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G. W. WALLACE

PROCESS OF CARBONIZING

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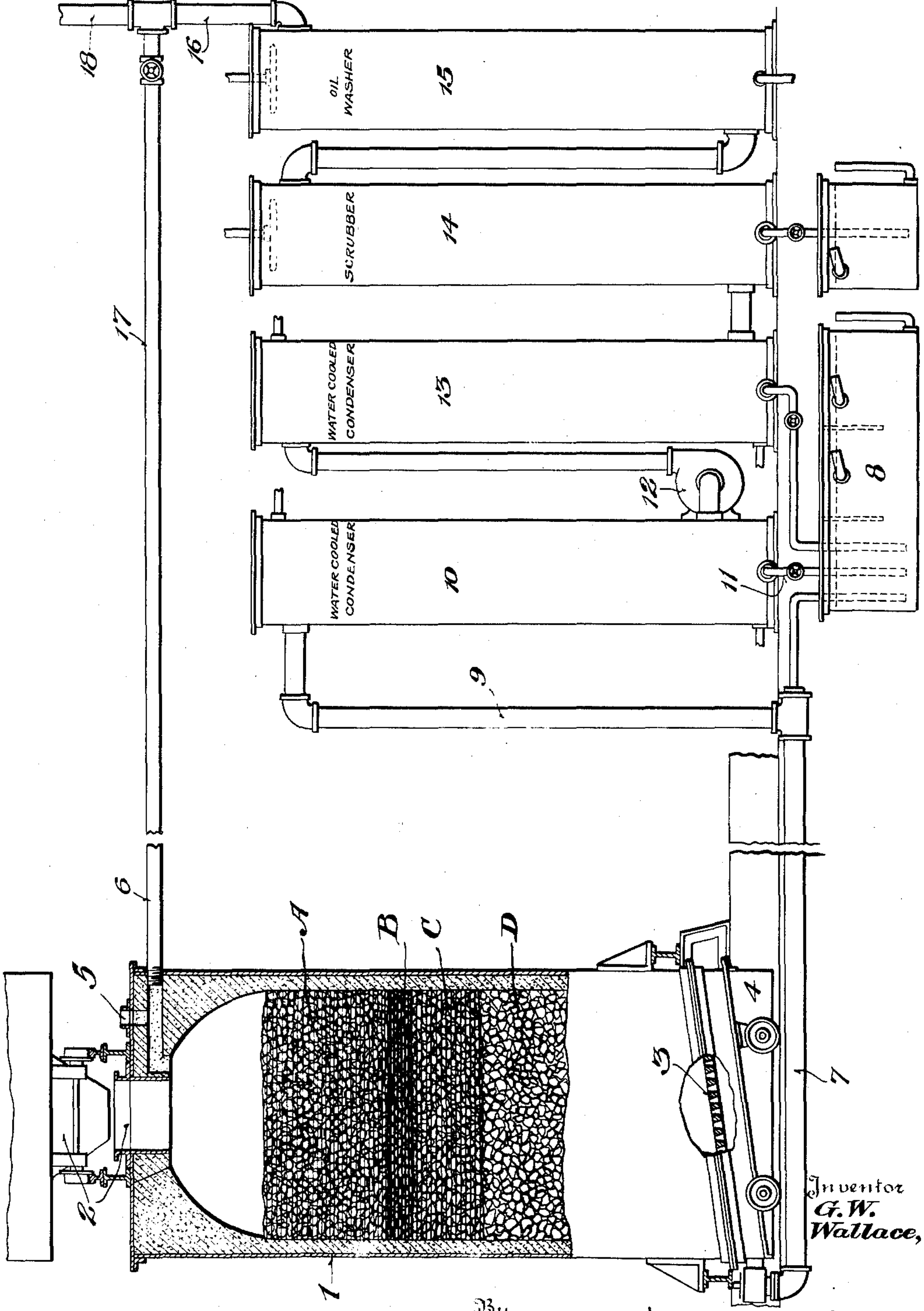

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PROCESS OF CARBONIZING.

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To all whom it may concern:

Be it known that I, George W. Wallace, a citizen of the United States, residing at San Francisco, in the county of San Francisco and State of California, have invented certain new and useful Improvements in Processes of Carbonizing, of which the following is a specification.

This invention relates to processes of carbonizing; and it comprises a method of carbonizing shale, lignite, coal, etc., to obtain valuable volatilizable products wherein shale, or the like (usually, but not necessarily, moist or moistened) is carbonized in a vertical column under conditions causing a transverse band or zone of carbonization to advance progressively downward towards and to the colder, moist lower end, the temperature in this zone being usually around 800° F and the the downward progression of the zone being effected by a hot down draft of returned combustible gases admixed with air; all as more fully hereinafter set forth and as claimed.

In distilling shale, lignite, coal, etc., to obtain oils and tars and ammonia, the bituminous bodies present break up primarily by an action analogous to the charring of wood; an action which, as a whole, if not actually exothermic, at all events requires the addition of very little foreign heat once the materials are brought to a reacting temperature. The action is the same as that forming the first stage in coking coal and is called carbonization; a term which may be here used. Once initiated at any point in a mass of hot fuel, the decomposition reaction tends to become self-propagating and advance elsewhere. Possibly the actual decomposition itself is always exothermic; but the net result of the complex of actions taking place and vaporization of the volatile products formed, with consumption of heat, may or may not be a liberation of heat. However, if added heat is required, the amount, in thermal units, is, as noted, usually very little. With various coals under various conditions, recorded results vary between a liberation of about 780 British thermal units per pound of coal to an absorption of about 170. One of the products of the primary decomposition is always combustible gas (ethylene, ethane, etc.); and if heating conditions be not carefully regulated, the amount of this gas is materially augmented by secondary decomposition of the oils and tars primarily produced. This is of course undesirable, except where gas is the product sought.

It is well recognized in the art that low temperature distillation is desirable in order to obtain a maximum of oils and tars; and many methods of distilling have been proposed with this end in view. For the most part, however, they have been unsuccessful in securing the full result sought because of the engineering and technical difficulties incident to heating any substantial mass of pulverulent or fragmentary nature evenly and to exact temperatures throughout; and particularly where, as in the present case, the result is, or may be, a self-propagating exothermic reaction. Ordinarily, moreover, the methods are, thermally speaking, expensive; they require much heat to be used and particularly with externally heated retorts; this being especially true where substantial yields of ammonia are sought and currents of steam are used to assist in its extrication. The question of the heat necessary is particularly serious in dealing with shales and lignites high in mineral matter, of low fuel value.

It is the object of the present invention to provide a method particularly applicable to the treatment of oil shales, but also useful with lignites and coals, in order to produce maximum yields of oils and tars, as well as of ammonia, with a minimum consumption of fuel. The solid product of the action may be mineral matter or ash, or it may be a carbonized mass of coky or semi-coky nature, having fuel value. In order to accomplish my end, I take advantage of the stated self-propagating nature of the carbonizing reaction, instituting a carbonizing reaction in the top of a column or body of shale in a suitable container and effecting a downward regulated travel of this zone of carbonizing towards and to the lower end of the column. The carbonizing action is, as stated, usually exothermic, that is, is attended with a local evolution of heat and an increase in temperature. In order to control the reaction and its propagation, I balance the heat and volume of a downdraft of burning gases traveling in the direction of propagation against the cooling effect of moisture in the line of advance. In so doing, I am enabled to achieve a new result: rapid carbonization at a controlled and low temperature. In practice, above (or in heat communicating relationship to) the head of the column of shale I burn gases to produce a higher temperature than that required to initiate carbonization, while the body of shale is wet or moist to a point just below the temporary locus of the zone of carbonization, and therefore at a temperature not exceeding 212° F. The exact distance between the moist zone where sudden cooling takes place and the advancing high temperature face of the carbonization zone depends on the volume of hot gases passing and drying out the material. The charge is usually in fragments of two inch size or less, though "run of mine" may be used and it holds whatever water will adhere, the rest draining downward. Hot gases are passed downward through the shale towards the cold end. By regulating the quantity of gases in the downdraft and their temperature, obviously I can exercise exact control of the progress of the carbonization zone. It is a matter of balancing the heat and the volume of the gases in the drowndraft against the cooling effect of the moisture in the shale below the zone.

Usually some of the combustible gases resulting from the action itself and collected beyond the condensers (which I may here call "tail gases") are returned to a point in the treating apparatus just above the mass of shale under treatment and are there burnt with air. The amount of heat developed depends upon the quantity of gas so introduced and burnt. The hot mixed body of gases passing downward through the mass of shale gives the heat necessary to initiate and maintain the carbonization; i. e., the heat required to compensate for radiation, for heating the solid materials to a somewhat higher temperature, for vaporization and the like. The downdraft carries heat, as well as vapors and gases, forward beyond the lower advancing face of the zone of carbonization and preheats the materials to be carbonized. The primary products of carbonization are cooled thereby. Under the circumstances, these products leave the advancing face really as a sort of fog or fume, well distributed through the draft current and there is no tendency for the shale to clog with tar. The zone of preheating below the advancing face of the carbonizing zone is limited in its length by the presence of liquid water therebelow. At some point not far below the advancing face of the carbonizing zone, which I usually keep at a temperature around 800° F., the temperature of the shale cannot exceed 212° F. because of evaporating water and liquids. Between these points is a preheating and drying zone of a length depending upon the gas speed. The moisture in the fuel is evaporated in the preheating zone with a corresponding consumption of heat units; but these heat units are largely given back to the shale when the water vapor passes downward and is again condensed by the underlying layers of cool shale. The presence of the water vapor just below the advancing face of the carbonizing zone aids materially in giving high yields of ammonia, and is also advantageous in producing a quick cooling of the vapors leaving the carbonizing face with the downdraft. Oil shale containing 15 to 20 per cent of oil or bituminous matter may carry as high as 8 to 12 per cent of water and retains a considerable amount of H_2O even when passed through a drier or preheater or heat exchanger. In the operation of the process as just described, the water naturally present in the shale, though not absolutely essential, is definitely advantageous, instead of being detrimental. In addition to the water or moisture in the shale, some H_2O is formed by the combustion of the returned tail gases and these gases are usually moist in any event; they leave the scrubber saturated with water vapor. It is, however, often useful to add some water with material not naturally carrying much water. The water in the material, or that added, while vaporizing during the process, is largely again liquified; and to this extent the vaporization does not involve any loss of heat units. Using a shale with, say, 10 per cent of water in it, much of this water is extracted from the shale in the present process in the liquid form.

At the base of the column pass away liquid water and liquid oily and tarry products, together with various gases and vapors resulting from the operation. Ordinarily, until the carbonizing and preheating zones approach the bottom of the column of shale, the temperature at this point is around 140–160° F. The gases drawn off at this point are a mixture of the hydrocarbon gases produced in carbonization with producer gas formed by the action of the air on the carbon, and are saturated with water vapor at the temperature obtaining at the base of the column. They carry much oil and water as a fog or fume. Ordinarily, I draw off liquid water and oils into a settling tank for separation and pass the gases through cooling and scrubbing towers, where there is a further recovery of liquid oils. The final gases may be oil-scrubbed to extract uncondensed vapors. The tail gases, or some portion of them, I may send to storage or return directly to the head of the column of shale to furnish the heating downdraft. Where there are several units under the present invention in operation, it is convenient to have them out of phase with each other, so that those furnishing much gas can supply it to those in which the development of gas is insufficient. Ordinarily, I find it better, where plenty of gases are available, to feed more gas than air to the head of the column, thereby giving a downdraft of what may be called a reducing nature; i. e., there is not enough air added to burn all the gas. But, as stated, at some stage of the operation there may not be sufficient gas to do this and in such event, I use such quantity of air as may be necessary to furnish heat and volume of draft gases. The air reacts with residual carbon to give producer gas.

While I have stated that the combustion of the gases takes place above the head of the column of material, yet actually more or less of the combustion may take place in the interstices of the top layers by a sort of "surface combustion" effect. The particular way in which combustion is effected above the column depends to some extent upon the material. Where the material is a shale high in mineral matter of fusible nature, I prefer not to have the combustion temperature go too high; and where the residue left by carbonization contains enough carbon to make it valuable as fuel, as in treating lignites and coals, I cut down the access of air as far as possible to that required for furnishing heat or draft volume. In either event, the presence of a comparatively large proportion of unburnt returned combustible gases is advantageous. Under familiar equilibrium principles, the presence of these gases tends to restrain the formation of like gases in carbonization. And they appear to act to "shield" the oils. Oxidation in the carbonization zone is not desirable.

The oils drawn off at the base of the column and those collected in the various scrubbing devices are distilled in the usual way to obtain commercial oils, gasoline, kerosene, lubricating oil, etc.

As the carbonization of the shale is effected in an atmosphere which contains water vapor, a large proportion of the nitrogen present in the original material reappears as ammonia—I secure excellent yields of ammonia. This ammonia is recovered from the effluent water by the usual processes.

In the accompanying illustration I have shown, more or less diagrammatically, certain apparatus within the purview of my invention and susceptible of use in performing the described process. This view is in central vertical section, certain parts being shown in elevation. In the showing,

Element 1 designates a casing or "generator" of any suitable material, such as brickwork, iron, etc., provided with charging means 2, grate 3 and oil receptacle 4. As shown, the casing is provided at a point above the normal level of solid material therein with air inlet 5 and gas inlet 6. At the bottom the casing is tapped by outlet pipe 7 leading gases and condensed liquids away. The liquids pass to separator 8 shown as provided with internal baffles where the oil and water are separated; each being withdrawn for suitable treatment elsewhere; the oil to be distilled and the water going to an ammonia separator. The gases in line 7 pass by branch 9 to water cooled condenser 10, where there is a separation of further oil and water, which may go back to 8 through valved outlet 11, or to similar separating devices. The cooled residual gases are withdrawn by suction fan 12, which produces suction on the whole line, and usually sent to a second water cooled condenser, indicated at 13. Where ammonia is to be recovered, as is generally the case, I next pass the gases through one or more ammonia scrubbers of the usual type. One is shown as 14. Ordinarily, I finally pass the gases through an oil scrubber or absorption tower 15. Tail gases leave this scrubber through pipe 16, as much as may be wanted being returned for the operation through valved pipe 17 forming the continuation of inlet 6 previously alluded to. Branch pipe 18 may be provided leading to gasometer means (not shown) for storage purposes or for averaging out fluctuations.

In the operation of the described device on oil shale, the "generator" may be filled with shale to the normal level marked A, and gas and air supplied to the top of the casing to produce a hot downdraft under the influence of suction from fan 12. They may of course be supplied under pressure, if desired. The hot downdraft of burning gases initiates a transverse zone of carbonization which travels steadily downward. In the drawing, I have indicated this traveling transverse layer somewhat below the top as B. Below is a drying and preheating zone which I have indicated as C. As the zone of carbonization travels downward, the hot draft gases passing ahead of it preheat and dry the material in zone C, and pass on into the untreated or cool shale below; this cooler layer being indicated as a whole by D. Here the gases drop their moisture, tar and oils, which trickle downward. This action continues until the zone of carbonization approaches the bottom of the column—zone D always remaining at a temperature somewhere below 212° F. until this time. When the zone of carbonization reaches grate 3, the operation is interrupted and the residual ash or coke (as the case may be) removed in any suitable manner. In the case of oil shale, the residue is usually of little heating value, but in treating lignites and the like, it is of considerable fuel value. The present invention is particularly applicable to these lignites, since it permits of the removal of much of their water in liquid form, i. e., without the consumption of heat incident to drying, or complete drying, in the usual ways.

While I have described the use of combustible gases arising from the operation itself, they may of course be replaced or supplemented by combustible gases from other sources, such as natural gas. As a component of the downdraft, natural gas, which is largely methane, has some advantages. The operation as shown and described is discontinuous; successive batches of shale being treated in the generator; but apparatus may be provided enabling the operation to be made continuous.

What I claim is:—

1. In the low temperature carbonization and distillation of shale and the like, the process of producing a controlled rapid low temperature carbonization which comprises initiating, maintaining and controlling a downwardly advancing zone of low temperature carbonization and distillation in a moist column of material by a downdraft of hot gases therethrough, said gases comprising returned combustible gases, arising from the operation, burning with admixed air and control of the advance of the zone being effected by regulation of the amount and proportion of the said gases and air.

2. In the low temperature carbonization and distillation of shale and the like, the process which comprises initiating, maintaining and controlling a downwardly advancing zone of low temperature carbonization and distillation in a moist column of material by a downdraft of hot gases therethrough, said gases comprising returned combustible gases arising from the operation, burning with admixed air in amount insufficient for their combustion and control of the advance of the zone being effected by regulation of the amount and proportion of the said gases and air.

3. In the low temperature carbonization and distillation of shale and the like, the process of producing and maintaining a regulated rapid low temperature carbonization and distillation which comprises transmitting downwardly through a pervious moist column of shale a burning draft of combustible gases and air, regulation of the carbonization being effected by control of the amount and proportions of such gases and air so burning.

4. In the low temperature carbonization and distillation of shale and the like, the process which comprises transmitting downwardly through a pervious moist column of shale a burning draft of combustible gases and air to give an advancing zone of carbonization and distillation; the bottom of the column being maintained at a temperature not above 212° F. until just before the downwardly advancing zone of carbonization approaches it and an intermediate zone of preheating and drying between the advancing face of the carbonizing zone and the portion of the column at a temperature not above 212° F. being maintained by suitable adjustment of the air and gases so introduced.

5. The process of carbonizing oil shale or the like in a closed vertical chamber which comprises initiating or setting up a zone of gaseous combustion above a body of shale in said chamber to initiate and maintain a zone of carbonization in said chamber and causing said zone of carbonization to progress downwardly through the column or body of shale in said chamber.

6. The process of carbonizing oil shale or the like in a closed vertical chamber which comprises initiating or setting up a zone of gaseous combustion giving a body of flaming gases of reducing nature, above a body of shale in said chamber to initiate and maintain a zone of carbonization in said chamber and causing said zone of carbonization to progress downwardly through the column or body of shale in said chamber.

7. The process which comprises initiating a zone of gaseous combustion at the top of a body of shale in a closed chamber, and setting up a downdraft of the products of said combustion through the body of shale, whereby a zone of carbonization is caused to progress through said body.

8. The process which comprises creating a zone of gaseous combustion by burning a mixture of air and gas in the top of a closed chamber containing a body of shale, causing the resulting flaming gaseous products to pass downwardly through said body, drawing off and treating in the usual way the condensed and uncondensed products of distillation from the bottom of said chamber, and returning some of the uncondensed gases in the form of combustible gas to the top of said chamber to maintain said zone of gaseous combustion.

9. The process of extracting oil from shale and the like which consists in creating a zone of gaseous combustion above a body of shale in a closed chamber, causing a downward draft of the products of said zone of combustion through the body of shale, recovering the distillation products from the bottom of said chamber, and returning some of the gaseous products to said zone of combustion therein.

10. In the low temperature distillation and carbonization of shale, the process which comprises introducing a burning mixture of combustible gas and air above a vertical pervious column of shale having a moist base and passing said mixture downwardly therethrough and thereby initiating and propagating a downwardly moving zone of carbonization and distillation with a substantial zone of preheating and

drying between said carbonization zone and said moist base until just before the advancing face of the carbonization zone reaches the bottom of the column, the heating action of the burning mixture and its volume being balanced against the cooling action of the moisture and liquids in the line of propagation to control the progress of the carbonization zone and to preserve a substantial zone of preheating and drying.

In testimony whereof, I have hereunto affixed my signature.

GEORGE WIGHTMAN WALLACE.