

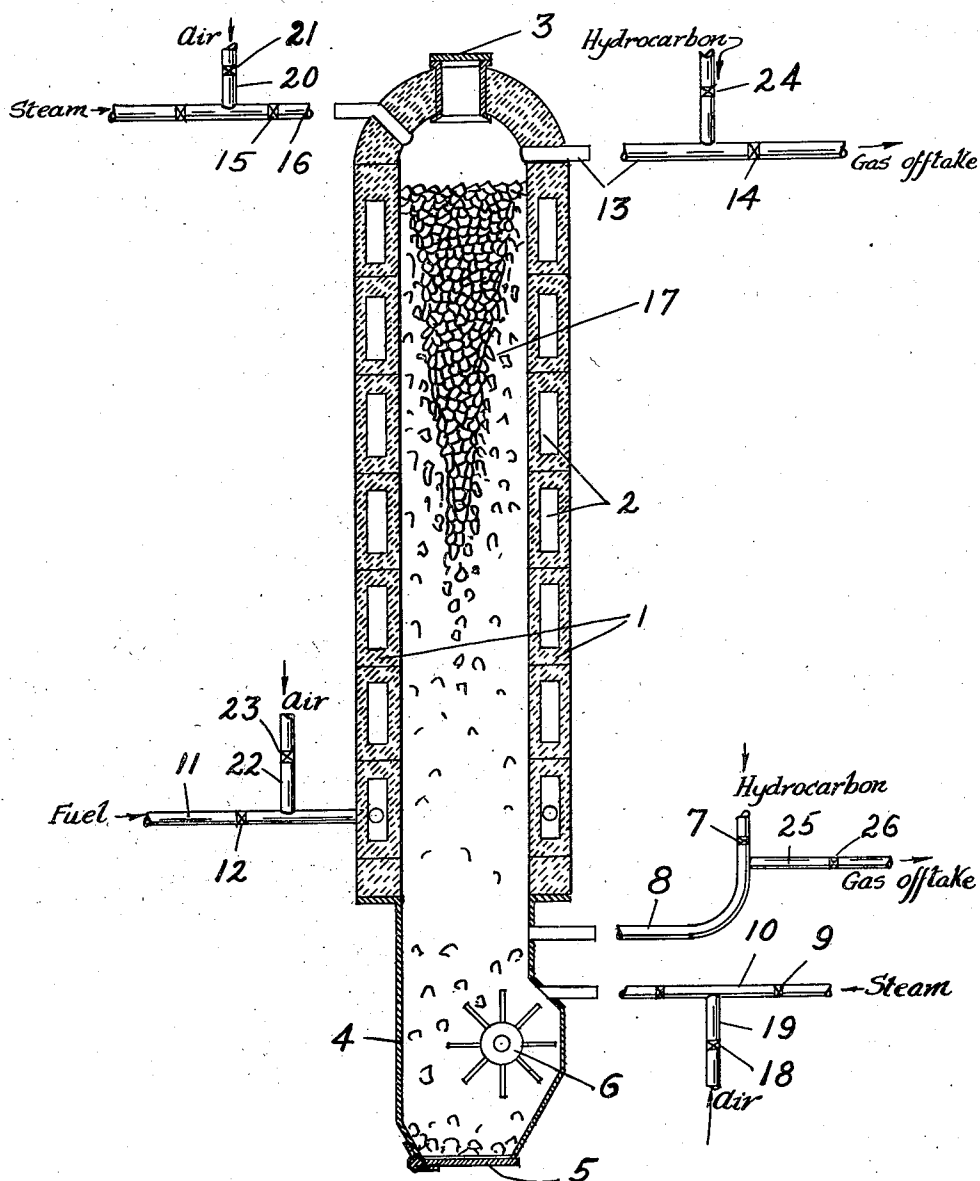
July 31, 1934.

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1,968,053

PROCESS OF MAKING COKE AND COMBUSTIBLE GAS

Filed Nov. 1, 1930



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UNITED STATES PATENT OFFICE

1,968,053

PROCESS OF MAKING COKE AND
COMBUSTIBLE GAS

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Application November 1, 1930, Serial No. 492,870

6 Claims. (Cl. 202-23)

My process relates to the method of increasing the gas making capacity of a coal carbonizing unit by causing reactions to occur between steam and hydrocarbons prior to and simultaneous with the cooling of the carbonized product which is usually coke. The reactions are caused to occur in the presence of incandescent carbonaceous material. The objects of this invention are:

1. To increase the gas making capacity of a coal carbonizing unit, such as vertical retorts.

2. Produce low-density gas having a high hydrogen content.

3. Make possible the more flexible use of a coal carbonizing unit in generating manufactured gas.

4. Cool the coke made simultaneous with the generation of gas by reactions which yield a greater volume of gas per unit of available heat stored in the coke mass.

5. Use hydrocarbon gases and hydrocarbon mists in a supplementary method of making gas in coal carbonizers.

The other objects will become apparent from the disclosures made herein.

I have shown in my Patent No. 1,762,100, issued June 3, 1930, that hydrocarbons react with steam in the presence of heated solids, forming carbon monoxide and hydrogen. In this instance I believe I have an invention in which particularly high efficiencies are obtained in the production of reaction products. For example, considering the carbonizing unit to comprise vertical retorts, it is common practice to steam the retorts after the carbonization is substantially complete, that is, steam is introduced preferably in the base of the mass of incandescent coke and passed upwardly therethrough. In passing through the hot coke chemical reaction occurs whereby carbon monoxide and hydrogen are formed by the well known water gas reaction which is endothermic, and the coke is simultaneously cooled. I find that by substituting a gaseous hydrocarbon or a very finely atomized hydrocarbon for a portion of the steam, and particularly during the early stage of the steaming operation, a larger yield of gas is obtained than when steam is used alone. The explanation of this result is to be found in the fact that less heat is required as heat of reaction in the formation of gas by the hydrocarbon reaction with steam than by the reaction of steam with carbon. I find, further, that with straight steaming the resultant mixed gas has a higher specific gravity than the ordinary coke-oven gas from coking coal, whereas when a hydrocarbon is employed along with steam as a cooling medium the resultant mixed gas has a specific gravity nearer

to that of the coke oven gas. This invention differs from the disclosure in my patent referred to above in that the operation is not performed in cycles with a given fuel bed and there is no initial air blasting to heat said fuel bed. In air blasting a bed of ignited coke, as in a water gas generator, the temperature zone immediately after the blast is a gradient, the highest temperature being at the bottom and the lowest temperature at the top. Therefore, in introducing steam and hydrocarbon either upwardly or downwardly, the reactants contact solids at different temperatures in the different zones, whereas in introducing steam and hydrocarbon into the base of a vertical retort when the charge is freshly carbonized the temperature throughout the mass in the retort is more nearly uniform, allowing a more complete conversion in the reactions of steam with said hydrocarbon and steam with the carbon of the incandescent coke. In other words, an excess of steam may be used beyond that required for chemical reaction with the hydrocarbon without a waste of steam and without burning fuel, and especially for bringing the carbon to incandescence. I, therefore, attain in practicing this process a higher thermal efficiency than can be obtained in alternately blasting an ignited fuel bed with air and with mixed steam and a hydrocarbon. This feature alone I believe makes the herein described method of procedure patently novel over the disclosures of my patent referred to above. In the process disclosed in that patent, it is not economical to pass higher hydrocarbons than methane or mixtures containing methane and higher hydrocarbons into the fuel bed under conditions whereby only partial decomposition or partial reaction occurs; in the present case hydrocarbons may be introduced into the retort along with steam even after the temperature of the coke mass has fallen to a point where only partial reaction occurs, and beneficial results are obtained. In this instance, the calorific value of the resulting gas is higher by virtue of the methane or other hydrocarbons that have been formed in the retort or which passed through the retort undecomposed. I find it is possible and economical to use highly atomized mists of hydrocarbons along with steam as a medium for partly cooling the incandescent coke in a carbonizer simultaneously forming besides carbon monoxide and hydrogen some hydrocarbon gas. Thus, not only is the volume of gas increased per unit of coal charged into the retort, but the calorific value of the resultant mixed gas is higher than would result with straight steaming.

Another difference between this process and the patented process enumerated above is the effect of the difference in temperature. In the patented process high temperatures are employed, namely: those suitable for the substantially complete decomposition of methane, whereas in this case the fuel bed is more uniformly heated but to a lower temperature. Under the conditions obtaining in the ordinary carbonization of coal in the production of coke, as in a vertical retort, any deposited carbon resulting from the employment of a hydrocarbon mist is not in the form of a carbon black but rather in the form of coke. This result is probably because of the lower temperature obtaining in the retort than in the hot zone of a water gas generator.

While I usually prefer to have the steam and hydrocarbon gas or the steam and hydrocarbon mist thoroughly mixed before they are allowed to contact with the incandescent coke in the carbonizer, it is not necessary to thus introduce it. In some instances it is preferable to introduce the hydrocarbon separately from the steam and when introduced from beneath the incandescent coke it is preferable to admit the hydrocarbons at a higher level than the steam. It is understood that the steam and hydrocarbons may be introduced into the carbonized fuel downwardly from the top, upwardly from below or in any other suitable manner; I prefer, however, to introduce them upwardly from beneath the charge.

Because of the difference in the readiness with which various hydrocarbons crack, it is possible by the selection of the hydrocarbon or hydrocarbons to obtain a varied effect in thus making gas, for example: when natural gas is passed through the fuel bed all of the ethane and a portion of the methane reacts with steam during the forward part of this phase of gas making, whereas in a subsequent phase the methane is not appreciably reacted, only the ethane and higher hydrocarbons being re-formed. When natural gas or similar mixture of volatile hydrocarbons is introduced along with steam, the resultant gas obtained during this phase of the gas making period comprises largely hydrogen, carbon monoxide and methane with more or less ethane accordingly as the temperature is relatively low or high in the bed of coke. It is understood that I may use in my process as a cooling agent in a carbonizer and preferably along with steam, natural gas, hydrocarbons obtained therefrom such as methane, ethane, propane, butane, pentane, higher paraffins, petroleum-refinery gas, light oil, atomized petroleum products and other hydrocarbons.

I find that the gas making capacity of a carbonizer adapted for carbonizing solid fuel can be further increased by introducing into the carbonizer during the carbonizing period a hydrocarbon gas or mist, preferably at a slow rate, whereby equalization of temperature in the coking mass is approached and the hydrocarbon is only partly decomposed. The free carbon liberated by the thermal decomposition is absorbed by the tar and does not appear in the outlet gas as a form of carbon black. It is of course recognized that when a large quantity of said hydrocarbon is rapidly introduced into a small volume of coking coal heated to incandescence so large an amount of carbon black may be liberated that some of it will appear in the gas. The amount of hydrocarbon I prefer to employ is that whereby substantially all of the liberated carbon is absorbed by the tar and the coking mass.

The thermal decomposition of hydrocarbons is,

in most cases, endothermic, that is, heat is absorbed during reaction. This means that the use of certain amounts of hydrocarbon during the coking period would tend to increase the coking time (time required for carbonizing the coal or other solid fuel) by virtue of the heat absorbed by reaction. The amount of hydrocarbon used can be so regulated that it functions as a means of controlling the time of carbonizing (duration of the period of carbonization) in such a manner that the volume of gas produced can be maintained simultaneous with a decrease in coke production per unit of time (by virtue of an increase in the duration of coking period) and the quality of coke made is improved as a result of greater uniformity in the rate of heating of the coal in the various parts of the coking mass. It is commonly desirable, on the part of coke oven operators, to slow the rate of carbonization during certain periods of the year when coke is not in great demand, without diminishing the output of gaseous heat energy or materially increasing the amount of heat consumed in the process per therm of gas produced. The described procedure permits this effect to be obtained.

When a maximum output of coke is desired it is preferable and in some cases essential to pre-heat the hydrocarbon used, prior to introducing it into the coking mass. This tends to neutralize the endothermic effect of the decomposition or partial decomposition of the hydrocarbon. Certain effects obtainable will become apparent from a scrutiny of the following table:

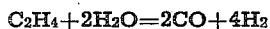
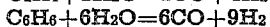
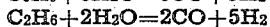
Approximate heat of formation at constant pressure

Hydrocarbon	Heat of formation B.t.u. per cubic foot	Yield of hydrocarbon by completely cracking 1 volume of hydrocarbon into its elements	Heat of reaction per foot of hydrogen evolved by cracking a hydrocarbon gas into its elements
		Volumes	B. t. u.
Methane— CH_4	+103	2	+51.5
Ethane— C_2H_6	+136	3	+45.3
Propane— C_3H_8	+167	4	+41.7
Butane— C_4H_{10}	+202	5	+40.4
Pentane— C_5H_{12}	+228	6	+38.0
Hexane— C_6H_{14}	+291	7	+41.4
Ethylene— C_2H_4	-13	2	-6.5
Propylene— C_3H_6	+15	3	+5.0
Butylene— C_4H_8	+51	5	+10.2
Benzene— C_6H_6	-47	3	-15.7

Attention is called to the fact that benzene, a by-product of the coal carbonizing industry, has a negative heat of reaction. This means that the only heat absorbed making gas from benzene is expressed in the heat capacity of the resulting gas plus the heat of reaction which is negative, making it possible with some superheating to generate gas from this material with substantially zero amount of absorption of heat from the coking mass. Some steam, preferably superheated, may advantageously be used with the hydrocarbon. Ethylene behaves in a manner similar to benzene in the coking mass except that there is less tendency for the formation of naphthalene. The relative heat requirements are indicated by the table.

The rate of introducing the hydrocarbon into the coking mass or into the incandescent coke may vary. The rate preferred depends upon the temperature in the solid fuel mass, the rate of input of heat, the amount of superheating of said hydrocarbon, the output of coke desired and the gasification effect desired. When steam is ad-

mitted simultaneously with the hydrocarbon, it also is a factor influencing the rate of introduction of the hydrocarbon. When the hydrocarbon is well superheated it can effectively be introduced at a faster rate than when not superheated, other factors remaining the same. Likewise, to obtain a given cracking effect the rate may be greater as the temperature of the coking mass rises. The greater the amount of steam used, the less the amount of hydrocarbon used other things remaining the same; this applies chiefly when steam is used in excess of the amount required to satisfy the chemical reaction with the hydrocarbon. Examples of the latter type of reaction, which are not carried to completion are as follows:



Normally I prefer to use chiefly the straight hydrocarbon during the coking stage of carbonization, but if steam is used simultaneously with it the relative amount of said steam used may be appreciably less than indicated by the equations above, that is, less than the molecular requirements in producing carbon monoxide and hydrogen, without producing carbon black in the outlet gas. The reason for this is two fold, namely, because some of the hydrocarbon does not completely crack or react and because a portion is decomposed yielding carbon, hydrogen and hydrocarbon, the liberated carbon being absorbed by the coking mass and the tarry matter. This is an advantage gained, in this manner of reforming, over other processes, so far as I am aware. Even when using bituminous coal in a water gas generator in producing gas, the steam requirements are greater than when the hydrocarbon is introduced into a coal carbonizer during the coking operation. My process is thus entirely different from that revealed in the patent referred to above, No. 1,762,100.

Although my process can be practiced in various types of coal carbonizers, retorts and ovens now in common use as well as in a wood charring apparatus, I prefer to show by an illustration how the process may be practiced. The accompanying figure is a diagrammatic sketch in vertical cross section, of one type of oven or retort wherein my process may be practiced; the connecting conduits are shown in elevation.

In the figure the retort has walls 1, with heating flues 2, fuel charging door 3, discharge hopper 4 for the residue or by-product coke or char, discharge door 5, discharge mechanism 6, steam supply lines 10 and 16 with control valves 9 and 15, fuel supply line 11, for supplying fuel to heat the retort, and gas off-take 13 with valve 14. Steam line 16 with valve 15 is provided for introducing steam from above the carbonizing fuel, and an air pipe for downwardly blasting with air is shown at 20 with valve 21. The down-run gas produced is removed through pipe connections 8 and 25 and valve 26. The solid fuel such as coking coal, lignite, petroleum refinery solid residuum commonly called coke, sub-bituminous coal or other solid fuel that does not become liquid upon heating in process of carbonizing is shown at 17; the connections for upwardly blasting with air include pipe 19 controlled by valve 18. Air inlet and valve for the combustion of the fuel gas are shown respectively at 22 and 23. The down-run hydrocarbon is introduced through

valve 24 and inlet 13; up-run hydrocarbon gas is introduced through valve 7 and inlet 8.

In the operation of the process I may proceed as follows: Charge the solid fuel to be carbonized into the retort through 3, close 3 and apply heat to the retort as, for example, by burning a gaseous fuel in the heating flues 2 by admitting fuel gas through 11 and 12, drawing in air for its combustion through 22 and 23 or by inspiration or other means. When a desired temperature is reached in the coking mass a hydrocarbon gas is introduced into 4 and into the coking mass through 8 by opening valve 7; the hydrocarbon thus admitted passes upwardly into the coking mass 17 and the reaction products are discharged with the gaseous products of carbonization through 13 and 14. The steam is admitted through 10 by opening valve 9. Air is introduced through 19 by opening valve 18. The relative amounts of steam, air and hydrocarbon used are controlled by regulating respectively, valves 18, 9 and 7.

When the hydrocarbon, with or without air, steam or both, is admitted to the retort from above the coking mass as through 24, the valve 14 is closed and the gaseous products are discharged through 8, 25 and 26. In this instance the inlet valves for air and steam are at 21 and 15 respectively.

When it is desirable to discharge the coke it is accomplished by opening the discharge door 5 and operating discharge device 6, rotating it.

It is understood that I do not limit myself to the use of the particular carbonizer shown in the figure in the practice of my invention; various modifications can readily be conceived in which a vaporized or gaseous fuel and steam, or an equivalent mixture, can be introduced into a bed of solid fuel during the process of its carbonization.

For the purpose of clearness I desire to describe my process, somewhat summarily as follows:

(1) Introduce a hydrocarbon in a fine state of subdivision, being preferably a gas or fog, into the mass of solid fuel confined in a carbonizer, during at least a portion of the carbonization period or directly thereafter.

(2) Introducing, when so desired, some steam simultaneous with said hydrocarbon for the purposes of producing an additional cooling effect, causing greater dispersion of said hydrocarbon and causing the formation of a denser gas by virtue of the carbon monoxide and hydrocarbon gas formed. The latter gas (hydrocarbon gas) is formed as a result of pyrolysis of the hydrocarbon introduced with the steam.

It is understood that the rate of introducing the hydrocarbon may be increased during the progress of carbonization, being as low as zero during an early stage and be so high during a subsequent stage that the composite gas made in the carbonizer per unit of time, other factors remaining substantially the same, is materially increased. An alternative effect is: the gas making capacity of the carbonizer is maintained substantially normal but the production of coke per unit of time is materially reduced. I claim that by the use of my process either periodically or continuously throughout the year in conjunction with a coal carbonizer one can operate with greater flexibility in the control of output of coke, gas and by-products. It is understood that the hydrocarbon may be introduced without

steam particularly when used in other stages than the last stage of carbonization. When using methane as the hydrocarbon, or a gas largely comprised of methane, I prefer not to introduce the hydrocarbon in the early stage of carbonization unless it is preheated. Under this condition very little methane is decomposed but a beneficial effect is obtained, namely, the middle of the mass of solid fuel is more readily and rapidly heated and the whole charge is more uniformly heated than without the use of said hydrocarbon. The volume of condensable matter produced is greater not only by the amount of hydrocarbon added but by the preservation of heavy hydrocarbons normally cracked in the process but which are not so completely cracked when swept from the carbonizer more rapidly than in ordinary practice.

Ethylene, propylene and other hydrocarbons such as propane, butane, and petroleum-refinery gas may be used and appreciably cracked at temperatures below that at which methane decomposes or reacts with steam. Thus with hot petroleum-refinery gas or the equivalent, I prefer to introduce it during a large portion of the carbonization period, increasing the rate of introduction as the temperature rises, introducing steam along with or simultaneously with it during the late stage of carbonization, finally discontinuing the admission of the refinery gas and continuing with the steaming for a brief period for the purpose of cleaning the coke or other product of carbonization.

I do not confine myself to the carbonization of coal in the practice of my process or to a particular type of carbonizer but the vertical retort or slot oven is referred to as being suitable for the purpose.

In my Patent No. 1,762,100 I claimed the process of making mixed gas comprising hydrogen and carbon monoxide by substantially complete reaction between steam and a hydrocarbon whereas in this application I claim the process of making a mixed gas comprising hydrogen, carbon monoxide and hydrocarbon gas. This process can be employed at lower temperatures than the enumerated patented process and therefore I believe that it should not be confused as a special case or special application of the former but rather as a distinctly and patentably different process.

I have stated that the hydrocarbon gas or the mist introduced into the solid fuel in process of carbonizing is admitted at a slow rate; this term is also used in the claims and therefore its meaning should be clarified. I have found that when a hydrocarbon such as ethane, propane, butane, refinery gas and other hydrocarbons having a greater molecular weight than methane are introduced into a coking bed of coal, the amount of decomposition of said hydrocarbon increases with rise in temperature, the hydrocarbons of high molecular weight cracking more readily than those of low molecular weight. When the temperature in the fuel mass is rather high, that is, above 1500° to 1800° Fahrenheit the percentage amount of decomposition is great. If the hydrocarbon is introduced too rapidly some carbon black passes through with the generated gas, particularly when no steam is used or when very little steam is used. I prefer to so control the rate of introducing the hydrocarbon into the coking or carbonizing mass that the amount of free carbon black entrained in the generated gas is substantially zero. It is recognized that at

relatively low temperatures the time of contact or time of exposure to the hot mass is a factor in completing cracking and therefore the percentage amount of cracking under low temperature conditions less cracking occurs per 1000 cubic feet of hydrocarbon passed at high rates than at slow rates but the amount of carbon carried out of the carbonizer entrained in the gas is also a function of velocity. Therefore when conditions are such that there is a tendency for carbon to pass out entrained in the gas the tendency can be reduced to substantially zero by decreasing the rate of admission of the hydrocarbon, or, at high temperatures increasing the amount of steam, or by both. By free carbon black is meant the carbon particles resulting from cracking of the hydrocarbon that are not absorbed by the tar produced during carbonization or deposited on the solid fuel. Methane does not decompose appreciably at relatively low temperatures hence carbon entrainment is not encountered using it as the hydrocarbon unless used at elevated temperature.

I commonly prefer to adjust the rate of introduction of the hydrocarbon or hydrocarbon and steam so that a definite volume of gas is made per unit of time, or so that a definite amount of solid fuel is carbonized per unit of time. By controlling the amount of preheating of the hydrocarbon and the rate of introduction of steam and hydrocarbon it is possible to accomplish this result. For example, using the hydrocarbon at a given rate over an appreciable portion of the carbonization period the time required for completely carbonizing coal is longer than is normal but the gas production is as great or greater than normal according to the amount of hydrocarbon used, whereas if the hydrocarbon is preheated the output of gas is increased and the coking time not appreciably decreased. The specific gravity of the gas made is controlled by controlling the relative amounts of hydrocarbon introduced during the high and the low-temperature stages of carbonization. Gas having the lower density is produced from the hydrocarbon used at a slow rate at high temperature, above about 1500° F. whereas at relatively low temperatures the specific gravity of the generated gas is higher.

Without preheating the hydrocarbon and using it (in this example natural gas) during the last stage of carbonization only along with some steam, for cooling the coke, I find that I can increase the gas-making capacity of a vertical retort, carbonizing bituminous coal, from 10 to 20 per cent without decreasing the carbonizing capacity of the retorts. The total amount of natural gas required in this case is about 6 to 12 per cent of the normal amount of gas made by straight carbonization, namely about 680 to 1320 cubic feet per ton of coal carbonized. When the natural gas is preheated a greater gas-making capacity can be obtained without reducing coke output. By a more extended use of the natural gas or the gasing period the gas-making capacity of the retort is further increased but the coke output decreased. The maximum capacity for coke and gas is obtained when using preheated unsaturates with a minimum amount of steam, other factors remaining the same.

The calorific value of the generated gas is, in all cases, greater than 300 B. t. u. per cubic foot. It may be that of average city gas, about 550 B. t. u. per cubic foot or, higher or lower according to conditions, under control. For example, when the hydrocarbon is admitted only during

the last period of carbonization, when the temperature is higher than about 1800° Fahrenheit, and at so slow a rate that cracking is fairly well complete the generated gas resulting from cracking or from the steam hydrocarbon reaction, has a calorific value of about 350 to 450 B. t. u per cubic foot and comprises hydrogen, methane and carbon monoxide. As the temperature falls, or rather at low temperature or at somewhat faster rates the amount of methane in the generated gas increases and with it the calorific value of said gas is increased.

By using a liquid hydrocarbon, preheated and under superatmospheric pressure, releasing the pressure by atomizing directly into the mass of coking fuel it is possible to obtain quite satisfactory results, particularly when it is desirable to make gas having a calorific value higher than 350 B. t. u, per cubic foot.

The term gaseous hydrocarbon as used in the claims is understood to include a gas or a highly atomized liquid hydrocarbon.

It should be noted that the yield of motor fuel per ton of coal carbonized is increased by the employment of hydrocarbons in the manner herein described. This is particularly true when using either the liquid hydrocarbons or the gaseous hydrocarbons having a high molecular weight.

It is indicated in the table above that the heat of formation and the heat absorbed by pyrolysis is different for the various hydrocarbons. In many instances pyrolytic reactions are endothermic, and this seems to be the case with many of the hydrocarbons or mixtures of hydrocarbons commonly available in commercially large quantities at a low price. Now, when such a material is introduced into a mass of coking coal or the equivalent at a rate whereby heat is absorbed in reactions at a greater rate than heat is transferred to the coking mass from the heating walls the coking mass cools to an equilibrium point at which the amount of decomposition of the hydrocarbon is substantially that corresponding to the amount of heat input. I find that I can very appreciably increase the output of gas, even without decreasing, in fact, even increasing the coke-making capacity of the carbonizer by introducing into the coking mass simultaneously with the hydrocarbon or with the hydrocarbon and steam a combustion-supporting medium such as air, oxygen, oxygen-enriched air or other reactant adapted to evolve heat by chemical reaction. In this manner the heat of reaction may be supplied by combustion reactions within the carbonizer. Although I normally prefer to use that amount only of oxidizing agent required to offset the cooling effect of the endothermic reactions, it is beneficial and hastens the rate of carbonizing, to introduce an excess of oxidizing agent during an early stage of carbonization, before maximum temperature in the mass of solid fuel is reached, and a lesser amount at the end of the carbonizing period when a cooling effect may be desired. I recognize that oxygen and carbon dioxide in the presence of freshly charged coking coal are not beneficial but are sometimes deleterious to the formation of first quality coke. However, after the plastic stage has been passed an oxidizing agent may be used without sacrificing the quality of the coke. I prefer, in carbonizing coking coal to proceed as follows: Introduce a hydrocarbon along with an oxygen-containing gas such as air, beginning after the plastic stage of carbonizing is past in the major portion of

the fuel mass, using the air in some excess of the amount required to neutralize or offset the cooling effect of the pyrolysis of the hydrocarbon used; continue with this procedure adding steam also in a subsequent stage as found desirable, increasing the amount of hydrocarbon in the late stage and post-carbonizing stage of processing, using steam alone for a brief period at the end of the cooling stage. The coke is preferably not completely cooled in the carbonizer but merely cooled relative to maximum temperature attained.

This step of introducing an oxidizing agent into the fuel mass along with the hydrocarbon is of particular benefit when using an atomized oil as the hydrocarbon. When using such a hydrocarbon more heat is required than when using a gas because of the latent heat of vaporization of the oil. By the use of a small amount of air, I am able to use more oil, and obtain a greater quantity of liquid by-products including motor fuel, and gas.

There are certain mixtures of air and any particular hydrocarbon or mixture of hydrocarbons that will not propagate flame at normal temperature and at atmospheric pressure even though an igniting flame be applied. In employing the oxidizing medium, usually air, in my process I choose to confine myself to these limiting mixtures. It is possible to employ explosive mixtures if the velocity of injection is greater than the rate of flame propagation.

It will be noted that, using a refinery gas as the hydrocarbon, the heat of decomposition is very low because of the large percentage of ethylene and propylene present and that accordingly only a very small relative amount of oxygen need be used to maintain a rate of heating of the mass of solid fuel comparable with that in normal carbonization. It follows that, unless a high output of coke or coke and gas are desired, only small amounts of oxygen need be used with such a hydrocarbon.

When using air-hydrocarbon mixtures that border on the range where the mixture will propagate flame it is distinctly advantageous to use steam with the hydrocarbon, the effect of the steam being to narrow the range between the inflammable limits in amount of gas in the mixtures with air. When the hydrocarbon used is preheated, care should be used to avoid the use of mixtures of air and hydrocarbon that will readily propagate flame.

The word "coke" is used in the claims in the broad sense, and designates the solid fuel residue resulting from the carbonization by heating solid carbonizable fuels to incandescence or to a carbonizing temperature which, as stated, is commonly 1500 to 1800° Fahrenheit.

Having described my invention so that one skilled in the art can practice it, I claim:

1. A process for carbonizing solid fuels and making combustible gas, comprising, heating a confined mass of a carbonizable solid fuel to a carbonizing temperature liberating volatile matter from it as a gas and simultaneously forming coke, introducing a substantially gaseous combustible hydrocarbon into said mass during at least a part of the heating operation, at a rate sufficiently slow for the pyrolytic formation therefrom of an additional amount of gas comprising hydrogen, withdrawing the gases as generated substantially free from entrained carbon resulting from pyrolysis of said hydrocarbon, and recovering the coke separate from said gases.

2. A process for making coke and combustible gas substantially free from suspended carbon largely from a carbonizable solid fuel comprising, heating a confined mass of said solid fuel to a carbonizing temperature liberating volatile matter from it as a gas and forming coke, introducing a gaseous hydrocarbon into said mass at a low rate simultaneous with the application of heat thereto causing pyrolysis of at least a portion of it thereby forming a gas containing hydrogen substantially free from suspended carbon resulting from said pyrolysis, withdrawing the gases substantially as generated, and recovering the coke separate from the gaseous products.
3. A process for making coke and combustible gas substantially free from suspended carbon from carbonizable solid fuel and a gaseous hydrocarbon, comprising, first heating a confined bed of said fuel to incandescence thereby evolving gas from said fuel, then continuing the heating operation and introducing into the heated bed a preheated gaseous hydrocarbon at a substantially definite rate forming an additional amount of gas comprising hydrogen, withdrawing the gases substantially as generated, and recovering the coke separate from said gases, said rate being so low that the hydrogen gas as withdrawn from said bed is substantially free from entrained carbon black resulting from the pyrolysis of said hydrocarbon.
4. In the process of making coke and combustible gas by carbonizing a carbonizable solid fuel and separately recovering said coke and gas, in combination the steps, passing through a confined heated bed of said solid fuel during the latter portion of the carbonizing period a gaseous stream initially consisting of a preheated gaseous hydrocarbon and steam at so slow a rate that said hydrocarbon reacts with said steam in contact with the heated solid fuel in process while heat is being applied to said fuel, thereby produc-

ing coke and an additional amount of combustible gas which is substantially free from suspended carbon resulting from hydrocarbon pyrolysis, and separately recovering the coke and combustible gas.

5. A process of making combustible gas and coke, comprising, heating a confined mass of carbonizable solid fuel to incandescence thereby evolving combustible gas and carbonizing said solid fuel, introducing at a slow rate a mixture of a substantially gaseous hydrocarbon and a gas containing free oxygen into the incandescent mass during the latter part of the heating period only, thereby forming an additional amount of combustible gas partly by exothermic reaction of oxygen with said hydrocarbon and partly by pyrolysis of said hydrocarbon, depositing the free carbon evolved by said pyrolysis on the surface of the heated solid fuel, removing and recovering the combustible gases substantially as formed and then separately recovering the coke.

6. In the process of making coke and combustible gas by carbonizing a carbonizable solid fuel and recovering coke separate from said gas, the step comprising, introducing substantially together both a preheated gaseous hydrocarbon and steam into a confined mass of said solid fuel while applying heat to said mass during a late stage of the carbonization period at so slow a rate that they react chemically with one another by virtue of heat absorbed by them in said mass thereby producing coke and forming an additional amount of combustible gas containing methane, hydrogen and carbon monoxide that is substantially free from entrained carbon black resulting from the pyrolysis of said hydrocarbon; withdrawing the gases as generated, discontinuing the steam-gas blast, and withdrawing and separately recovering said coke.

WILLIAM W. ODELL.