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METHOD OF HEATING AND FLUIDIZING FOR A
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1 Claim. (Cl. 202—14)

This invention relates to the carbonization and destructive distillation of carbonaceous solids, particularly coking coals. More particularly, it refers to improvements in methods of processing finely divided coal, while it is suspended in a liquid or gaseous fluid, in such processes as carbonization, complete gasification, producer gas operation, coal hydrogenation and liquefaction, or production of feed gases for hydrocarbon synthesis.

The coking or gasification of coal may be handled with improved facility by suspending finely divided coal in a fluid so that a bed of dispersed solids will be maintained in a reaction zone and each coal particle will be separately supported in the fluid. In some processes, such as coal hydrogenation, the finely divided coal can be suspended in a liquid such as an oil. In others, finely divided coal is supported in a gas stream and is thus caused to form a turbulent, dense phase bed of fluidized coal particles through which flows the supporting gas stream. The aforementioned fluidized beds exhibit, as is well known, the characteristics of a liquid and consequently are easily handled.

When a coking coal is heated to a temperature within its plastic range it becomes somewhat plastic and sticky, sometimes expands, and in a fluid bed it immediately agglomerates. The formation of these agglomerates interferes drastically with the maintenance of the fluid bed and usually makes it impossible to maintain fluidization. The difficulty of maintaining a fluid bed of coking coal at temperatures within its plastic range is so crucial that investigators have resorted to introducing into the bed inert finely divided solids in volumes from 15 to 30 times the volume of the fresh finely divided coal in order to keep separate the sticky coal particles and prevent their coherence and defluidization. The obvious expense of this expedient demonstrates the seriousness of the problem.

Similarly, the swelling and stickiness exhibited by coking coals during heating causes a swelling and agglomeration and undesirable increase in viscosity when such coal is dispersed in a liquid. The difficulty in the latter case has been such that in present experimental operations there has been devised a method of rapidly increasing heat supply to coal-oil suspensions while passing through the plastic range (about 285° to 325° C.) so as to raise the temperature from 285° to 350° C. as quickly as possible. As reported by Hirst and Chaffee, *Industrial and Engineering Chemistry*, vol. 41, No. 5, 1949, p. 872, this rapid heating of plastic coal reduces the danger of coking, swelling, and equipment failure.

The primary object of this invention is the elimination of the above described difficulties in the utilization of coking coals at elevated temperatures. It is an additional object of the invention to provide an improved method of carbonizing coal in a fluidized bed. Other objects will appear in the following specification and in the claims hereinafter made.

The described difficulties can be eliminated and the stated objects readily accomplished by the simple method

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of subjecting finely divided coal, preferably while in a fluidized state, to a treatment comprising contacting the said coal with oxygen or an oxygen containing gas at temperatures between about 80° and 300° C. and for a time which can range from a few seconds to an hour or so depending upon the employed temperature, the particle size of the treated coal, and the degree of treatment desired. This treatment effects a surficial oxidation of the coal particles and an apparent reaction with certain more active constituents in the coal. Coal treated by this process can be heated to coking temperatures and above without agglomeration or excessive swelling of the coal. Fluidization of coal in a gaseous medium can be readily maintained, and fluid coal-liquid mixtures exhibit substantial elimination of increased viscosity difficulties, and the like.

Absorbed oxygen even at low concentrations alters the coking properties of the coal and at increased concentrations destroys the coking property entirely. While coal will vary considerably in its coking characteristics and in the effect which absorbed oxygen will have on it, about 0.2% of absorbed oxygen by weight based on the weight of the coal will exhibit some deterioration of coking quality. The maximum amount of oxygen that need be absorbed by a coal or reacted therewith in order to destroy entirely the coking property of the coal is about 2.6% by weight of the coal. In general, however, the cohering property of even strongly coking coals will be destroyed by the absorption of, or reaction with, about 0.8% of oxygen based on the weight of the coal.

The pretreatment of coals with oxygen or an oxygen-containing gas is most effective when employed with finely divided coals and preferably the coal to be treated should be so pulverized that about 80% of it will pass through a one-eighth inch screen. Increased comminution of the coal to sizes ranging from, for example, 100% through a 10 mesh to 100% through a 100 mesh screen (U. S. Bureau of Standards, Standard Screen Series 1919) will greatly increase the effectiveness of the treatment.

The temperature of the pretreatment largely controls the rate of oxidation of the coal. The maximum employable temperature is one just below the softening point of the coal being treated. Although the softening point of different coals varies somewhat, it generally falls within the range of about 285° to 325° C. The minimum temperature is one that will provide an adequate effect in a practicable length of time. At 110° C. a coal, which will substantially entirely pass through a one-eighth inch screen, will lose one-half its coking property in fifty minutes. Inasmuch as it is usually unnecessary to destroy the coking or agglutinating property of the finely divided coal to that extent, lower temperatures, for example, 80° C. can be employed for an equivalent length of time or a shorter time period of, for example, about 5 to 10 minutes can be effectively utilized. Thus, pulverized coal is preferably treated with air or oxygen at temperatures between about 150° and 285° C. for periods between about 5 and 50 minutes. Higher temperatures within the range are most suitable for continuous operation because at the higher temperatures near the softening temperature of the coal a contact time of only a few seconds may sufficiently reduce agglomeration of fluidized coking coal to permit fluid carbonization.

The rate of oxidation decreases rapidly with time and consequently rapid treatment is most efficient and the first few moments of contact are the most effective. Nevertheless, coals which already contain an appreciable content of oxygen and are found to be weakly coking will absorb oxygen rapidly and will lose coking strength more rapidly than low-oxygen coal.

Fluidization of the coal particles and treatment of the coal in a fluid bed through which is passed the oxygen

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bearing gas is a particularly advantageous method of carrying out the present treatment. The turbulence of such fluid beds provides that the particles are rapidly changed in position and provide uniform temperature level throughout the bed. Fluid bed operation is particularly adaptable to continuous operation. Heated air can be passed into a fluid bed contained in a heated or insulated chamber and the gas will pass through the dense zone constituting the said fluid bed, through a settling zone of greater cross section and lower gas velocity, and then through a cyclone separator or the like where remaining solids are separated from the gas stream and returned to the said bed. The hot air is preferably recycled (at a rate of at least about 4 volumes of recycled air to that of fresh feed) to the fluid bed as only a very small content of the oxygen contained therein will be consumed with each pass. Make-up oxygen or air can be added to the cycle stream at a rate that will maintain a high enough oxygen content to insure a favorable equilibrium condition in the reactor. The fluid bed is preferably supported in a concurrently flowing gas stream, and superficially oxidized coal is preferably removed as overflow from the top of the bed. The larger coal particles will tend to remain for a longer time in the fluid bed and, by absorbing more oxygen, compensate for a smaller relative surface area.

Partially oxidized coal can be drawn off from the fluid bed and pretreater and thereafter be directed to carbonizing apparatus, to an oil paste mixing step, or to a total gasification step for the preparation, for example, of hydrocarbon synthesis feed gases.

A process according to the present invention in which coal is carbonized is described with relation to the accompanying drawing, the single figure of which is a diagrammatic sketch of a flow diagram of the coal carbonization process.

Referring now to the drawing, particulate coal which has been crushed to a size that will pass through a 50 mesh screen is transported by means of belt 7 or like conveying device into a storage bin 8. Finely divided coal in the bin 8 flows through downcomer pipe 9 and can be fluidized by a gas introduced through line 10 in which is disposed control valve 11. Fluidized coal flows through the said downcomer 9 having disposed therein gate valve 12 which governs the rate of introduction of the coal through line 13 into a pretreater 14. The pretreater 14 contains a dense turbulent bed of finely divided coal that is fluidized in a concurrent stream of hot air. The air is pumped by a blower 15 through a line 16 and a heater 17 or suitable means for heat interchange wherein the air is heated to a temperature between about 160° to 200° C. The heated air is flowed through line 18 and is introduced into line 13 wherein it admixes with and fluidizes coal being fed into the pretreater. The said heated air flows through the fluid bed maintained in the pretreater 14 and leaves the surface of the said turbulent bed passing into an upper dilute phase 20, wherein the air is separated from the said fluid bed. The heated air passes through a cyclone 21 wherein suspended solid particles carried over with the gas stream are separated therefrom and are returned through the leg 22 of the cyclone into the said fluid bed. Separated air passes through line 23 from which excess gases can be bled through valved line 24. The heated air is recycled through line 25. The excess gases which are bled through line 24 can be instead employed in heat interchange or as a source of primary air in combustion apparatus.

Partially oxidized coal which has absorbed about 0.3% oxygen and been in contact with heated air for a period of from about one to ten minutes flows from the said pretreater 14 through a fluidized downcomer pipe 26 that is fitted with an aerator jet 27 having a valve 28. The fluidizing medium introduced through jet 27 can be any inert gas but is preferably steam or flue gas. This gas is introduced through the said jet pipe 27 at an adequate

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pressure to maintain a column of fluidized coal in a standpipe 29 and a back pressure adequate to form a seal against the flow of air from the pretreater 14 into subsequent carbonizing apparatus.

The fluidized coal rises in the standpipe 29 and overflows therefrom into the upper, dilute phase section 30 of a continuous retort 32. Retort 32 consists of a coking chamber 33, insulated walls 34 and concentric flue 35. The flue 35 extends along the vertical axis of the retort at the center thereof. At the top of the central flue, passages 36, indicated in dotted lines on the drawing, convey hot combustion gases from the central flue 35 to outer concentric flue 35a. Fuel gas and air pass upwardly through the inner flue 35 and the hot gases of combustion or flue gas can be caused to flow through ports 37 arranged concentrically around the base of the coking chamber 33 by opening or closing sliding brick, not shown. This portion of the flue gas serves to fluidize the pulverized coal in the concentric coking chamber 33 and also to introduce heat directly therein. The remainder of the flue gas flows from the concentric flue 35a through outlet line 38 and a portion thereof can be used to fluidize the coal in standpipe 29. The flue gas can be vented or the heat thereof can be employed in heat interchange or like conventional operation. If in any particular operation it is necessary to avoid entirely dilution of the effluent coke-oven gas, a portion of this gas can be recycled from the by-product gas stream and be used to fluidize the coal in the retort. In such a case substantially all the coking heat will be obtained indirectly from the flues and oven walls. Dilution of the coke-oven gases with other non-condensable gases can also be avoided by fluidizing the particulate coal in steam. Steam can also be used not only to fluidize the coal but, when superheated, to supply part or the entire requirement of coking heat.

A fluid bed of finely divided partially oxidized coal is maintained in the said coking chamber 33 at temperatures ranging from 480° to 1200° C. Gases evolved during carbonization of the fluidized coal aid in its fluidization. These gases pass into the upper dilute phase section. The evolved carbonization gases pass through line 40 into a cyclone 41 wherein entrained solid particles are substantially completely separated therefrom. The hot carbonization gases flow from the cyclone 41 through a line 42 to conventional by-product recovery apparatus 43 that is merely indicated on the drawing. Coke-oven fuel gas flows from the by-product recovery apparatus 43 through a line 44 from which a portion thereof is directed through a line 45 in which is disposed valve 46 and burner 47. Burner 47 is disposed in the base of the inner concentric flue 35 of the continuous retort 32.

Coke is withdrawn from the concentric coking chamber 33 through a passage 50 having disposed therein a gate valve 51 or like means for releasing the carbonized coal and permitting flow through the said passage 50.

Where, by the process of invention, the agglutinating power of coking coal has been greatly reduced or destroyed, coking can be simply performed by passing the fluidized treated coal in a gas stream through an externally heated coil.

The finely divided coke produced by the process can be used for any one of the several purposes well known to the prior art. For example, it can be used as a fuel and the sensible heat of its ash can be used in fluid state by means of heat interchange. The coke can be completely gasified in produced gas apparatus, or it can be employed in the production of hydrocarbon synthesis feed gas.

In an example of operation according to this invention, a Pocahontas coal having a volatile matter on a dry basis of 20%, a fixed carbon of 70% and 5% oxygen by ultimate analysis is crushed and screened so as to provide a comminuted coal, all of which will pass through a 10 mesh standard screen. The coal is fluidized in a stream of air heated to a temperature of 280° C. in a

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pretreater (as shown in the drawing) in which the coal is retained as a fluid bed. Fresh coal is fed to the said fluid bed and treated coal is withdrawn as an overflow from the surface of the bed at such a rate that the average time of contact will be approximately 10 minutes. So-treated coal is then flowed into an indirectly heated coking zone wherein it is carbonized in a fluid bed at a temperature between about 800° and 1200° C., the coal having been heated through the temperature range in which it ordinarily exhibits plasticity without defluidization of the fluid bed.

A Southern Illinois coal of 34% volatile matter and 16% oxygen on the dry basis requires less intensive pretreatment according to the process of invention than the more strongly coking Pocahontas coal. This coal is crushed to a size such that 80% by weight will pass through a one-eighth inch screen. It is then fluidized in a pretreating zone in hot air that is preheated to a temperature of about 110° C. The coal is maintained in the said fluid bed for approximately one hour and is thereafter permitted to overflow by the introduction of fresh coal into the bed and is conveyed to a carbonization zone. The coal is thereafter carbonized in a fluid bed at a temperature of about 900° C.

A method of determining the required time effectively to oxidize a given coal may be approximated by considering that each 10° C. rise in pretreating temperature will effect a doubling of the rate of surficial oxidation of the coal. The rate of oxidation will also increase as approximately the 0.7 power of the oxygen concentration in the treating gas. If pure oxygen is employed the treating temperature must be kept below 200° C. to avoid combustion.

I claim:

The method of carbonizing finely divided coal which has been pretreated with an oxygen-containing gas at a temperature below about 285° C., below the softening point of the coal and below combustion temperature with said oxygen-containing gas for a time sufficient to incorporate at least about .2 weight percent oxygen in said coal and to render the coal relatively non-agglomerating, which method comprises introducing finely divided coal in the absence of appreciable amounts of oxygen into

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a carbonizing zone, passing a gasiform stream upwardly through the carbonizing zone for maintaining solids therein in dense phase fluidized condition, burning a fuel gas in a zone surrounded by said fluidized solids and in indirect heat-exchange relationship therewith, passing combustion gases downwardly around at least a portion of the fluidized solids in heat-exchange relationship therewith, introducing a minor amount of the downwardly flowing flue gases at a low point into the fluidized solids to supply a part of the fluidizing gas therein, withdrawing a major amount of the combustion gases at a low level, withdrawing coke from the bottom of the carbonizing zone and withdrawing fluidizing gas and gasiform products from the upper part of the carbonizing zone.

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