

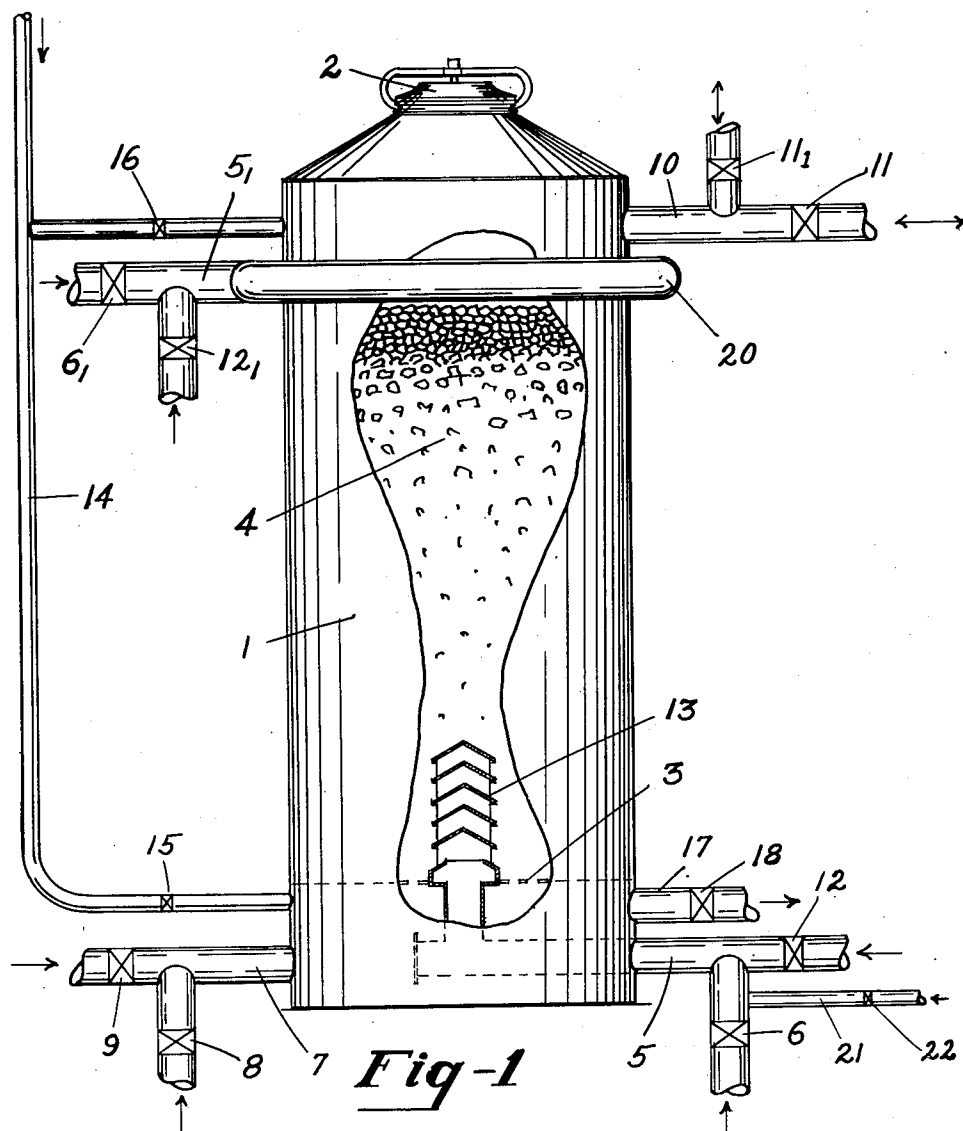
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W. W. ODELL

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PROCESS OF MAKING COMBUSTIBLE GAS

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William W. Odell
INVENTOR.

BY William W. Odell

ATTORNEY.

UNITED STATES PATENT OFFICE

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PROCESS OF MAKING COMBUSTIBLE GAS

William W. Odell, Chicago, Ill.

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7 Claims. (Cl. 48—196)

The process relates to the re-forming of hydrocarbons and the production therefrom of combustible gas having a lower calorific value. It is concerned with the introduction of one or more than one hydrocarbon, along with a relatively quite definite amount of air, into a mass of heated contact material, which may be coke, carbon, a catalyst comprising a metal or metal compound, or a combination of them, and the production of a combustible gas having a low nitrogen content, substantially free from suspended carbon resulting from pyrolysis of said hydrocarbon.

One of the objects of this invention is:

To produce at high thermal efficiency a gas having a low percent of nitrogen, using as a raw material a hydrocarbon compound. Other objects will become evident from the disclosures and claims.

The operation, which may be conducted in a water-gas generator, preferably is intermittent. It comprises heating an ignited bed of solid fuel confined in the generator by air-blasting it, subsequently discontinuing the air-blasting and introducing into the heated mass a hydrocarbon and a quite definite amount of an oxygen-containing gas. The hydrocarbon may be an atomized oil or a gaseous hydrocarbon, and the oxygen-containing gas may be air, an oxygen-enriched air or the equivalent. Although it is evident that a gas can be made by this process having a low calorific value, the combustible constituents comprising chiefly hydrogen with a relatively small amount of carbon monoxide and methane, I prefer to operate in such a manner that the gas generated has a calorific value approximating 400 B. t. u. per cubic foot or higher; 800 B. t. u. is about the upper limit with most gaseous hydrocarbons.

It is known that the hydrocarbons dissociate into their elements when heated to a high temperature in contact with heated surfaces, and that the higher hydrocarbons (those of higher molecular weight than methane) decompose at temperatures lower than that at which methane dissociates. I utilize these principles in my process. I find that at a temperature lower than about 2000° F. methane is not completely decomposed by contact with heated surfaces, even at equilibrium. At about 1300 to 1600° F. the

rate of reaction is very slow; it is possible to pass methane through a fuel bed heated to about these temperatures, at such a velocity that very little dissociation occurs. Moreover higher hydrocarbons dissociate more readily and more rapidly than methane at about these temperatures, yielding methane, hydrogen, some unsaturated and some condensable hydrocarbons. The nature of the surface contacting material (catalyst) has considerable bearing on the amount of unsaturated hydrocarbons formed. The composition of the resulting gas also depends upon the rate of flow of hydrocarbons through the contact mass, temperature of said mass, nature of the hydrocarbon or hydrocarbons used and the amount of oxygen used simultaneously therewith. These variable factors are controlled to give the desired result.

In the treatment of natural-gas products such as pentane, for example, it is sometimes desirable to make a gas having a low nitrogen content, a calorific value of 450 to 600 B. t. u. per cubic foot and recover liquid by products. To accomplish this I proceed as follows: A mass of contact material such as ignited coke, carbon or other carbonaceous material confined in a suitable generator, is heated to a temperature above about 1400° F. but preferably not appreciably above 2000° F. The heating may be done by air-blasting. Subsequently the mass is blasted with the hydrocarbon, preferably preheated, and a relatively definite amount of air. The maximum amount of air used is that required to maintain the temperature in said mass above about 1300° F. and below about 2000° F. The oxygen is most effectively used, with regards to the storing of heat, when the temperature is appreciable below 2000° F., because the equilibrium between CO₂, carbon and CO is then favorable for the formation of CO₂, whereby the maximum amount of heat is liberated per unit volume of oxygen used. Accordingly, it develops that less oxygen is required in operating at the preferred low temperature than at temperatures of 2000° F. and higher. Likewise the higher the temperature of the hydrocarbon used the less the relative amount of air required. I prefer to have the hydrocarbon preheated to about 1000° F., or rather, usually below its ignition temperature. In all instances the amount of air (oxygen)

used is less than that required to form a gas-air mixture in which flame will propagate at ordinary temperatures. Using oxygen-enriched air, the most satisfactory results are obtained when its oxygen concentration is less than 50 per cent and preferably less than about 40 per cent. In the re-forming of the pentane heat is absorbed, the reaction being endothermic, and there is formed, hydrogen and methane with smaller amounts of carbon monoxide and ethane if the temperature is close to 2000° F. but at the preferred lower temperature 1300° F. to 1600° F., the gas contains hydrogen, methane, ethane, carbon dioxide and some unsaturated hydrocarbons; the carbon, which would normally be evolved without the use of air or oxygen, is largely consumed in the process forming carbon dioxide and liberating heat. After the fuel bed has cooled below the desired gas-making temperature the cycle is repeated.

It is noted that when the hydrocarbon is preheated, low operating temperatures are maintained and both (alternate) up and down runs are made the run period may be long relative to the air-blasting period. The amount of heat energy required to completely dissociate a given hydrocarbon into its elements is or may be much greater than that required to crack it into hydrocarbons of lower molecular weight. Likewise, the cracking of hydrocarbons having moderate to high molecular weights occurs at a lower temperature than that required for complete dissociation. Thus by operating at the lowest possible temperature and by preheating the hydrocarbon used to a temperature as high as feasible less heat energy is required per unit volume of hydrocarbon treated. The gas thus made has a higher calorific value than that produced at higher temperatures; this is the result commonly sought.

I find that certain metal catalysts such as chromium, and copper aid in the conversion of hydrocarbons at low temperatures into hydrocarbons having lower molecular weight. Other materials, chiefly metals, or metal compounds, are also catalytic to the reactions, and aid in reaching equilibrium at relatively low temperatures. By the use of a metal catalyst such as chromium, in conjunction with a fuel bed, and causing the hydrocarbon higher than methane under superatmospheric pressure to contact the fuel and catalyst at a temperature above 1300° but below about 1700° F. the percentage of unsaturates (largely olefins) in the resultant gas is higher than is obtained at atmospheric pressure. At high pressure and with a high rate of flow of hydrocarbon contacting the catalyst a very high yield of unsaturates can be obtained. This, I find, is an economical method of producing unsaturates from saturated hydrocarbons or from unsaturates having high molecular weight. Chromium, copper, alloys or similar catalyst may be used to promote these reactions and, differing from many catalytic processes, it is not necessary for the catalyst to be in a fine state of division to obtain commercial yields; the surface may be provided by employing pellets or balls of the alloy. A larger quantity of catalyst is thus required than when it is used in a fine state of subdivision but it is more readily adapted for use in a fuel bed than the subdivided catalyst. So far as I am aware this process of making unsaturates offers the simplest method of utilizing in the process the

carbon normally liberated by the reactions involved.

I prefer not to limit my process to the particular method of primary heating hereinbefore described, namely, by air-blasting. Any known means of heating may be used, such as electrical, or the combustion of gases in contact with the fuel bed. In order to reduce the amount of solid generator fuel (contact mass) consumed during the primary heating stage to a minimum, a gaseous fuel can advantageously be used during primary heating.

When sufficient catalyst (chromium or chromium alloy containing copper) is used the time of contact required to obtain the optimum yield of unsaturates varies from less than one second at about 1650° F. to several seconds at 1300° F. The nature of the catalyst, nature of the surface of the solid fuel used, and the character of the hydrocarbon used, as well as the temperature, are factors that are related to the time of contact required to obtain high yields of unsaturates. Using pentane, about 0.7 to 0.8 second time of contact with the catalyst contact-mass at about 1650° F. was sufficient to obtain a satisfactory yield of propylene and butylene. At a longer time of contact or at higher temperature, or both, less butylene is formed and appreciable amounts of ethylene are formed. The relative amounts of ethylene and higher olefins formed can be controlled by adjusting the rate of flow of reactants, the temperature and the composition of the catalyst. The higher temperatures and longer time of contact favor the production of the hydrocarbons of lower molecular weight; contrariwise, the lower temperatures and high velocities of flow are favorable to the formation of the hydrocarbons having a higher molecular weight than ethylene. High pressure is favorable to the formation of unsaturates.

I do not limit myself to a particular apparatus in the practice of my invention because various types of gas producers and water-gas sets may be equipped for the purpose. Nevertheless the figure is presented for the purpose of illustrating one means of practicing my invention.

The figure is an elevation of a gas generator with a portion of the wall cut away to show the interior in section; the drawing is somewhat diagrammatic, connections for air, gas and steam are clearly shown.

In the figure, the generator is shown at 1, with fuel charging door 2, grate 3, fuel bed 4, inlet 5 for air, gas, steam or a combination of 2 or more of them, valve 6 for controlling the air, valve 12 for controlling the gas, valve 22 controlling the steam, entering generator through 5; the lower outlet for generated gas 17 has control valve 18. A tuyère 13, shown diagrammatically, is adapted to receive the fluids admitted through 5. Another connection for admitting air and gas at base of generator is shown at 7, the valves for controlling the respective fluids are 8 and 9. Steam line 14 has control valves 15 and 16 for controlling the flow of steam to the generator. An upper gas offtake 10 is provided for removing generated gas from above the fuel bed through 11 or 11_i. The valves 11 and 11_i may also be used for introducing air and hydrocarbon gas to the generator when the generated gas is being removed from beneath the grate. A bustle pipe 20 is provided for admitting air and gas to the generator above the fuel bed, the air being

introduced to the latter pipe through 6₁ and 5₁, the gas through 12₁ and 5₁.

Various combinations or operating cycles can be practiced by the proper manipulation of valves after the fuel 4 is kindled. An example is given, referring to the drawing, as follows:

The ignited fuel 4 is air-blasted by opening valve 8, removing the blast gas through 10 and 11. After the desired temperature is reached in the bed, as herein described, the air valve 8 is closed and valves 6 and 12 are opened to admit the described amounts of air and hydrocarbon or other gaseous fuel through 5 and tuyère 13, removing the generated gas through 11. Additional amounts of air, hydrocarbon, steam or combinations of them may also be admitted to generator through 8, 9 and 15. After a period the gas-making run is discontinued and the fuel bed is again heated by air-blasting it from beneath or from above it after which a down run is made by introducing the air and gas through 6₁ and 12₁ and bustle pipe 20 into generator; the gas in this instance is removed through 17 and 18.

An alternative method of introducing air and gas into the fuel bed is to introduce one of them through the tuyère 13 and the other through the grate by opening valves 6 and 9 or 12 and 8.

Although the figure portrays only a generator and the pipe connections it may be operated in conjunction with checker chambers such as are used with carbureted water gas sets or with other heat-exchange devices or catalyst chambers; these devices are not of themselves claimed as patentably new and are not shown. The generator may be connected in series with another similar generator. Means for preheating the gas-making fluids are not shown because they are not claimed by me to be patentably new.

When refractory material or other non-combustible catalyst is substituted for the fuel bed 4 of the figure, the heating of the mass is accomplished by burning the fluid fuel in contact therewith instead of blasting it with air alone.

It has been shown that I prefer to operate by my process intermittently for the purpose of limiting the relative amount of oxygen used in processing. However, I find that I can operate continuously, or substantially so, by externally heating a mass of contact material, for example coke, confined in a chamber such as a pipe, or in a plurality of pipes, by a known method, and introducing the hydrocarbon into said contact mass at a controlled rate with a small amount of an oxygen-carrying gas. Thus the heat supplied to conduct the operation is derived from two sources, namely from the external heating, and from the internal heating or combustion. In attempting to make this process continuous by the application of external heat only to tubes containing the coke (tubes confined in a furnace) I found that the tubes sometimes became heated to a temperature at which it is dangerous to employ high internal pressures. By a combination of internal and external (simultaneous) heating, excessive temperatures are avoided and a minimum amount of oxygen is required, the hydrocarbon and the air may be preheated by the sensible heat of the effluent gases by employing suitable heat exchange apparatus. This application is confined to process only and therefore apparatus illustrations are not presented;

it is believed that one skilled in the art can understand and practice the invention without the aid of illustrations.

A very high yield of condensable, valuable products are obtained by passing the hydrocarbon and reaction products serially through a plurality of confined, heated masses of contact material, maintaining a high temperature and pressure (about 1800° F. and superatmospheric pressure) during contact with the first mass of said series, maintaining the reactants at a lower temperature (800° to about 1650° F.) during contact with subsequent masses. The pressure may be appreciably lower during the latter phase of operation, particularly when catalysts are employed. The rate of flow of fluids should be higher through the first mass of the series than through subsequent masses. The sensible heat of the effluent gases from the first mass is sufficient to maintain the desired temperature in the subsequent masses provided the pressure drop is not too great, thus external heating or internal heating is not necessary for any but the first mass. During the first stage of the gas-making run, that is, during contact with the first mass in the series, both unsaturates and hydrogen are formed, subsequently hydrogenation and some polymerization occurs yielding condensable products some of which are suitable for use as motor fuel. The nature of the end products formed in the high pressure stage vary according to: the character of the hydrocarbon initially used, temperature, pressure and rate of flow of the fluids in the different stages, as well as according to the nature of the contact surface and catalyst employed. Splendid results are obtained using chromium, copper or a chromium alloy in the portion of the catalyst mass to be contacted by the gas stream first, preferably in conjunction with a solid fuel, and nickel, phosphoric acid, metal phosphates, cobalt or other particular catalyst in a subsequent stage. When phosphates, phosphoric acid or alumina are thus used as or in the contact mass it is commonly advantageous to introduce some steam into the fluid stream prior to its contact therewith, that is, subsequent to its passage through the first contact mass of the series. Oxygen is admitted to the system preferably in the first stage only. When steam is used as described, the readily condensable end products may comprise a mixture of a hydration product of an unsaturate, a hydrogenation product and a polymerization product of an unsaturate.

Although it is recognized that high pressures favor the maximum production of polymerization products and hydrogenation products, I find that at moderate pressures it is possible, with the aid of a catalyst, to polymerize and to hydrogenate the gum-forming and resin-forming unsaturates and other unsaturates having high molecular weights. In this manner it is possible to a certain extent to purify the gas substantially during its generation, making useful products therefrom. Although, in the production of a gas containing appreciable amounts of unsaturated hydrocarbons it is necessary to operate with temperatures in the fuel bed favorable for the formation of certain unsaturated hydrocarbons that slowly form gums and resins in the gas, these compounds are largely, or entirely removed by exposure, particularly under pressure greater than atmospheric, to the action of a suitable catalyst at a temperature below

about 1650° F. and preferably somewhat higher than 800° F.

The contact mass or masses used in my process may be solids that are strictly catalysts, solids containing catalysts or largely carbonaceous material. However, benefits are derived from using coke, charcoal, or active carbon such as carbonized peach pits, particularly in the first of a plurality of masses used in series. Not only does the carbon aid in the pyrolysis of hydrocarbons, but it is an ideal filtering medium for carbon particles suspended in gas; it is also a fuel which can be used to a limited, controlled extent in the process. Coke is a good contact material; coke containing a catalyst such as copper, chromium or both incorporated therein is an excellent material for the purpose. Briquets containing catalytic material incorporated therein are satisfactory.

Gaseous hydrocarbons lend themselves more readily than heavy liquid hydrocarbons to treatment by my process in making gas substantially free from suspended carbon, using a minimum amount of oxygen during the gas-making period.

A more specific example of the operation and results obtainable with my process is presented, with reference to the processing of butane as follows: Referring to the figure, and considering that the contact mass 4 is comprised of alumina and/or aluminum phosphate, gas and air are admitted to generator 1 through valves 9 and 8 respectively and combustion of the gas is promoted in the mass 4, and the combustion products are removed through offtake 10 and valve 11. After the mass is heated to approximately 1300° Fahrenheit valves 8 and 9 are closed and the gaseous butane is introduced into the heated mass under superatmospheric pressure by opening valve 12; valve 6 is also opened to let some air also under superatmospheric pressure into the gas (butane) stream. The butane and air are mixed in the stream leading to the tuyère 13 and the mixture is introduced through the tuyère into the heated mass 4. The pressure in the generator during the gas-making period is approximately 1 to 5 pounds gage. In this example 100 volumes of butane gas are mixed with 30 volumes of air and the amount of gas generated is 260 volumes having a composition substantially as follows:

Composition, calorific value and specific gravity of the generated gas

Per cent by volume	
Carbon dioxide	1.7
Carbon monoxide	1.7
Hydrogen	14.2
Methane	20.2
Ethylene	26.3
Ethane	3.8
Propylene	19.1
Propane	3.8
Nitrogen	9.2
Total	100.0
Specific gravity	0.880
Calorific value	1285
B. t. u. per cubic foot	

At a somewhat higher temperature the higher hydrocarbons, namely propane, propylene and ethane in this example, are pyrolyzed yielding a larger volume of gas having a lower specific gravity and a lower calorific value. More air

is required under these conditions to produce a gas substantially free from suspended carbon resulting from pyrolysis of the hydrocarbons. The heating operation may be accomplished in 2 to 4 minutes and the gas-making run is about 8 to 20 minutes, being adjusted so that the time of contact of the gas stream with the heated mass is approximately 3 seconds or slightly less than 3 seconds.

The following is an example of the results obtained operating similarly as in the foregoing example except that the temperature in the contact mass in this case is approximately 1450° Fahrenheit at the start of the gas-making run and 100 volumes of butane gas were used along with 80 volumes of air. The yield of combustible gas was 365 volumes having a composition substantially as follows:

Composition, specific gravity and calorific value of the generated gas

Per cent by volume	
Carbon dioxide	2.5
Carbon monoxide	7.7
Hydrogen	14.0
Methane	24.5
Ethylene	30.2
Ethane	1.6
Hydrocarbons of higher molecular weight	2.5
Nitrogen	17.0
Total	100.0
Specific gravity	0.767
Calorific value	885
B. t. u. per cubic foot	

In this case a little more than half of the heat required to make the operation continuous is supplied by the exothermic reactions involving the oxygen used with the butane. The heating operation is accomplished in approximately 2 minutes whereas the gas-making run is 10 to 15 minutes in length when the reactants are not preheated; however a very much longer run can be made when the reactants are preheated before introducing them into the heated mass in the generator. A duration of contact of the reactant stream with the contact mass is of the order of 2 seconds. The composition of the gas varies somewhat as the duration of exposure to heat increases; the longer the exposure the more complete is the pyrolysis.

Employing 100 volumes of butane with 90 volumes of air, operating substantially as in the foregoing example, the calorific value of the resulting gas is somewhat less than 800 B. t. u. per cubic foot, the amount of ethylene in the gas is less and the amount of hydrogen greater than in the above analyses.

An example of operation and results obtained using both air and steam is as follows: Proceeding as in the foregoing example, 100 cubic feet of butane gas are introduced into the contact mass heated approximately to 1500° to 1600° Fahrenheit along with 98 cubic feet of air and two pounds of steam under superatmospheric pressure of the order of 1 to 5 pounds gage. With a duration of contact of the reactant stream with the contact mass of approximately 2.5 seconds the yield of gaseous reaction products—generated gas—is 740 cubic feet having a composition substantially as follows:

*Composition, specific gravity and calorific value
of the generated gas*

	Per cent by volume	
5 Carbon dioxide.....	2.0	
Carbon monoxide.....	8.0	
Hydrogen.....	50.4	
Methane.....	11.4	
Ethylene.....	15.3	
10 Ethane.....	.7	
Hydrocarbons having greater molecular weight than ethane.....	.2	
Nitrogen.....	12.0	
Total.....	100.0	
15 Specific gravity.....	0.483	
Calorific value.....	560	
	B. t. u. per cubic foot	

20 It will be noted that the amount of air used during the gas-making run is insufficient to react completely with all of the butane and is also insufficient to make the operation continuous. The amount of steam used is insufficient to react chemically with all of the butane. The gas-making run is discontinued after the temperature of the contact mass has fallen below a satisfactory gas-making temperature; in this example the lower limit is about 1300° Fahrenheit. Even though insufficient air is used to make the operation continuous it is possible to make long gas-making runs because the air used is sufficient to prevent the sudden cooling of the outer surfaces of the elements comprising the contact mass below the temperature of the inner portions. The duration of the run in this example is 10 to 15 minutes; it may be appreciably longer if the air and butane are preheated before they are introduced into the heated contact material.

40 Similar results are obtained at higher pressures, 50 to 200 pounds gage, or more, the chief difference being that as the pressure is increased the per cent of hydrogen decreases, the olefin content increases, the amount of readily condensable reaction products increases and the volume of gas produced is somewhat less than in the foregoing example. At 200 pounds gage pressure more than 2 gallons of condensate, liquid at atmospheric pressure and 60° Fahrenheit, are obtained per 1,000 cubic feet of butane gas processed.

50 When a mass of solid fuel such as coke is used as the contact material with or without an added catalyst, the procedure is much the same as in the foregoing; however it is commonly preferable to promote combustion in the fuel mass by air-blasting it without the simultaneous addition of gaseous fuel as was used in the foregoing examples. When operating at low temperatures, 800° to 1300° Fahrenheit it is necessary to use other fuel than the coke as a heating medium because the ignition temperature of the coke is usually high; at higher temperatures, 1300° to 1700° Fahrenheit, the gaseous fuel need not be used unless it is desirable to preserve the coke mass because of the catalyst thereon or for other reasons.

70 Employing a coke bed as a contact mass, an example of operation is as follows: Heat the mass to approximately 1300° to 1600° Fahrenheit by promoting combustion within said mass for a brief period, about 2 minutes, discontinue the heating operation, introduce in a stream both a gaseous hydrocarbon, in this example propane, and air into the heated mass at a rate

adapted to allow the gases of said stream about 2 seconds time of contact with said mass as the stream passes therethrough. The pressure in the generator during the gas-making period is 1 to 2 pounds gage. The amount of air used per 100 cubic feet of propane gas is 60 cubic feet and the yield of gas is approximately 310 cubic feet per 100 cubic feet of propane used. A long run of about 10 to 12 minutes is made. The generated gas has a composition substantially as follows:

*Composition, specific gravity and calorific value
of the generated gas*

	Per cent by volume	
Carbon dioxide.....	2.5	
Carbon monoxide.....	8.0	
Hydrogen.....	20.4	
Methane.....	25.5	
Ethylene.....	16.3	
Ethane.....	5.3	
Hydrocarbons having greater molecular weight than ethane.....	1.0	
Nitrogen.....	21.0	
Total.....	100.0	
Specific gravity.....	0.696	
Calorific value.....	698	
	B. t. u. per cubic foot	

Employing a somewhat larger relative amount of air the hydrogen content and gas yield increase and the per cent of ethylene and ethane decrease but the nitrogen content does not appreciably increase.

By "gas of low nitrogen content" is meant gas that does not contain appreciably more than 21 per cent of nitrogen.

Before presenting my claims, I refer to some possible uses for my process with the intent to clarify the purpose of my invention. I find that large quantities of propane butane, petroleum still gases and similar gaseous products are being wasted in locations where there is a demand for gas having a lower calorific value, lower density and different burning characteristics. These gases I propose to use without installing large steam-generating boilers, as hereinbefore described. In distributing mixed gas it is desirable at certain times in the year (for example when large volumes of natural gas are available) to make a rather lean gas by my process, namely about 400 to 450 B. t. u. gas, whereas at other seasons of the year it is desirable to produce a gas for mixing having a higher calorific value and a larger percentage of hydrocarbons; this condition is met by merely changing the operating temperature and proceeding as outlined above. Thus the hydrocarbons in the re-formed gas may comprise merely methane, or methane, ethane and ethylene or these and still higher hydrocarbons.

Having described my invention I claim:

1. Process of making combustible gas having a calorific value greater than 400 B. t. u. per cubic foot, comprising, heating a confined, porous bed of solid fuel to a temperature of 1300° to 1650° Fahrenheit by promoting combustion within said bed, discontinuing the heating operation, introducing into the heated bed a stream of substantially gaseous hydrocarbon and sufficient combustion-supporting gaseous fluid to prevent the formation of substantial amounts of carbon black by pyrolysis of said hydrocarbon but insufficient to continuously maintain said tem-

perature in said bed, thereby forming said combustible gas.

2. The intermittent process of making low-nitrogen-content combustible gas having a calorific value greater than 400 B. t. u. per cubic foot, comprising, heating a confined, porous bed of solid, refractory contact material comprising a metal catalyst to a temperature of about 1300° to 1650° Fahrenheit by promoting combustion within said bed, discontinuing the heating operation, then introducing into said bed a stream of a substantially gaseous hydrocarbon and sufficient air to prevent the formation of substantial amounts of free carbon black by pyrolysis of said hydrocarbon but insufficient to continuously maintain said temperature in said bed, thereby forming said combustible gas, and subsequently repeating the cycle.

3. Process of making combustible gas having a calorific value greater than 400 B. t. u. per cubic foot, comprising, heating a confined, porous bed of solid contact material comprising solid fuel to a temperature of approximately 1300° to 1650° Fahrenheit by promoting combustion within said bed, discontinuing the heating operation, introducing into the heated bed a stream of substantially gaseous hydrocarbons chiefly those having a greater molecular weight than that of ethylene with a lesser definite amount of a combustion-supporting gas thereby forming said combustible gas largely by pyrolysis of said hydrocarbons, and repeating the cycle, said definite amount of combustion-supporting gas being sufficient to prevent the liberation in the gas stream of substantial amounts of carbon black by hydrocarbon pyrolysis but insufficient for continuously maintaining said temperature in said bed.

4. Process of making low-nitrogen-content combustible gas having a calorific value greater than 400 B. t. u. per cubic foot largely by pyrolytic reaction, comprising, heating a porous bed of solid, refractory contact material to a temperature of approximately 1300° to 1650° Fahrenheit by promoting combustion within said bed, discontinuing the heating operation, introducing into the heated bed a stream of substantially gaseous hydrocarbons having a greater molecular weight than that of methane and sufficient air to prevent the liberation in said stream of substantial amounts of carbon black resulting from hydrocarbon pyrolysis but insufficient to continuously maintain said temperature in said bed, thereby forming said combustible gas, and repeating the cycle.

5. Process of intermittently making combustible gas having a calorific value greater than 400 B. t. u. per cubic foot of low nitrogen content largely from hydrocarbons having a greater molecular weight than that of methane, comprising, heating a confined, porous bed of solid fuel to a temperature approximating 1300° to 1650°

Fahrenheit by promoting combustion within said bed for a brief period, discontinuing the heating operation, introducing into the heated bed for a relatively long period a substantially gaseous hydrocarbon having a greater molecular weight than 16 and a lesser definite amount of a combustion-supporting gas mixed in a common stream thereby generating said combustible gas having a low nitrogen content largely by pyrolysis but in part by exothermic reactions, the amount of said combustion-supporting gas used being insufficient to continuously maintain said bed at the gas-making temperature but sufficient to maintain it at the latter temperature for a prolonged gas-making run, subsequently repeating the cycle.

6. The intermittent process of making combustible gas having a calorific value greater than 400 B. t. u. per cubic foot from petroleum refinery gas having a relatively high calorific value, comprising, heating a confined, porous mass of solid fuel to a temperature of about 1300° to 1650° Fahrenheit by promoting combustion within said mass for a brief period, discontinuing the heating operation, introducing into the heated mass for an appreciably longer time a stream of said refinery gas and a definite amount of air, thereby causing incomplete pyrolysis of the hydrocarbons initially present in said refinery gas, forming said combustible gas substantially free from suspended carbon black resulting from pyrolysis and subsequently repeating the cycle, said definite amount of air being insufficient to continuously maintain said mass at said temperature but sufficient to prevent the liberation in said stream of substantial amounts of carbon black by hydrocarbon pyrolysis.

7. The intermittent process of making combustible gas of low nitrogen content which gas is substantially free from suspended carbon resulting from hydrocarbon pyrolysis, comprising, heating a confined porous mass of solids comprised essentially of carbonaceous fuel to a temperature of 1300° to 1650° Fahrenheit by promoting combustion within said mass, discontinuing the heating operation and then simultaneously introducing into said mass for a prolonged gas-making run a gaseous hydrocarbon having a greater molecular weight than 16 and a gas containing an amount of free oxygen insufficient to continuously maintain said mass at the aforesaid temperature but sufficient to make a gas-making run of long duration relative to the duration of the heating period being less than that required to form a gas-oxygen mixture that will propagate flame at ordinary atmospheric temperature, thereby forming said combustible gas.

WILLIAM W. ODELL.