STAGED HEAT HARDENING OF FLUID COKE BRIQUETTES

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Application July 27, 1955, Serial No. 524,793
3 Claims. (Cl. 44—23)

This invention relates to improvements in the heat hardening of fluid coke briquettes. More particularly it relates to a process of this nature wherein the briquettes are heat hardened by a staged process which first immerses them in hot finer fluid coke particles. The fines are then removed from the briquettes by hot inert gases which also subject the briquettes to a second higher temperature operation.

There has recently been developed an improved process known as the fluid coking process for the production of "fluid coke" and the thermal conversion of heavy hydrocarbon oils to lighter fractions, e. g. see Patent No. 2,725,349, granted November 29, 1955, and Patent No. 2,721,169, granted October 18, 1955. For completeness the process is described in further detail below although it should be understood that the fluid coking process itself is no part of this invention.

The fluid coking unit consists basically of a reaction vessel or coker and a heater or burner vessel. In a typical operation the heavy oil to be processed is injected into the reaction vessel containing a dense, turbulent, fluidized bed of hot inert solid particles, preferably coke particles. A transfer line or staged reactors can be employed. Uniform temperature exists in the coking bed. Uniform mixing in the bed results in virtually isothermal conditions and effects instantaneous distribution of the feed stock. In the reaction zone the feed stock is partially vaporized and partially cracked. Effluent vapors are removed from the coking vessel and sent to a fractionator for the recovery of gas and light distillates therefrom. Any heavy bottoms, other heavy hydrocarbonaceous matter is burned in the burning vessel. The coke produced in the process remains in the bed coated on the solid particles. Stripping steam is injected into the stripper to remove oil from the coke particles prior to the passage of the coke to the burner.

The heat for carrying out the endothermic cracking reaction is generated in the burner vessel, usually but not necessarily separate. A stream of coke is thus transferred from the reactor to the burner vessel, such as a transfer line or fluid bed burner, employing a standpipe and riser system; air being supplied to the riser for conveying the solids to the burner. Sufficient coke or added carbonaceous matter is burned in the burning vessel to bring the solids therein up to a temperature sufficient to maintain the system in heat balance. The burner solids are maintained at a higher temperature than the solids in the reactor. About 5% of coke, based on the fuel, is burned for this purpose. This may amount to approximately 15 to 30 wt. percent of the coke made in the process. The net coke production, which represents the coke make less the coke burned, is withdrawn.

Heavy hydrocarbon oil feeds suitable for the coking process include heavy crudes, atmospheric and crude vacuum bottoms, pitch, asphalt, other heavy hydrocarbonaceous residues or mixtures thereof. Typically such feeds can have an initial boiling point of about 700° F. or higher, an A. P. I. gravity of about 0° to 20°, and a Conradson carbon residue content of about 5 to 40 wt. percent. As to Conradson carbon residue see A. S. T. M. Test D—189—41.

A problem in the marketing of the fluid coke product is the small size of the particles, predominantly, i. e., about 50–90 wt. percent, in the range of 20 to 60 mesh. The production of substantially larger particles is inconsistent with satisfactory operation of the fluid bed. On the other hand industrial requirements for coke often necessitate particles having a diameter of about at least 1/16 inch to 1 inch. These fluid coke particles have accordingly been compacted into briquettes using various carbonaceous binder substances. The agglutinating carbonaceous binder substances that can be utilized include suitable hydrocarbon binders, such as asphalt and other heavy petroleum residues, aromatic tars, e. g. vacuum reduced thermal tars, heavy ends of coal tar, such as coal tar pitches having a minimum softening point of about 100° C., and heavy ends from the coking operation, i. e., 1000° F. + material. Some specific trade examples of the binders are Elk Basin residuum (160° F. softening point), Enjoy 160 asphalt and Hawkins coker bottoms. These substances are utilized in an amount of about 5 to 25 wt. percent based on the coke charge and preferably 8 to 15 wt. percent.

The fluid coke can be used as is to make briquettes, but the behavior of briquettes during heating and the strength of the final products are improved by grinding part or all of the coke to produce finer particles. This mixture with binder at a temperature of 200°—300° F., after cooling to 150°—250° F. is then briquetted by molding in a hydraulic press at a pressure of about 2100 to 20,000 p. s. i. Roll presses such as those commonly employed to make briquettes from coal and other materials can be used. Such machines are described in the Chemical Engineering article "Agglomeration," October 1951. The mixtures pass directly to the pressing rolls. These briquettes require heat hardening at a temperature of about 700° F. to decompose the binder to a carbonaceous residue and to produce adequate strength and cohesion. Treating at these temperatures, however, because of the melting of the binder material results in the deformation of the compactions and also adherence to each other. In addition elevated temperatures tend to oxidize the compactions undesirably.

This invention provides an improved method of thermally hardening the compactions of fluid coke which overcomes these difficulties. The method comprises a staged operation wherein the briquettes are first immersed in a non-fluidized bed of finer coke particles at an elevated temperature. The mixture of briquettes and fines is then fed to an upper portion of an elongated heating zone maintained at a higher temperature by countercurrent contact with hot inert gases which enter at a lower portion thereof. The velocity of the inert gases is such that the briquettes flow downwardly in the form of a moving bed while the coke particles are entrained. The heat hardened briquettes are removed and the coke particles returned to the first stage. Further details follow.

The first stage of the heat hardening is conducted by immersing the briquettes in a non-fluidized bed of finer coke particles. The temperature of the bed is in the range of 600° to 1200° F. The coke particles utilized for the heat treating are preferably the finer "fluid coke" particles and the size distribution can be substantially the same as the fluid coke obtained from the fluid coking process without grinding. This heat treating step is conducted for a time interval of about 5 to 20 minutes. Conveniently about 3 lb. of fine coke particles are utilized for about 1 lb. of briquettes. The term "non-fluidized bed" is used generally herein to cover fixed and moving beds as no ageration gas is supplied (see Fluidization Nomenclature, Industrial and Engineering Chemistry, volume 41, page 1249, June 1949).
The mixture of fines and briquettes are then fed to a vertical elongated second stage heating zone in which they are heated to a temperature in the range of 1200° to 2000° F. The time of heat treatment in this zone is of about 12 hours. The requisite temperature is provided by hot inert gases which enter the heat treatment zone at a lower portion thereof. The hot inert gases include materials like CO₂, CO, N₂ etc. Preferably the inert gases are flue gases from combustion systems. Combustible material can be fluid coke itself or an extraneous fuel such as fuel oil or natural gas. The combustion is supported by an oxygen containing gas such as air but no excess oxygen contacts the agglomerates. The superficial velocity of the inert gases is in the range of 3 to 15 ft/sec so that the briquettes flow downwardly in the form of a moving bed countercurrently thereto while the coke particles are entrained and separated from the briquettes.

This invention will be better understood by reference to the following example and descriptions in connection with the flow diagram shown in the drawing.

Referring now to the flow diagram, briquettes prepared from fluid coke and 15 wt. percent Elk Basin vacuum residuum binder by molding at a pressure of about 4000 p.s.i. and a temperature of 200° F. are fed by conveyor 1 onto moving grate 2. Finer fluid coke is fed onto the grate from hopper 3 through lines 4 and 5. The briquette 1 to 2 inches thick is immersed in the fines bed of fine coke particles which are at 800° F. The speed of the moving grate is adjusted so that the heating hardening operation in this stage is conducted for 10 minutes. During this heat treatment each briquette is supported in a protective surrounding which transfers the heat by conduction.

When the briquettes’ surface is hardened the mixture of briquettes and fines is dumped into an upper portion of a vertical elongated heat treatment zone 6 by means of hopper 7 and line 8. Hot upwardly flowing flue gas from line 9 from an auxiliary furnace not shown contacts the mixture and reheat the fine coke to 800° F., the temperature of the fine coke having been reduced by contact with the cold briquettes. The briquettes pass downwardly and are heated to 1600° F. by countercurrent contact with the hot inert gas. The velocity of the flue gas is, e.g. 10 ft/sec, such that the briquettes flow downwardly in a moving bed through heating zone 6 and are removed as stable heat hardened briquettes through line 10 and feeder 15. Cooling gas in the form of wet steam is injected into the bottom of the furnace through line 16. The finer coke particles, however, are entrained through line 11 and sent to cyclone or other vapor separating device 12. The fines return to the reservoir in the hopper through dipleg 13 whereas the flue gas is removed through line 14 and can be recycled. Both briquettes and fines collect in hopper 7. Sufficient pressure is built up in hopper 7 and line 8 to introduce the coke into heating zone 6 at about 1 p.s.i. or less.

The following data demonstrate the superiority of fluid coke briquettes pretreated with hot fluid coke as compared to briquettes heated with hot inert gas. After pretreatment with fluid coke at the indicated temperature the briquettes were heated to 1800° F. in an inert atmosphere to duplicate conditions in the second heating stage, the shaft furnace.

<table>
<thead>
<tr>
<th>Temperature of Fluid Coke Used in First Stage, °F</th>
<th>Percent Loss in Tumbling Test</th>
<th>3 in. Briquettes</th>
<th>1 in. Briquettes</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Pretreatment</td>
<td></td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>800</td>
<td></td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>1,000</td>
<td></td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

These results show the markedly improved abrasion resistance obtained by the staged process of this invention.

The tumbling test is used as an indication of abrasion or dusting resistance. The test is carried out in a porcelain jar 7 inches in diameter and 7½ inches in length. The jar is rotated at 70 R. P. M. for 2400 revolutions. The size distribution is then measured and losses ascertained.

The conditions usually encountered in a fluid coker for fuels are also listed below so as to further illustrate how the “fluid coke” was prepared.

<table>
<thead>
<tr>
<th>Conditions in fluid coker reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F.</td>
</tr>
<tr>
<td>Pressure, Atm.</td>
</tr>
<tr>
<td>Superficial Velocity of Fluidizing Gas, ft/sec</td>
</tr>
<tr>
<td>Coke Circulation (Solids/Col Ratio)</td>
</tr>
</tbody>
</table>

The advantages of this invention will be apparent to the skilled in the art. Deformation of the briquettes is avoided during the initial heating operation so that the advantages of hot flue gas heating can be obtained. The loss of strength and adhesion of the briquettes in the flue gas heater is thus avoided.

If it is desired the fluid coke can be devolatilized, calcined or activated prior to processing into briquettes. The consequent reduction in the volatile content permits a reduction in size and treating time in the second stage, flue gas heating step and also improves the quality of the agglomerated product.

For example, pellets or extruded forms may be heat hardened by use of this invention. Fine solids other than fluid coke may be used.

It may also be desirable to supply heat to the moving grate by burning fuel directly above the grate. This would normally be injurious to the agglomerates but the presence of fine coke provides adequate protection.

Following the primary heat hardening step the fine coke may be separated from the agglomerates by screening or by use of a separate elutriation system which does not make use of the hot flue gas from the shaft furnace. This would make it possible to recover valuable hydrocarbons from the shaft furnace gas. Similarly, valuable hydrocarbons may be recovered from the gas evolved in prehardening on the moving grate.

The moving grate may be replaced by more simple equipment such as a batch treating vessel.

It is to be understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. In the heat hardening of fluid coke briquettes with an agglutinating carbonaceous binder substance at temperatures at which the briquettes normally tend to deform and oxidize, the improvement which comprises the steps of first immersing the briquettes in a non-fluidized bed of fine coke particles at a temperature in the range of 600° to 1200° F., then feeding the mixture of coke particles and briquettes to an upper portion of an elongated, vertical, heat treating zone in which the briquettes are heated to a temperature in the range of 1200° to 2000° F. by hot inert gases entering the heat treating zone at a lower portion at a superficial velocity in the range of 3 to 15 ft. per second, the velocity of the inert gases being such that the briquettes flow countercurrently downwardly in the form of a moving bed while the coke particles are removed and entrained therefrom and re-
5 turning the coke particles at a temperature in the range of 600°F to 1200°F to the immersion step.

2. The process of claim 1 in which the immersing step is carried out for a time interval of 5 to 20 minutes.

3. The process of claim 2 in which the heat treating step is carried out for a time interval in the range of 1 to 12 hours.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,776,935 Jahnig et al. ----------- Jan. 8, 1957