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METHOD OF HEATING COKING RETORT OVENS WITH ENRICHED MIXTURES OF FUEL GAS

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The present invention relates in general to improvements in the heating of such combustion apparatus as coke ovens, and is more particularly concerned with the heating of those coke ovens which, by reason of their design, construction, or provided features of equipment, are restricted for their effective heating solely to fuel-gases of relatively higher calorific values; for example coke-oven gas, or its equivalent.

In the heating of coke ovens that do not belong to the so-called "combination" class, in consequence of their lacking, for example, either regenerators or combustion-media flow-passageways adequate to supply, to the heating flames, fuel-gases of low calorific values at a rate requisite for their effective heating, merely lacking equipment for distributing fuel gas of low calorific value to existing regenerators, circumstances frequently arise making it not only desirable, but urgently necessary, to heat such coke ovens, if only periodically for a limited period, with an extraneously derived fuel-gas that, by reason of the above-referred limitations of the coke ovens, must belong to those characterized by their relatively high calorific values. An instance where, for example, such circumstance can become particularly critical is in those populous districts where coke-oven gas serves as the exclusive source of industrial and domestic heating. If the coke-oven installation for supplying such district constitutes solely coke ovens of the above-stated type and there is only a limited capacity of productive reserve, serious situations can arise when gas-distribution demands reach or exceed for any considerable period the daily or seasonal demands the coke ovens are adapted to meet. Since the distributed gas must be kept relatively constant in respect to such properties as, amongst others, calorific value and specific gravity, because the usual appliances, or the existing settings thereof throughout the district for burning the gas, are relatively limited in their effective tolerance of fluctuations in these characteristics, the utility of any of the usual low calorific value fuel gases, such as producer- or blast-furnace gas, for meeting the increased demand, is, even in the event there were a source of supply, thus precluded either for purposes of oven heating or for any extensive dilution of the coke-oven gas to be distributed because, for the latter purpose, it is so radically different from coke-oven gas in respect of calorific value and specific gravity. In view of the foregoing, there is in the art obviously a need of a flexible method and means whereby coke ovens not of the combination type can be cheaply and quickly converted from their heating with coke-oven gas to one employing an extraneously derived gas of similar or greater calorific value, thereby releasing their usual requirement of the former said gas, with its requisite physical properties, for delivery to the district to be supplied.

An object of the present invention is the provision of cheap, novel, and effective method whereby coke ovens requiring for any reason a fuel gas of high calorific value for their effective underdriving can be easily and quickly converted from a heating with coke-oven gas itself to a heating with an extraneously derived fuel-gas of the same or equivalent heating characteristics, thereby releasing for useful purpose the coke-oven gas otherwise requisite for their heating.

Natural gasoline is a liquid petroleum product consisting of the heavier hydrocarbons present in natural gas and extracted therefrom by such means as compression, absorption, and other processes. One of the grades of natural gasoline available, for example, on the market in ample supply at a relatively reasonable price is a so-called 37-70 natural gasoline. It contains as important ingredients quantities of aliphatic hydrocarbons containing from five to seven carbon atoms in their molecular constitution. These substances have at 60° F. individually in pure form, respectively, a partial pressure less than atmospheric and of from about one-half to seven pounds per square inch absolute. They are thus rather volatile but are easily storable even in the hottest summer weather in containers having walls of moderate thickness. When they are dissolved in hydrocarbons having higher molecular weights their pressures are accordingly reduced. They are per se, however, of relatively limited utility in the usual hydrocarbon market, being to limited extent employed to lower flash-points of motor fuel for winter use but are usually disposed of by their extensive chemical alteration; for example, by polymerization.

It has now been demonstrated in the practice that these Cs to Cs aliphatic hydrocarbons are themselves of important economic value, when in dispersion in a carrier gas, for the underdriving of coke ovens. Sufficient quantity thereof are dispersible in an inert carrier gas or in combustion media of low calorific value, to form a fuel gas having a calorific value equal to and even greater than coke-oven gas, without their dew-point at such calorific values being reached during distribution of the resultant gaseous mixture, under ordinary operating conditions, to the coke ovens. As a carrier-gas, there may be employed
blast-furnace gas and producer-gas, which normally require preheating to at least about 1700° F. for effective coke-oven heating, and air, combustion-products, or the like, can be also used for the purpose.

Ordinarily, it is preferred to buy the said hydrocarbons in the form of a solution; for example, the above-mentioned natural gasoline, or a 26–70 natural gasoline, wherein they are present in major proportion; these natural gasolines are common refinery products and are readily available on the market; they are preferred principally because of ease of storage and relatively low transport risk, the said C₅ to C₇ hydrocarbons being then removed from their said solution at the coke-plant site by simple fractionation, and thereafter directly used.

For the present purpose it has been found practical to remove the said C₅ to C₇ hydrocarbons by a continuous fractional distillation of the employed natural gasoline, the C₅ to C₇ hydrocarbons being removed as overhead vaporous product and, while not necessarily, they are, for obtaining all advantages of the present improvement, in such vaporous form intimately admixed with the chosen carrier-gas in that proportion which produces a mixed fuel-gas having the preferred calorific value. It is in this wise relatively simple continuously to produce the novel fuel-gas of the present invention with a substantially uniform calorific value that can be even considerably higher than ordinary coke-oven gas without normally exceeding the dew-point of the C₅ to C₇ components thereof. The resultant novel fuel-gas is then distributable to the usual fuel-gas distribution system of the coke-ovens wherein it can be employed in the usual fashion of fuel gases that do not require regenerative preheating for their effective combustion therein. All coke-oven gas produced in the coking chambers is thus released for other commercial uses.

The required equipment, by which the said C₅ to C₇ hydrocarbon fraction can be separated from the natural gasolines, is simple and requires a relatively small investment especially in view of the greater economic value of the coke-oven gases which can be released for other purposes.

In the accompanying drawings forming a part of this specification and showing for purposes of exemplification a preferred apparatus and method in which the invention may be embodied and practiced but without limiting the claimed invention specifically to such illustrative instance or instances:

Fig. 1 is a diagrammatical elevational view of apparatus for practicing the present invention, and showing also in vertical section crosswise thereof, a coke-oven battery wherein the present improvement can be advantageously practiced; and

Fig. 2 is a vertical section taken longitudinally of the battery along line II—II of Fig. 1.

The same characters of reference designate the same parts in each of the views of the drawings.

Referring now to the drawings, particularly to Fig. 1, tank 11 serves as a storage container for the natural gasoline received at the plant and for the reserve supply of said gasoline to the header described separating plant and the subsequent gas-mixing apparatus. Because of the relatively low vapor pressure of the said natural gasoline at normal atmospheric temperatures, the said storage tank 11 can be of the strength usually employed for gasoline storage, and a high-pressure tank is not required. Connected to said storage tank 11 is a discharge pipe 12 through which a predetermined flow of the said natural gasoline is withdrawn by a metering pump 13. The natural gasoline is pumped by the said metering pump, through pipe 14 and column-inlet pipe 15, which is equipped with thermostatically controlled automatic valves 16 and 17, respectively, into fractionating column 20. Inlet pipe 15 connects into the said column 20 at a point near the bottom thereof, and inlet pipe 16 is connected at approximately the middle of said column. The inflow of natural gasoline can thereby be directed into either the middle section or the bottom of the column, or, in predetermined ratio, to both, the rate of flow thereto being automatically controlled by a thermorestat 21 that is connected to both automatic valves 16 and 17, and is located at approximately the midpoint of the column. By such proportioning of the charge to two points in the column the relative quantities and the range of molecular weights of the hydrocarbon constituents of the overhead fraction and bottoms residue can be closely controlled.

The fractionating column 20 is a Raschig-ring packed column comprising: an indirect steam-reheater 22 with its thermostatically controlled inlet valve 23, a free space 24, which is between a lower section of packing 25 and an upper section 26, and receives the natural gasoline charged into the column through the said pipe 16 for its vaporization; and a set of water-cooled coils 27 disposed in the topmost section of the said column 20, and serving for cooling reflux therein. Beneath said lower section of packing 25 and at a level sufficient to cover the said reheater 22, there is maintained a constant volume of bottoms fraction by means of a liquid-level control 28, which automatically controls a valve 29 in bottoms discharge pipe 30. The said bottom discharge is directly connected to a bottoms pump 31 which pumps the bottoms fraction through pipe 32 into a bottoms cooler 33, that is disposed in said line 32, whence they flow into storage tank 34 and from which the bottoms fraction can be directed to any desired destination. It is also feasible to employ a spring-operated valve in the said discharge pipe 30, and to set such a valve at a pressure slightly higher than column pressure, in order to prevent bottoms fraction flowing through the said pump 31.

Any over-head fraction of up to and including C₅ hydrocarbons which is separated in vapor phase from the charged crude natural gasoline, by the above-described fractionating means, flows from the top of the column through a vapor line 35 in which is disposed pressure-regulator valve 36 for maintaining a constant pressure on the said column 20, to a Venturi inspirating mixer 37 whereby it is intimately mixed with the employed carrier-gas, which is delivered from appropriate supplying means through pipe 37a into gas-holder 38 thereof. The said carrier-gas flows through pipe 39 into the said Venturi inspirating mixer 37. The said carrier-gas and vaporous hydrocarbons are delivered into the said Venturi mixer in such relative positions that, irrespective of their respective pressures in said lines 32 and 39, their rapid and thorough mixing is assured.

The resultant novel fuel-gas, comprising said intimate admixture and issuing from the Venturi mixer 37, is flowed thence from through pipe 40 into
indirect steam-heater means 41 having the conventional steam coils 42 and inlet and outlet steam pipes 43 and 44 respectively. Thence the heated, novel fuel-gas is drawn from the said heater through pipe 45 by a booster pump 46 whereby it is pumped through fuel-gas delivery pipes 47, gas-distribution headers 48 at either coke-oven battery side, and manifold pipes 49, as shown by the arrowed lines, to the heating flues of waste heat coke-oven battery 50 of which a vertical cross section, taken longitudinally through an oven, is shown in Fig. 1, and a vertical section, taken longitudinally of the battery, is shown in Fig. 2.

The said waste-heat coke-oven battery 50, illustrated herewith for purpose of example only as representative of the class of combustion apparatus wherein the present improvement can be advantageously employed, is of the type having horizontal heating flues 55 and simple passages ways adjacent below the oven soles for recuperatively preheating combustion-air. The flow of air is indicated on the drawing by simple arrows; it enters the battery structure through tunnel-like sub-soles passages ways 52, whence it passes into and along sub-soles flues 53 and at the outlet ends thereof divides and returns in reverse flow at a higher level in those parallel flues 54, 55, that extend longitudinally of the ovens on each side of each of those sole flues 55 whereby combustion-products are delivered from the oil-heating flues 50 to waste heat tunnel 56. From each of the parallel flues 54 the preheated air rises up through take flues 55 which are so branched as to supply such air through ports 58 individually to each end of each of the superposed horizontal heating flues 59, of adjacent oven-heating walls of adjacent coke ovens 60.

The fuel-gas of the present improvement is supplied at one end only of each horizontal flue by a nozzle 61, the nozzles for the heating flues at one end of each wall being supplied by a manifold pipe 49. The said gas flows under the influence of stack draft along the said horizontal heating flues 55, burns therein with the said adjacenty delivered preheated air from ports 58, and the combustion-products for all the flues of the heating walls enter sole flues 55 through sole flue bull's eyes 63 and leave the battery through passages ways 54 and waste heat tunnel 65. The flow of collected combustion-products just prior to leaving the battery is indicated in the drawing by circled arrows.

In one example of battery operation in accordance with the present improvement, approximately 127 B. t. u. producer gas, having a 0.9 specific gravity, was continuously mixed in the diagrammatically shown apparatus with the top fraction of a natural gasoline to produce the present new fuel-gas which had an average heating value of 800 B. t. u. per cubic foot under standard conditions. The natural gasoline employed was of the grade which is termed 31–70 natural gasoline, that is, one having a vapor pressure of thirty-one pounds per square inch absolute at 100° F. and of which 70% distills at 140° F. The 31–70 natural gasoline that is available as a commercial product in the market under that designation varies in composition, its A. P. I. gravity, for example, ranging from 83 to 94; it contains variable minor proportions of low boiling butane, and the like, which are frequently disposed of in said trade products. Despite such variations it was possible with the illustrated apparatus simple and continuously to produce the present new fuel-gas with substantially the same heating characteristics at all times.

The above employed natural gasoline was continuously pumped at an average rate of seven gallons per minute by adjustable metering pump 12 into the illustrated fractionating column 50 which was operated under a vacuum-temperature of approximately 15 pounds per square inch gage. Therein the said gasoline was continuously separated into an overhead fraction that constituted 80% of the charge, over 80% of said fraction comprising aliphatic hydrocarbons having five to seven carbon atoms in their molecular constitution. The bottoms residue consisted substantially only of some heptane with the heavier hydrocarbons. The temperature of the heavier hydrocarbons in the re-boiler 22 in the base of the column was continuously maintained at about 240° F. by thermostatically controlled automatic operation of the supply of steam to the heating coils therein.

The vapors leaving the top of the column were maintained at a temperature of about 140° F. by means of the cooling coils 47.

From the top of the column these vapors passed to the Venturi mixer 37 wherein they were admixed with producer-gas from holder 38 in such proportion as to produce the new fuel-gas having a calorific value of substantially 800 B. t. u. per cubic foot, under standard conditions, and having a dewpoint in respect of the admixed hydrocarbons less than 0° C.

The so-formed new fuel-gas was then warmed in heater 41 merely to prevent condensation of water therefrom, contained in the carrier-gas, by cooling during its transmission to the ovens, and was thereafter flowed under pressure from booster pump 46 to the ovens where it was burned in the heating flues. Hydrocarbon vapors representing about 7,600 gallons of liquefied hydrocarbon fraction per day were burned in the oven flues of the illustrated battery. This new gas released approximately 1,400,000 cubic feet of coke-oven gas per day for other purposes.

In a second example of operation wherein two coke-oven batteries of the type described were heated by the fuel-gas of the present improvement, four million cubic feet of coke-oven gas per day were released to consumers' use. The fuel-gas was formed by mixing producer-gas and the vapidous hydrocarbons as above described; it had a calorific value of 800 B. t. u. per cubic foot under standard conditions. During winter operation the atmosphere temperature reached −10° F., and yet no hydrocarbon condensate was found in the gas transmission pipes for said gas mixture.

One of the special advantages of the present process resides in the fact that the special carbonaceous hydrocarbons are continuously prepared as required in vapor form in situ and are immediately introduced, without any condensation step thereafter, into the carrier-gas. There is thus no opportunity, after their separation from the natural gasoline, for them selectively to evaporate into the carrier-gas and give a resultant fuel-gas product that varies from time to time in its calorific value due to the tendency of lower-boiling constituents preferentially to evaporate. This latter disadvantageous circumstance is especially apparent in any procedure where liquid mixed hydrocarbons are vaporized by their contact with a carrier-gas.
In the above-given examples, producer-gas has been employed as the carrier-gas; the present improvement is not however limited thereto and, in fact, it may often be found preferable to employ air, combustion-products, or blast-furnace gas, for the purpose. For example, an 800 B. t. u. per cubic foot gas formed by admixing air and the C3 to C1 natural-gasoline hydrocarbons is a non-explosive mixture.

The invention as hereinabove set forth is embodied in particular form and manner but may be variously embodied within the scope of the claims hereinafter made.

I claim:

1. In coke-oven operation, heating said coke oven with a fuel-gas, by the steps of: storing in liquid state at the coke-oven site a natural gasoline, withdrawing and fractionally distilling as a product from the stored natural gasoline a vaporeous stream of a hydrocarbon mixture comprising the hydrocarbons of the natural gasoline having up to six and seven carbon atoms in their molecular constitution, admixing a stream of a carrier-gas, chosen from the group consisting of air, blast-furnace gas, producer-gas, and combustion-products, with a vaporeous stream of the hydrocarbon mixture separated from the natural gasoline as product including hydrocarbons having up to six and seven carbon atoms in their molecular constitution, the rate of said admixing being such as to provide a carrier gas admixture of a calorific value effective to heat said coke oven but insufficient to raise the dewpoint temperature of the so-formed admixture above a temperature point reached therein during its traversal of a distribution system to the heating flues in said coke oven; applying heat to said admixture to maintain the temperature thereof, during its traversal to said coke oven, above the dewpoint temperature with respect to the condensible constituents of said admixture; and continuously delivering said admixture as fuel-gas from the distribution system to heating flues of said coke oven battery without preheating for combustion for effecting coking aforesaid and burning the same therefrom in quantity to generate the heat required for coking charges in the coke chambers of said battery.

2. In coke-oven operation, generating the heat for coking oven-charges in a masonry coke-oven battery comprising coke chambers and contiguous heating walls therefor comprising combustion flues, by the steps of: storing in liquid state at the coke-oven site a natural gasoline having a vapor pressure of about one atmosphere and of which about 70% distills at 140°F; withdrawing from said storage and fractionally distilling the natural gasoline so as to separate therefrom in vaporeous form a mixture of hydrocarbon compounds containing substantially all of the hydrocarbons up to, and including also hydrocarbons having seven carbon atoms in their molecular constitution while leaving as bottoms substantially only heavier hydrocarbons; admixing the so-separated hydrocarbon mixture with a carrier-gas chosen from the group consisting of air, blast-furnace gas, producer-gas, and combustion products, and in proportion to provide a mixture having a calorific value sufficient to generate by its combustion in the combustion flues in the heating walls of contiguous coke chambers in the masonry coke-oven battery aforesaid, the heat required for coking oven-charges in the oven chambers contiguous to the heating walls but insufficient to raise the dewpoint temperature of the so-formed admixture above a temperature point reached therein during said admixture traversal of a distribution system therefor to the combustion flues in the heating walls of said masonry coke oven; maintaining heat in said admixture to maintain the temperature thereof during its traversal to said coke oven, above the dewpoint temperature with respect to the condensible constituents of said admixture; flowing the admixture through a distribution system therefor to the combustion flues in the heating walls of contiguous coke chambers in the aforesaid battery; delivering said admixture as fuel gas from the distribution system to the combustion flues in the heating walls of said masonry coke-oven battery without preheating for combustion for effecting coking therein; and burning the same therefrom in quantity to generate the required heat for coking oven-charges in the coke chambers contiguous to the heating walls fed by said gas mixture.

4. The method of operating a masonry coke-oven battery, comprising coke chambers and contiguous heating walls therefor comprising combustion flues, which involves: storing a mixture of hydrocarbons of natural gasoline having from five to seven carbon atoms in their molecu-
lar constitution, and having at 60° F. individually a partial pressure less than atmospheric, in liquid state at the coke-oven plant site in a container of the strength not greater than that usually employed for gasoline storage; withdrawing and introducing the same in measured quantities in vapor form into a carrier-gas of the group consisting of air, blast-furnace gas, producer-gas, combustion products, in proportion to form a fuel-gas mixture having a dewpoint in respect of the hydrocarbons less than 0° C., and a calorific value of substantially 800 B. t. u. per cu. ft. effective to generate the coking heat required for coking oven-charges in said oven battery when burned in the combustion flues therefor without substantial preheating of the gas mixture therefor; distributing the fuel-gas mixture to the combustion flues of the aforesaid oven battery in proportionate amounts required through a fuel-gas distributing system therefor comprising headers, manifolds, and nozzles leading to the individual combustion flues that are primarily designed and adapted for feeding solely thereto, optionally, the proportionate quantities of coke-oven gas that the oven-chambers themselves generate, and are required to meet the underliring requirements in said combustion flues: applying heat to said admixture to maintain the temperature thereof, during its traversal of the distribution system to the heating flues in said coke oven battery, above the dewpoint temperature with respect to condensible constituents of said admixture; and burning said fuel-gas mixture in said combustion flues as thus fed thereto in the proportionate amounts required to meet the underliring requirements of the individual combustion flues.

5. In coke-oven operation, heating said coke oven with a non-regeneratively-preheated fuel-gas, by the steps of: withdrawing from reserve, in liquid state, at the coke-oven plant site and heating to vaporize a mixture of hydrocarbons containing up to and including hydrocarbons having seven carbon atoms in their molecular constitution; continuously flowing the heated vaporous mixture of hydrocarbon compounds containing up to and including hydrocarbons having seven carbon atoms in their molecular constitution, into admixture with a producer-gas having too low a calorific value effectively to heat said coke oven without a regenerative-preheating step for said producer-gas, and in proportion to provide the producer-gas with a calorific value effective to heat said coke oven but insufficient to raise the dewpoint temperature of the so-formed admixture above a temperature point reached therein during its traversal of a distribution system to the heating flues in said coke oven; applying heat to said admixture to maintain the temperature thereof, during its traversal to said coke oven, above the dewpoint temperature with respect to the condensible constituents of said admixture; and continuously delivering said admixture as fuel-gas to heating flues of said coke oven without a regenerative preheating step and burning the same therein.

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