

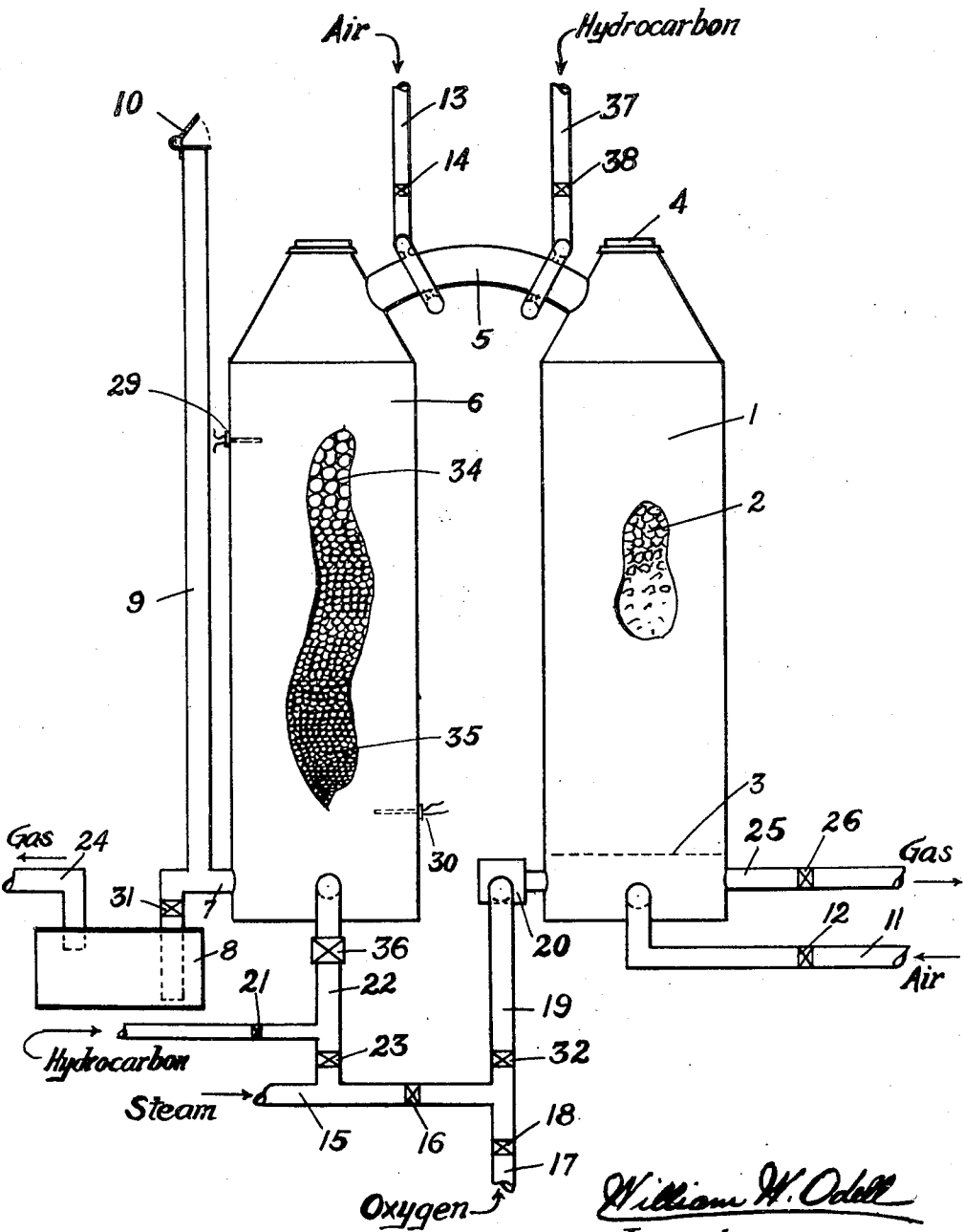
Jan. 17, 1950

W. W. ODELL

2,494,576

PROCESS AND APPARATUS FOR MAKING COMBUSTIBLE GAS

Filed May 17, 1946



William W. Odell
Inventor

Mumma Han atty

UNITED STATES PATENT OFFICE

2,494,576

PROCESS AND APPARATUS FOR MAKING
COMBUSTIBLE GAS

William W. Odell, Washington, D. C.

Application May 17, 1946, Serial No. 670,408

8 Claims. (Cl. 48—208)

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This invention relates to a process and apparatus for making combustible gas. It has to do with the production of a gas rich in hydrogen and deals with controlled water gas reactions and also reforming of hydrocarbons in the vapor phase.

One of the objects of this invention is to economically produce a gas largely in a water gas generator that has a high volumetric ratio of H_2 to CO. Another object is to increase the gas making capacity of the generator. Another object is to utilize coal or mixtures of coal and coke as generator fuel without the difficulties commonly encountered in so using such fuels, namely, without excessive difficulties due to caking and matting of the generator fuel, severe clinker troubles, and with less gum-forming hydrocarbons in the gas made.

In ordinary practice employing bituminous coal as generator fuel for making water gas by the customary air blast alternated with up and down steam runs the gas-making capacity is much lower than when operating with coke fuel. One of the reasons for this is the great difficulty in heating the coal in the upper or top zones of the bed as quickly or to as high a temperature as desired. Another difficulty is that, because of the lower mean temperature prevailing in the fuel bed the gas made therein contains tarry matter and unsaturated hydrocarbons, some of which may be classed as gum-forming hydrocarbons. The organic sulphur content of the gas thus made is higher than that in gas made from coke. Because of the lower mean temperature in the fuel bed attempts have been made to improve conditions by employing an extended air blast; this results in increased clinker troubles and an increase in generator fuel per one thousand cubic feet of gas made since more fuel is thus burned during the portion of the air-blast period when the CO_2 content of the blast gas is very low.

This invention greatly minimizes the difficulties experienced in the gasification of coal and it also materially improves efficiencies in gasifying coke, briquets and other solid fuels, by maintaining better temperature conditions in the fuel bed, while simultaneously controlling the ratio of H_2 to CO in the gas made.

One form of apparatus in which this invention may be practiced is shown diagrammatically, in elevation, in the figure in which the generator 1, containing solid fuel 2 supported as on grate 3, has a fuel charging door or lid 4, and a gas off-take 5 leading to stabilizing and re-forming chamber 6 which is substantially an efficient heat exchanger. The off-take 7 from the base of the exchanger leads to wash box 8 and also has a connecting conduit 9 to stack valve or lid 10. Means for air-blasting the generator are shown by conduit 11 and valve 12, whereas the secondary

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duit 13 and valve 14. The steam line 15 supplies steam to the generator for up runs through valve 16 and conduit 19, whereas oxygen or an oxygen rich gas is supplied thereto through conduit 17, valve 18, and conduit 19. The steam and oxygen mix in mixing chamber 20 in their travel to the generator. Conduit 22 supplies vapor phase hydrocarbon through control valve 21, whereas steam is supplied through valve 23 to the heat exchanger. The off-take for down run gas is shown at 25 with control valve 26. The latter valve can be submerged or a part of a two-way valve in a common wash box, this is not new; this also applies to off-take valve 31 ahead of wash box 8. In chamber 6 the contact solids, which are preferably small and preferably uniformly sized in any particular layer, form a bed. The solids adjacent the bottom layer are preferably smaller than those in the top layer as indicated at 35 and 34. Thermocouple connections 29 and 30 are guides in temperature control; 36 is a mixing box for steam and combustible gas (hydrocarbon gas) and 24 is the off-take from the wash box. A second supply line for hydrocarbon gas 37 has control valve 38.

In starting operations in the apparatus shown in the figure with all valves initially closed, a fire is kindled in 1 in the usual manner and lid 10 is opened. Air blasting is started by opening valve 12 and after the fuel in 1 becomes hot the gas generated during air-blasting is mixed with air by opening valve 14 in conduit 13 and burned. The products of combustion are conducted down through exchanger 6, heating the contact solids therein, and pass out through 7 and 9. Now a brief up-steam run is made by closing valves 12 and 14 and lid 10, and opening valve 31 and steam valve 16. The steam run is then discontinued by closing valves 16 and 31 and the apparatus is now ready for regular operation.

Example 1

Generating gas having a volumetric H_2 to CO ratio of approximately 1.5 to 1.

Open lid 10, open air-blast valve 12 and after about one-half to one minute open valve 14 to admit sufficient air to burn the combustible matter in the blast gas from 1 and thereby heat the refractory solids 34 and 35 in heat exchanger 6, conducting the products of combustion out through 9. The solids at 34 should preferably be heated to 2200° to 1600° F. and the solids 35 to a temperature varying from about 1600° F. at the top to 400° to 600° at the bottom. Air valves 14 and 12 are closed; steam valve 16 and valves 31 and 32 are opened, and lid 10 is closed. In this manner an up-steam run is made for about one minute to 1.5 minutes; then valves 16, 31 and 32 are closed and valve 26 is opened and steam is introduced through valve 23 and conduit 22 to exchanger 6 wherein it is heated to a high tem-

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perature and passes through conduit 5 to generator 1 and down into the fuel bed, the gas being removed through 25 and 26. This is continued for about two to three minutes, until the temperature in the hot zone of the fuel bed is lowered to about 1400° to 1600° F. Steam valve 23 and gas offtake valve 26 are now closed and valve 31 is opened. A special prolonged up run is now made as follows: Open steam valve 16 and valve 32 and also open oxygen valve 18 sufficient to let through an amount of O₂ equivalent to about one-fourth the volume of the steam simultaneously introduced into generator through mixing box 20. The exact ratio of steam volume to oxygen volume is determined by gas analysis, since it will vary with the reactivity of the fuel. The temperature should preferably be such that the fuel bed temperature in the hot zone does not rise appreciably during this up run, thereby making gas having a higher than normal H₂ to CO ratio. This prolonged run, which may be three to ten minutes or more, helps also to carry the heat into the fuel in the upper layers of the fuel bed by prolonged exposure to a stream of hot gases. This run is discontinued and another air blast started as follows: close oxygen valve 18, then after a few seconds close steam valve 16 and valve 32, open air-blast valve 12 and after about five to eight seconds open lid 10 and close valve 31. This starts another cycle. By conducting all of the make gas to a common holder it will be found that the H₂ to CO ratio is a little less than 1.5 to 1. If it is much less than this the defect can be overcome by using somewhat less O₂ during the prolonged up run. This will result in a lower temperature in the hot zone of said bed during that run. On the other hand, if the H₂ to CO ratio is too high a shorter steam-oxygen run should be made.

With some fuels, such as some high temperature cokes, there is not enough gas evolved during the normal or desired length air-blast period when checker bricks are used in the heat exchanger 6 such as are used in a carbureted water gas set, and for that reason also the contact mass in exchanger 6 of the figure is preferably filled with small uniformly sized solids with greater surface per cubic foot of exchanger space than when checker bricks are used. However, in the event that sufficient blow gas is not generated during a normal air-blast period to heat the solids in the heat exchanger 6 it is preferable, with fuels of low ash softening temperatures, to refrain from making a much prolonged air blast but instead to introduce a little steam during the air-blast period, thus making a richer gas. Usually this will not be required.

The solids, of which the bed is comprised in exchanger 6 of the figure, are larger in the upper portion 34 than in the lower portion 35 because it has been found that this facilitates more uniform heating and prevents overheating in the top zone; the use of very small solids in the lower zone prevents the gases from leaving the exchanger at too high a temperature. The use of these small size solids also provides for high efficiency and economy of fuel; no waste heat boiler is needed.

Before giving another example it is perhaps desirable to offer what is believed to be an explanation of the reactions occurring whereby the high H₂ to CO ratio and high output are obtainable. In the ordinary operation of a water gas set employing a five to six foot depth of fuel bed in the generator, only a small portion of the fuel

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bed is hot at the end of the steam run portion of the cycle and a prolonged run at this point would cool the fire too much. However, at the temperature prevailing at the end of the steam run the reaction (1) $C + 2H_2O = CO_2 + 2H_2$ occurs more rapidly than the reaction (2) $C + H_2O = CO + H_2$ and thus the more of the former that occurs the greater the H₂ to CO ratio. Normally steam is not so completely reacted at the relatively low temperature as at high temperatures and it is therefore not economical to operate at temperatures appreciably lower than 1450° to 1600° F. in the hot zone of the fuel bed. It will be noted that the long steam-oxygen run is made after the fuel bed has been cooled by an up and down steam run; in this manner reaction (3) $CO_2 + C = 2CO$ is kept at a minimum. During the steam oxygen run the steam is in such excess that the fuel temperature does not rise to the ash softening temperature in the hot zone. When the extra high H₂ to CO is not required this steam-oxygen run may be made when the generator fuel bed is at a higher temperature.

In one case proceeding as described above the gas made during the steam-oxygen run had a composition as follows:

	Percent by volume
CO ₂ -----	24.0
CO -----	29.4
H ₂ -----	46.0
CH ₄ -----	.2
N ₂ -----	.4
	100.0

The materials consumed per one thousand cubic feet of gas made, as closely as could be measured, during this oxygen-steam run, were:

Generator fuel, calculated as carbon.....	lbs. 17.4
Steam.....	lbs. 25 to 27
Oxygen.....	cu. ft. 160

A deep generator fuel bed is desired more than seven feet, and preferably at least ten feet.

Since the steam-oxygen run is usually conducted at temperatures lower than normal in making water gas, ash does not melt or clinkers form during this period. In other words the fuel is thus consumed below its ash softening temperature.

Example 2

Production of a gas having a H₂ to CO ratio of 2 to 1 using some hydrocarbon gas during the back run or down run. In this example the gas thus used was coal gas having a composition as follows:

	Percent by volume
CO ₂ -----	3.0
CO -----	6.8
Illuminants -----	2.6
H ₂ -----	49.0
CH ₄ -----	33.6
N ₂ -----	5.0
	100.0

Operations were conducted substantially as in Example 1 at the start. That is, an air blast was made and the fuel bed heated to a good gas making temperature and the contact solids in the upper portion of exchanger 6 of the figure were heated to 2200° F. The blast was discontinued and the up steam run was made as before. Then a back run was made by opening valve 23

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and also valve 21, which latter permits the oven gas to mix with the steam and pass into the exchanger 6, up through the contact solids, thereby becoming heated to a high temperature and largely re-formed to CO and H₂, the resulting stream, containing excess steam above that chemically required by the re-forming reactions, passes down through the generator fuel bed 2 and out through 25 and 26. The gas made on this run is a mixture of water gas and re-formed gas and has a very high H₂ to CO ratio. Following this run the up run is made with steam and oxygen as described in Example 1. The composition of the total "make" gas exclusive of the air-blast gas is approximately:

CO ₂ -----	6.0
CO -----	30.0
H ₂ -----	61.3
CH ₄ -----	0.2
N ₂ -----	2.5
	100.0

This composition is obtained when the amount of steam used during the back run has the same volume as the oven gas used, computed as at 60° F. and when the amount of oven gas used is approximately fifteen to eighteen percent of the total gas made, and the amount of gas made during the steam-oxygen run is approximately 30 percent of the total gas made.

The total materials consumed during the gas-making runs, per one thousand cubic feet of gas made, were:

Steam -----	pounds-----	30
Oven gas -----	cubic feet-----	150
Oxygen -----	do-----	50

Carbon approximately 16 pounds not including the carbon consumed during the air-blasting period.

When gas of higher H₂ to CO ratio is desired more oven gas can be used or a low molecular weight hydrocarbon can be substituted in part or fully for the oven gas. In either case the hydrocarbon reacts substantially completely with steam in exchanger 6.

It will be noted that an appreciable excess of steam is used during the gas re-forming stage (the back run of Example 2) but this excess is not wasted; on the contrary it is superheated in heat exchanger 6 of the figure and then reacts with the generator fuel as it passes down into the fuel bed. This same economy of steam can be practiced when making the steam-oxygen run (up run) wherein an excess of steam is used, by introducing a vapor phase hydrocarbon through 37 and 38 of the figure into the gas stream passing through 5 into 6. The hydrocarbon thus admitted is completely re-formed in the highly heated contact solids in 6. In either case the hydrocarbons re-formed are used in amounts required to increase the H₂ to CO ratio above that of water gas, usually to about 2 to 1.

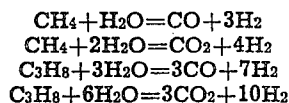
The novelty claimed for this invention lies in part in the combination of steps and the particular arrangement of the generator with a deep heat exchanger filled with a bed of small size solids adapted to withstand high temperatures. A plurality of sizes of solids are required in order to make the economies indicated. A hot valve is not required. Oxygen is used in a most economical manner and under temperature conditions favorable for maximum heat generation and high H₂ to CO ratio as well as below the ash

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softening point of the fuel. The high temperatures employed cannot be used in an ordinary carbureted water gas set because the valves will not stand it. Again, in common practice widely spaced checker bricks are arranged in chambers which are used as heat exchangers with the result that the gases leave at a high temperature; this is not the case in this invention. The prolonged oxygen-steam up run at the relatively low temperature heats a large portion of the fuel in the upper fuel bed to a higher temperature than is normal in ordinary water gas practice with the given fuel. In other words, in common practice the upper zones of the fuel bed using coal or low temperature coke do not become nearly as hot as desired during the air-blast period and they cool too quickly during the down steam run, whereas in this invention the down-run steam strikes the top zone at a high temperature, and during the prolonged oxygen-steam up run the gas formed passes up through the bed below the ash softening temperature and close to 1600° to 1800° F. Less trouble is experienced with caking and matting of the fuel, less trouble from clinker formation and from blow-holes in the fuel bed probably because of the better temperature conditions which prevail with the described method of operating.

The steam used during the steam-oxygen runs will vary from about three to about five times the volume of the oxygen used in admixture therewith, according to the temperatures of the oxygen and steam and according to the reactivity of the generator fuel and other variables. With less steam than about three volumes to one of oxygen there is a pronounced tendency for the temperature in the lower portion of the fuel bed to rise and thereby increase the tendency for clinkers to form as well as alter the H₂ to CO ratio of the gas made. Tests show that it is uneconomical to use an appreciably greater amount of steam than five times the volume of the oxygen used during the up runs (oxygen-steam runs) described.

A very economical manner of operating the apparatus shown in the figure, making a high-hydrogen gas, is briefly described as follows: Starting with the generator fuel at a gas making temperature and the solids in exchanger 6 at a satisfactory high temperature, make an up run by admitting steam through 15, 16, 32 and 20 to generator 1, removing the gas made through 5, 6, 31, 8 and 24, then make a back run using steam through 15, 23 and 22 and hydrocarbon vapor, in this example methane, propane, butane, ethane, natural gas or other hydrocarbon of low molecular weight, through 21 and 22, causing the said vapor and steam to mix in chamber 36 and causing the said vapor to react with some of the steam in passing up through the bed of solids in 6 by such reactions as:



The thus produced re-formed gas with an appreciable amount of excess steam is passed out of 6 at a high temperature, above about 1650° F., through 5 and down through the fuel bed in 1 and out through 25 and 26; the said excess steam from 6 reacts to a large extent with carbon of the fuel bed forming water gas. Now an up run is made using oxygen and steam as described but a relatively small amount of a hydrocarbon in the

vapor phase is introduced into 5 from 37 and 38 during this run for the double purpose of reacting excess steam from the up run through the fuel bed and to increase the H_2 to CO ratio. The hydrocarbon thus introduced reacts with the excess steam in passing down through 6; the gas made is removed through 31, 8 and 24. A small amount of hydrocarbon only is used during the latter run, namely an amount equivalent to a small percent by volume of the gas made during the oxygen-steam run is introduced through 37 and 38 as described.

The upper temperature limit for the solids 34 in the figure is, for practical reasons, about 2350° F., but even with this temperature prevailing in 34 the solids in the lower zone 35 are always very much below this temperature; this is because of the selection of small size solids as heat exchange units. Solids at the top layer of the bed can be three to four inches mean diameter, and spheres are preferable; at the bottom layer the solids can advantageously be as small as one inch mean diameter. Layers between top and bottom should be sized intermediately.

Again referring to the figure, the exchanger is shown, for simplicity, as being cylindrical; experiments indicate it preferably should taper downwardly or that the lining preferably should be so constructed that the bed of solids in 6, particularly in the lower half portion, tapers appreciably downwardly.

Having defined this invention so that one skilled in the art can practice it with variations to meet conditions, and without limitation to procedures of operation given as examples, I claim:

1. The cyclic process of making combustible gas having a high hydrogen content, comprising, first heating a deep, ignited bed of solid fuel confined in a generator by blasting it with a combustion supporting fluid meanwhile burning the producer gas thus made in an adjacent deep bed of small size heat-exchange solids confined in a heat exchanger and heating the solids in the upper portion of the latter bed to a temperature in the range 1650° F. to 2350° F. then discontinuing said blasting and making a series of gas-making runs namely, first passing a stream initially comprised of steam up through the heated fuel bed from beneath forming water gas therein, conducting the stream out the top of said bed and down through said bed of solids with increasing intimacy of contact therewith in which bed it reaches a temperature in the range 1600° to 2350° F. and is then cooled to an appreciably lower temperature in the lower portion thereof, discontinuing this up run and making a back run by passing a stream initially comprising essentially steam up through said bed of heat exchange solids with decreasing intimacy of contact therewith becoming heated therein to said temperature and down through said fuel bed forming additional water gas, then discontinuing the back run and making a relatively long steam-oxygen up run by passing a fluid initially containing oxygen and steam in the respective volumetric proportions of 1 to 3 to 1 to 5 up through the said fuel bed and down through said bed of heat exchange solids with increasing intimacy of contact therewith thereby making additional combustible gas which latter gas is serially heated to said temperature and partly cooled in passing through said bed of solids, and recovering the combustible gases made.

2. The cyclic process of making combustible gas of high hydrogen content, which includes the

steps, passing a stream initially comprising steam up through a confined deep bed of solid fuel heated to a gas making temperature thus making water gas, passing the stream containing the latter gas down through a confined bed of hot small size heat-exchange solids thereby storing some heat in said solids and partially cooling said gas, then making a back run by passing a stream comprising essentially steam up through said bed of hot solids superheating the latter stream to 1650° to about 2300° F. and down through said fuel bed forming an additional amount of water gas, then passing a stream initially comprising oxygen and steam in respective volumetric proportions of 1 to 3 to 1 to 5 up through said fuel bed for a prolonged period and down through said bed of hot solids thereby generating an additional amount of combustible gas and partially cooling it by contact with the solids in the latter bed while passing therethrough.

3. In a process of making combustible gas having a high hydrogen content employing reactions of carbon with steam and with steam-oxygen mixtures, in combination the steps, first heating a deep confined, ignited bed of solid fuel to a gas making temperature by blasting with a combustion supporting fluid, then discontinuing said blasting and making a series of gas-making runs, namely, an up steam run for a period removing the gas made from above said bed, a down steam run for a period admitting the steam from above said bed at about 1650° to 2300° F. removing the gas thus made from beneath said bed, and making a prolonged up run with mixed steam and oxygen, the amount of the latter steam used being more than three volumes for each volume of said oxygen, and recovering the gas made during the different runs.

4. In the process of making combustible gas of high hydrogen content employing water gas reactions and making up and down steam runs by passing a stream initially comprising essentially steam up and down through a confined deep bed of solid incandescent fuel, the step making a prolonged up run following a down steam run by passing a fluid stream initially containing essentially oxygen and steam in the respective volumetric proportions of 1 to 3 to 1 to 5 up through said bed, and recovering the combustible gas thus made.

5. In the process of making combustible gas of high hydrogen content employing water gas reactions and making up and down steam runs by passing a stream initially comprising essentially steam up and down through a confined deep bed of solid incandescent fuel, the step making a prolonged up run following a down steam run by passing a fluid stream initially containing essentially oxygen and steam in the respective volumetric proportions of 1 to 3 to 1 to 5 up through said bed, and recovering the combustible gas thus made.

6. In the process of making combustible gas wherein the stream initially containing gas-making fluids flows alternately upwardly and downwardly through a bed of incandescent solid fuel confined in a generator, the steps comprising, passing the hot up-run gases exiting from above the confined fuel bed downwardly through and with increasing intimacy of contact with a mass of refractory solids confined in a heat exchanger whereby heat is imparted to said solids by the latter gases which gases are simultaneously cooled correspondingly, and preheating at least some of the down-run stream of gas-making

fluids which stream is subsequently passed downwardly through said fuel bed, by first passing it upwardly through the heated mass of said solids with decreasing intimacy of contact therewith, thereby economizing heat energy.

7. The process of making combustible gas in cycles, one cycle comprising first up-blasting with air a deep bed of ignited solid fuel confined in a generator for a brief period to heat it to a gas making temperature, discharging the resulting gas from above said bed, introducing air into the discharged gas to burn the combustible content thereof and passing the hot products of the latter combustion down through a deep porous bed of refractory solids confined in a connected heat exchanger with increasing intimacy of contact with the refractory solids whereby an upper portion of said bed of solids is heated to a temperature of the order of 1650° to 2200° F. and the bottom portion is heated to a much lower temperature, then discontinuing the air blasting and making an up-run by passing a stream initially comprising essentially steam upwardly through said fuel bed making gas therein, passing the latter hot gas downwardly through said porous bed with increasing intimacy of contact with the refractory solids thereby partially cooling it while imparting some of its sensible heat to the latter bed, recovering the partially cooled gas thus made, discontinuing the up-run, now making a down-run by passing a stream initially comprising essentially steam upwardly through said porous bed with decreasing intimacy of contact

with said refractory solids thereby preheating it to a temperature of the order of 1650° F., passing the thus heated stream downwardly through the said fuel bed thereby making additional combustible gas, recovering the latter gas, then discontinuing the down-run and making a prolonged up-run by passing a fluid stream initially comprising steam and oxygen in a ratio of 3 to 5 volumes of steam to 1 of oxygen upwardly through said fuel bed thus making combustible gas comprising largely CO and H₂, passing the latter gas initially hot down through the said bed of refractory solids with increasing intimacy of contact therewith thereby partially cooling it while simultaneously storing additional heat in the latter bed, and recovering the thus cooled gas.

8. The process defined in claim 7 in which a hydrocarbon vapor is introduced, during the down run, into the said heated stream prior to its passage downwardly through the said fuel bed.

WILLIAM W. ODELL.

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