was substantially as follows:

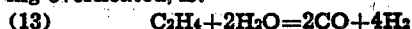
	Per cent by volume
CO ₂ -----	3.5
CO-----	15.3
H ₂ -----	29.6
CH ₄ -----	4.0
N ₂ -----	47.6
Total-----	100.0

Calorific value — 190 B. t. u. per cubic foot. Thus, with methane, in order to lower the nitrogen content of the make gas it is necessary to supply heat to the fuel bed by either preheating the air, preheating the methane, or both, or by making occasional straight air-blasts for the purpose of heating the fuel bed, discharging the blast gas produced separate from the make gas.

It is important to note that when ethylene or propylene, gases commonly present in large amounts in refinery gases, are substituted for natural gas a different heat effect is obtained. Using C_2H_4 for example the equation corresponding to (10) is:



and there is liberated heat equal to about 290 B. t. u. per cubic foot of C_2H_4 reacted. This amount of heat is more than sufficient to raise the temperature of the end products to that necessary in the fuel bed for gas-making purposes. It is therefore possible in this instance to utilize the excess available heat (heat of reaction), by introducing a small amount of steam, thereby making the operation continuous, maintaining suitable temperatures in the fuel mass without burning appreciable amounts of solid fuel and without generating a gas containing appreciable amounts of suspended carbon resulting from the pyrolysis of the hydrocarbon. This permits the production of a gas of lower nitrogen content with a given consumption of fuel than can be produced by similar reactions with saturated hydrocarbons (paraffins). The reaction whereby the generator fuel-bed is cooled, that is, prevented from becoming overheated, is:



whereby 360 B. t. u. are absorbed per cubic foot of C_2H_4 reacted, as heat of reaction, and 0.1128 B. t. u. as sensible heat of the reaction products per degree Fahrenheit above 70 F. per cubic foot of C_2H_4 reacted. I find that there is an optimum amount of steam that can be used economically with C_2H_4 and that there is an optimum amount of reaction (13) which should accompany reaction (12). The combined optimum proportions are about:

C_2H_4	1000 cubic feet of
Steam.....	10.0 to 24.0 pounds
Air.....	3600 to 4200 cubic feet

The approximate yield of gas is about 7200 cubic feet per 1000 cubic feet of C_2H_4 used, varying with the temperature of the steam, air and gas used and other variables. When no steam is used the amount of air used may be appreciably less than 3600 cubic feet per 1000 cubic feet of ethylene. When the air, or ethylene or both are preheated more steam can be used and less air per 1000 cubic feet of ethylene, thus decreasing the nitrogen content and increasing the thermal efficiency. In this case there is a practical working limit. The gases in the example given leave the generator fuel mass at about 1800° F. more than half of the sensible heat of the gases at that temperature can be recovered by counter flow recuperation or regeneration. Thus the optimum amount of air used per 1000 cubic feet of ethylene is 3600 to about 4000 cubic feet for substantially continuous operation.

Petroleum refinery gas which contains appreciable amounts of ethylene and propylene, or of either one, are particularly well adapted to be used in this process and the resulting gas has a lower nitrogen content other things being the

same than when methane, ethane or propane are used; this is true chiefly because of the negative heat of formation of ethylene and the low positive heat of formation of propylene. Without preheating the refinery gas and air or air alone, the amount of steam required or used is substantially zero for ordinary refinery gas; when the air is preheated some steam may advantageously be used.

When oxygen-enriched air is used instead of straight natural air the nitrogen content of the make-gas is still further reduced, the quantities of materials used, gas and oxygen are substantially as indicated by the equations. Similar equations can be written for propane, butane, etc. Because propane, butane and other higher hydrocarbons readily break up into CH_4 , C, H_2 and sometimes other compounds, it is possible to so regulate the proportions of air and hydrocarbon used that an appreciable amount of methane is obtained in the finished gas without proportionally increasing the carbon dioxide content of the re-formed gas.

Referring to Figure 1, I operate as follows: Ignite the carbon or coke 4 and heat the fuel mass by air-blasting it as through 5 and 6. After the mass 4 is well heated the air-blasting for heating purposes alone is not necessary. Hydrocarbon gas is introduced through 7 in controlled amounts relative to the air supply, so that the temperature in the fuel bed is maintained and the CO_2 and N_2 contents of the make gas are minimum. The make gas is removed through offtake 10, above the fuel bed. If the temperature rises, as it will with ethylene, some steam is introduced through 14 and 15 in amounts as given above. The steam increases the yield of gas and is a means of controlling temperature besides lowering the nitrogen content of the make gas. Under these conditions the make gas is removed through 10 and there is a tendency for the hot zone to travel upwardly towards the top. After a period of up-running it is therefore necessary to make a down run in order to maintain high operating and thermal efficiencies. This, I find, is particularly true when the consumption of generator fuel is maintained at or near a minimum; thus the operation differs from that of producer gas practice. The down run is made by shutting off the supply of air and hydrocarbon through 5 and 7 respectively of Figure 1, closing the steam valve 15, and introducing air, hydrocarbon and any necessary steam into the upper portion of the fuel bed as through 5', 10 and 16 of Figure 1; the make gas is now removed from beneath the fuel bed as through 17 instead of offtake 10. The cycle (up and down runs) is repeated at intervals as desired, in maintaining the fuel bed in the desired condition and the temperature of the exit gas at the desired level.

The down run hydrocarbon, or air or both may be introduced directly into the fuel bed instead of into the chamber space directly adjacent (above) the fuel bed. Means for accomplishing this are not shown because it is believed that there is no specific apparatus novelty therein. A tuyère may be used in the upper zone of the fuel bed for making down runs when desired. Under some conditions this may be considered a precautionary step.

In varying the proportions of hydrocarbon, air and steam, I find that the amount of hydrocarbon that can be used relative to the steam, air or both is greater on down runs than on up runs

without the entrainment of carbon or "lamp-black" in the make gas, so long as sufficient air is used to maintain the desired operating temperature in the fuel bed. Accordingly it is sometimes desirable to take advantage of this fact, particularly when it is preferred to make a gas having a relatively low density and having a relatively high content of hydrogen, by introducing a larger relative amount of hydrocarbon on the down runs than on the up runs. Another advantage accruing from this practice is that the increased amount of hydrocarbon makes the mixture above the fuel bed less explosive and, therefore, when the air and hydrocarbon are not preheated and when a tuyere is not used in the upper zone (on down runs) the operation is safer because flame cannot propagate through rich mixtures of gas and air; there is less probability of spontaneous ignition and less pressure developed if such ignition should occur. With this method of operation I am able to keep the top zone of the fuel bed relatively cool and the outlet gas at a lower temperature than otherwise. With this conservation of heat in the fuel bed less preheating is required in order to obtain a given result.

Although the amount of solid fuel used in my process per 1000 cubic feet of gas generated is almost nil when the amounts of air and hydrocarbon, or air, hydrocarbon and steam are properly proportioned to give this result, it is noted that carbon, coke and prepared "carbons" are catalytic to the chemical reactions involved in the generation of gas. Results are attainable using coke or carbon as contact material that are not attainable at the same temperature using ordinary refractory material as a contact medium. A gas containing a minimum amount of carbon dioxide more readily can be made using coke or carbon contact material (carbonaceous contact material) under a given set of conditions.

One of the reasons why the amount of solid fuel used per 1000 cubic feet of gas made is very small, is that the oxygen of the air used can more intimately mix and react with the gas (hydrocarbon) used than with solid carbon. When coke, coal, carbon and similar solid fuels are expensive it is preferable to operate so that the consumption of solid fuel is substantially nil. The carbon used may be an especially activated carbon, or one containing incorporated therewith or thereon a material catalytic to the reactions involved. Nickel, cobalt, with or without alumina are example catalysts that may thus be used.

A waste-heat boiler or other heat-exchange apparatus can be used with high efficiency using my process because it is continuous or at least substantially so thus eliminating one of the annoying features in the use of such equipment that is commonly experienced in the intermittent water-gas process.

One of the uses for which I claim that my process is particularly well adapted is in the stabilizing of the calorific value of natural gas at a standard such as 700, 800, 900 or 1000 B. t. u. by incorporating a lean gas in a richer natural gas in amounts sufficient for the purpose; the lean gas being made by my process, preferably using hydrocarbon gases when they are available at a low price. In this manner the natural gas may be stabilized by using a waste product produced from it, namely, propane, butane, pentane or natural gasoline.

Although the reactions involved in my process are in the aggregate exothermic, it is recognized

that by operating somewhat intermittently a similar result may be obtained at lower efficiency whereby the reactions are slightly endothermic or thermally neutral; the operation in this instance comprising increasing the relative amount of hydrocarbon or steam used or of both, and making occasional straight air-blasts. I prefer to operate with air and hydrocarbon, or the air, steam and hydrocarbon so proportioned that the heat evolved is close to nil. This can only be done when the air or hydrocarbon, or both are preheated, unless the operation is intermittent. Without using preheated gas-making fluids or when they are only slightly heated, I prefer to so operate that the effect of reactions is exothermic, otherwise the operation must be intermittent or appreciable carbon will deposit in the fuel bed.

Somewhat summarily it may be said my process comprises introducing a hydrocarbon, preferably in the gaseous state, into a heated bed of contact material, preferably carbonaceous solid material, simultaneously introducing therein an oxygen-containing gas such as air in amounts usually not greatly in excess of that required to convert the carbon of said hydrocarbon into carbon monoxide, and preferably in amounts not appreciably less than is required to form carbon monoxide by reaction with the hydrocarbon; the hydrocarbon and oxygen-containing gas used are preferably preheated and under conditions as described a relatively small amount of steam is sometimes used simultaneous with the hydrocarbon and oxygen-containing gas. The process is substantially continuous and both up and down runs are made. When the hydrocarbon is used somewhat in excess of that required to form carbon monoxide by reaction with the oxygen it is done preferably on the down runs; similarly when the oxygen used is in excess, the excess is introduced preferably during up runs. In all cases the amount of steam used by volume is much less than that of the air or oxygen-carrying gas.

The rate of flow of the gas-making fluids into the fuel bed and the rate of flow of reaction products through the fuel bed has considerable to do with the composition of the finished gas produced. In other words, a definite amount of time is required to reach the desired equilibrium in the reactions involved; the time required is greater as the temperature in the contact mass decreases and this is particularly noticeable below about 2000° F. With insufficient time of contact, namely, with too high a rate of flow of the gas-making materials, the resultant gas (make gas) contains a higher percentage of carbon dioxide and less carbon monoxide than when more time is allowed. In the operation of my process the time of contact is controlled so as to be compatible with the temperature of the contact surface of the fuel bed; this is accomplished by regulating the rate of flow of the reactants in accordance with the end sought. Under certain conditions the end sought is the formation of maximum amounts of hydrogen and carbon dioxide and a minimum amount of carbon monoxide. In this instance the contact mass is maintained at a lower temperature than otherwise and the rate of flow of reactants is increased. For a given hydrocarbon the optimum rate can readily be determined by experiment using a chosen contact mass. Under this condition if oxygen-enriched air is used instead of normal air, an amount of steam is introduced into the contact mass simultaneous with the hydrocarbon and oxygen to maintain the desired temperature. Be-

cause the amount of solid fuel (generator fuel) used per 1000 cubic feet of gas made is low in my process, the chief fuel being the hydrocarbon used in processing, it is feasible to use prepared fuels, briquetted or otherwise prepared in which a catalyst is incorporated. This is an ideal means of employing a catalyst, namely, in conjunction with a solid fuel. Coke and carbon are catalytic to the reactions involved in my process, but the incorporation therein of a metal or oxide catalyst is beneficial. When a metal oxide or salt is used in the preparation of such a fuel it is largely reduced to the metallic state when the fuel mass is heated to incandescence. This is true of all of the heavy metals commonly used as catalysts with the exception of aluminum compounds.

The gas made in my process differs from that made in other processes, so far as I am aware, in that it does not contain an appreciable amount of unsaturated hydrocarbons commonly referred to as "illuminants". When a temperature approximating 2000° F. is maintained in the fuel bed and natural gas, butane, or natural gasoline is used as "the hydrocarbon gas" the amount of illuminants in the gas made is approximately 0.4 to 1.6 per cent, whereas when the temperature of the fuel-bed hot zone is lower illuminants may be present in somewhat greater amounts. I prefer to operate at the higher temperature because illuminants formed at appreciably lower temperatures contain gum-forming constituents, particularly when the hydrocarbon used has a high molecular weight and a metal catalyst is not employed.

When using a given average amount of oxygen relative to the hydrocarbon used, I find it sometimes is advantageous to use a greater amount on up runs and a lesser amount on down runs. This is an aid in keeping the top of the fuel bed from becoming excessively hot and also is an aid in producing gas free from suspended carbon when using a minimum average amount of oxygen, because the fuel bed functions more efficiently as a filtering medium on down runs than on up runs; it also makes the down-run operation safer when a tuyère is not used in the upper zone of the fuel bed. Using butane, I am able to produce in this manner, a gas comprising hydrogen, carbon monoxide and methane, with only small amounts of carbon dioxide and illuminants; the nitrogen used with the oxygen appears in the finished gas.

Having described my invention, I claim:—

1. Process of making combustible gas having a relatively low calorific value largely from fluid hydrocarbons having a higher calorific value, in repeated cycles, one cycle comprising, first heating a confined porous bed of solid refractory contact material to incandescence by conducting combustion in contact with the surface of said material, then discontinuing the heating operation and making a prolonged gas-making run by introducing into the heated bed at a controlled velocity proportioned definite amounts of steam, air and a fluid hydrocarbon in a fine state of subdivision, causing them to react chemically in said bed forming a gas substantially free from suspended carbon resulting from hydrocarbon decomposition which gas comprises largely carbon monoxide and hydrogen, the volume of air used being greater than the vapor volume of said fluid hydrocarbon but insufficient for the complete combustion of said hydrocarbon, the amount of steam used being less than 1 mole for each carbon atom of said hydrocarbon, said velocity being

lower than that at which appreciable amounts of carbon appear suspended in the generated gas.

2. Process of making combustible gas having a relatively low calorific value largely from hydrocarbons having a higher calorific value, in repeated cycles, one cycle comprising, first heating a porous bed of confined, solid, refractory contact material to incandescence by conducting combustion in contact with the surface of said material, then discontinuing the heating operation and making a prolonged gas-making run by introducing into the heated bed of said material proportioned amounts of steam, air and a volatile liquid hydrocarbon at a controlled low velocity, causing them to react chemically in said bed forming a gas by catalytic action which is substantially free from suspended carbon resulting from hydrocarbon decomposition, said gas comprising largely a mixture of carbon monoxide and hydrogen in which the hydrogen to carbon monoxide ratio is greater than 1 but less than 2, the amount of air used being insufficient for the complete combustion of said hydrocarbon, the amount of steam used being less than 1 mole for each carbon atom of said hydrocarbon, said velocity being lower than that at which said suspended carbon appears in the gas.

3. Process of making combustible gas having a relatively low calorific value partly from solid fuel and partly from hydrocarbons having a higher calorific value, in repeated cycles, one cycle comprising, first heating a confined, ignited bed of solid fuel to incandescence by air-blasting it, then discontinuing the heating operation and making a prolonged gas-making run by introducing into the heated fuel bed proportioned amounts of steam, a fluid hydrocarbon and air, causing them to react chemically in and with said fuel bed forming a gas that is substantially free from suspended carbon resulting from hydrocarbon decomposition comprising largely carbon monoxide and hydrogen, the volume of air introduced being less than that required to cause complete combustion of said hydrocarbon and insufficient to maintain the temperature of said bed high enough for a continuous gas-making run, the amount of steam used being less than 1 mole for each carbon atom of said hydrocarbon, subsequently, repeating the cycle.

4. Process of making combustible gas which gas is substantially free from suspended carbon resulting from hydrocarbon decomposition, comprising, first air-blasting a confined, ignited bed of solid fuel to incandescence, then discontinuing the heating operation, making a prolonged gas-making run by separately introducing into the heated fuel bed definite relative amounts of air, steam and a gaseous hydrocarbon, causing chemical reactions to occur between them and the carbon of the fuel bed forming a gas the combustible components of which comprise largely carbon monoxide and hydrogen with a lesser amount of methane, the amount of said air used being less than 1 atom of oxygen to every carbon atom of said hydrocarbon and less than the minimum amount required to form an explosive mixture with said hydrocarbon, the amount of steam used being less than 1 mole for each atom of said hydrocarbon, and subsequently repeating the cycle.

5. Process of making combustible gas largely from fluid hydrocarbons but in part from solid fuel, comprising, air-blasting a confined, ignited bed of solid fuel to incandescence, discontinuing

the heating operation, making a prolonged gas-making run by introducing into the heated fuel bed air, a gaseous hydrocarbon and a small amount of steam being less than 1 mole for each carbon atom of said hydrocarbon, causing reaction to occur between said steam, hydrocarbon, air and incandescent fuel within the fuel bed forming a gas that is substantially free from suspended carbon resulting from hydrocarbon decomposition in which gas the volume ratio of free hydrogen to carbon monoxide is within the limits 1 to 1, to 2 to 1.

6. Process of making combustible gas largely from fluid hydrocarbons but in part from solid fuel, comprising, first heating a confined, ignited bed of solid fuel to incandescence by air-blasting it, then discontinuing the heating operation and making a prolonged gas-making run by introducing into the heated bed substantially definite amounts of steam, a gaseous hydrocarbon and air, causing them to react chemically within said bed simultaneous with the oxidation of some of said solid fuel forming a gas that is substantially free from suspended carbon resulting from decomposition of said gaseous hydrocarbon in which gas the volume ratio of free hydrogen to carbon monoxide is less than 2 to 1 but greater than 1 to 1, said relative amounts being substantially one volume of hydrocarbon, a lesser amount of steam than one mole for each carbon atom of said hydrocarbon, and sufficient air to preserve the fuel bed temperature sufficiently high to make possible the said prolonged run but insufficient to continuously maintain said bed at a gas-making temperature, subsequently repeating the cycle.

7. Process of making combustible gas in cycles largely from a fluid hydrocarbon having negative heat of formation but in part from solid fuel, comprising, first heating a confined, ignited bed of solid fuel to incandescence by air-blasting it, then discontinuing the heating operation and making a prolonged gas-making run by introducing into the heated bed steam a fluid hydrocarbon having negative heat of formation and an amount of air sufficient to produce said gas substantially free from suspended carbon resulting from hydrocarbon decomposition, which gas comprises hydrogen and carbon monoxide in substantially equal volumes, subsequently repeating the cycle.

8. In the intermittent process of making combustible re-formed gas largely from fluid hydrocarbons but in part from solid fuel by alternately blasting a confined, ignited bed of solid fuel with air and with steam, air and fluid hydrocarbon, in combination the steps, introducing said hydrocarbon into said bed from beneath it and introducing said air into said bed from within said bed.

9. In the intermittent process of making combustible re-formed gas largely from hydrocarbons but in part from solid fuel, by alternately blasting a confined, ignited bed of solid fuel with air and with steam, gaseous hydrocarbon and air, the step introducing definite relative amounts of the reactant fluids during the gas-making run, said relative amounts being substantially 1000 cubic feet of a gaseous olefin, approximately 0.72 to 0.84 as much air as that chemically required to oxidize the carbon of said 1000 cubic feet of olefin to carbon monoxide, and approximately 0.34 as much steam as that chemically required to oxidize all of the carbon of said olefin to carbon monoxide.

10. In the intermittent process of making re-

formed combustible gas largely from fluid hydrocarbons by thermally incompletely oxidizing a fluid hydrocarbon while passing in a stream through a confined incandescent fuel bed, in combination, the steps, introducing an oxygen-containing gas into the incandescent fuel bed in a stream from within said bed, and substantially simultaneously introducing the fluid hydrocarbon and steam from without said bed.

11. In the intermittent process of making re-formed combustible gas largely from fluid hydrocarbons by thermally incompletely oxidizing a fluid hydrocarbon while passing in a stream through a confined incandescent fuel bed, the step, introducing air into the incandescent fuel bed from within said bed while steam and a fluid hydrocarbon are introduced into said bed from without it.

12. In the intermittent process of making re-formed combustible gas largely from a fluid hydrocarbon fuel by thermally incompletely oxidizing said fuel while passing it in a stream through a confined, incandescent, porous bed of refractory solids, in combination, the steps, introducing a fluid hydrocarbon along with steam in a stream into the incandescent bed of solids from without said bed, introducing a stream of air into said bed of heated solids from within said bed, and causing the streams to unite within said bed.

13. In the intermittent process of making re-formed combustible gas largely from a fluid hydrocarbon fuel by thermally incompletely oxidizing said fuel while passing it in a stream through a confined, incandescent, porous bed of refractory solids, in combination, the steps, introducing both a fluid hydrocarbon and steam in a stream into the incandescent bed of solids from without said bed, introducing a stream of air into said bed from within said bed, and causing the streams to unite within said bed.

14. The intermittent process of making combustible re-formed gas largely from fluid hydrocarbons, which gas is substantially free from suspended carbon resulting from hydrocarbon decomposition, comprising, first heating a confined, porous bed of refractory solids to incandescence by promoting combustion in contact with said solids, then discontinuing the heating operation and making a prolonged gas-making run by introducing into the heated bed from without said bed a fluid stream comprising essentially steam and a fluid hydrocarbon while introducing air into said heated bed from within said bed, causing said steam, air and hydrocarbon to react in said heated bed forming said combustible gas, and subsequently repeating the cycle, the amount of air used being sufficient to maintain the necessary gas-making high temperature in said bed substantially throughout said prolonged run but insufficient to make the operation continuous.

15. The intermittent process of making re-formed combustible gas largely from fluid hydrocarbons, which gas is substantially free from suspended carbon resulting from hydrocarbon decomposition, comprising, first heating a confined, porous bed of ignited solid fuel to incandescence by promoting combustion within said bed in contact with said solid fuel, then discontinuing the heating operation and making a prolonged gas-making run by introducing into the heated bed from without said bed a fluid stream comprising essentially steam and a fluid hydrocarbon while introducing air into said bed from within said bed, causing said steam, air and hydrocarbon to react in said heated fuel bed forming said com-

5 bustible gas comprising largely hydrogen and carbon monoxide, the amounts of steam, air and hydrocarbon used being so proportioned that the volumetric ratio of hydrogen to carbon monoxide in said gas is somewhat greater than one but less than two.

10 16. The intermittent process of making reformed combustible gas, which gas is substantially free from suspended carbon resulting from hydrocarbon decomposition, largely from a gaseous hydrocarbon but in part from solid fuel, comprising, first heating a confined, porous bed of ignited solid fuel to incandescence by air-blasting it, then discontinuing the heating operation and making a prolonged gas-making run by introducing into the incandescent fuel bed from

without said bed a stream comprising largely a gaseous hydrocarbon and steam, meanwhile introducing into said bed from within it a stream of air, causing the streams to unite within said incandescent bed and to chemically react with one another, causing a portion of the oxygen of the said air stream to combine chemically with carbon of said fuel bed, withdrawing the gaseous reaction products in the united stream, the amount of air used during said run being sufficient to maintain the high gas-making temperature in said bed for the duration of said run but insufficient for continuously maintaining said bed at said temperature.

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