

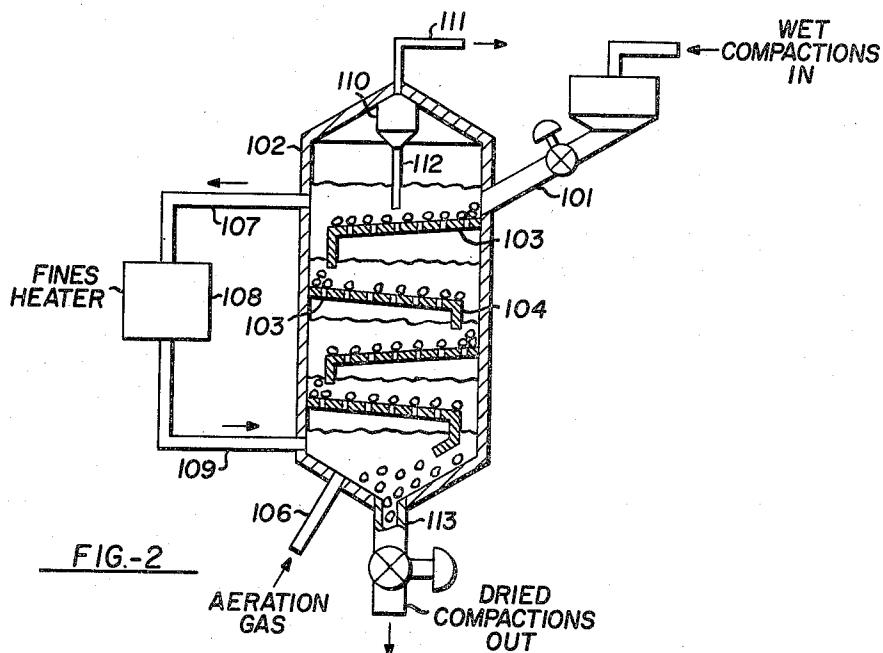
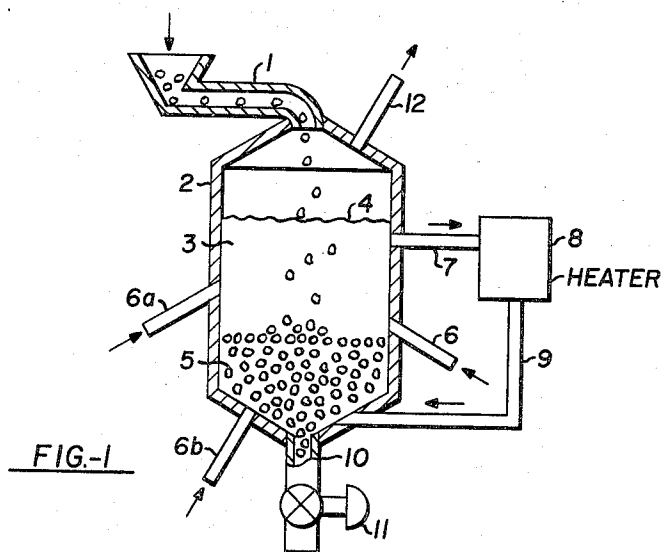
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HEAT TREATING FLUID COKE COMPACTIONS

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HEAT TREATING FLUID COKE COMPACTIONS

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This invention relates to improvements in the heat hardening of fluid coke compactions. More particularly it relates to a process of this nature wherein the compactions are heat hardened by treating them while in the form of a moving bed countercurrent to fluidized coke particles. It also relates to a process wherein this treatment is carried out in a plurality of superposed beds.

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 Serial No. 375,088 filed August 10, 1953. 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. Product vapors are removed from the coking vessel and sent to a fractionator for the recovery of gas and light distillates therefrom. Any heavy bottoms is usually returned to the coking 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 coking 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 feed, is burned for this purpose. This may amount to approximately 15% to 30% 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 hydrocarbon petroleum residua 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 60-90 wt. percent, in the range of 20 to 80 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 1/8 inch to 1 inch.

Compactions of the indicated size made from fluid coke are of several types, i. e., pellets, extrusions, and briquettes. All have in common the utilization of an agglutinating carbonaceous substance as a binder.

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., 1050° F.+ material. Some specific trade examples of the binders are Elk Basin residuum (160° F. softening point), Enjay 160 Asphalt and Hawkins coker bottoms. These substances are utilized in an amount of about 5 to 20 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.

If the coke is to be pelletized by tumbling, it must be ground. Pellets in general are prepared by grinding the fluid coke to give a fines fraction, e. g., minus 100 mesh, and mixing the coke with about 10% binder by tumbling. The binder is ground either separately or in mixtures with the coke. Enjay 160 asphalt can be ground by itself. Elk Basin and Hawkins coker bottoms may become too sticky, even when mixed with coke, to enable grinding at normal temperatures. Consequently, artificial cooling may be used to grind mixtures of these asphalts and coke. These mixtures (about 85% to 90% coke and 10% to 15% asphalt) are ground in a ball or other mill with about 25% water or similar liquid. Artificial cooling may be used to hold the temperature below 75° F. The ground mixture is filtered and the product containing about 25% water is passed through a screen to break up the lumps. These pellets are then charged to a rotating drum for balling so as to subject them to a rolling motion on a horizontally rotated surface.

The briquettes are prepared by admixture of the fluid coke as is or partially ground with about 10% of an agglutinating carbonaceous substance at a temperature of about 200° to 300° F. The mixture is briquetted in a hydraulic press at a pressure of about 2100 to 9600 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 machines are equipped with steam-heated mixers when briquettes are made with tar binders. The hot mixtures pass directly to the pressing rolls.

All these compactions require heat hardening at temperatures of above 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 of course 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 contacting the compactions, while in the form of a moving

bed, countercurrently to fluidized coke particles at heat treating temperatures. In a preferred modification the heat treatment is carried out in a plurality of superposed zones in which the compactions are in the form of shallow moving beds contained in dense, turbulent, fluidized beds of coke particles. The coke particles utilized for the heat treating are preferably fluid coke particles and the size distribution can be substantially the same as the fluid coke obtained from the fluid coking process without grinding.

The heat hardening temperature utilized is in the range of 700° F. or higher, preferably 1000° to 1800° F. The time is for about 15 minutes to 2 hours.

Countercurrent heating provides:

1. Slow evolution of the vapors so the briquettes are not exploded or cracked.

2. Products from cracking binder are not so severely cracked (e. g. less low value gas).

3. Better heat economy on the heater.

4. Lower circulation rate required on hot solids.

The efficacy of this very specific method of heat treating the compactions is surprising in that other heat treating methods give distinctly inferior results. Thus more than substituting one method of heat treating for another is involved. The reducing atmosphere present in the fluidized coke particles maintained at this temperature also contributes to the desired results.

This invention will be better understood by reference to the following examples and descriptions in connection with the flow diagrams shown in the drawings.

Figure 1 is a flow diagram of the heat treating of the compactions in a single, dense, turbulent, fluidized bed.

Figure 2 is a flow diagram of an alternative modification utilizing a plurality of superposed beds.

Referring now to Figure 1 briquettes prepared from fluid coke and 10 wt. percent Elk Basin residuum binder by molding at a pressure of about 9000 p. s. i. and at a temperature of 275° F. are fed through line 1 into an upper portion of elongated vertical heat treating vessel 2. The compactions fall countercurrently through a dense, turbulent, fluidized bed of fluid coke 3 at a temperature of 1200° F. having an upper level 4. The compactions are thus heat treated for 30 minutes. The compactions form a moving bed with more packing at a lower portion 5 of the heat treating vessel where there is no longer any problem of adhesion or deformation.

Fluidizing gas such as steam, light hydrocarbon, or inert gas is added through line 6 to give a superficial velocity of .1 to 3 ft./sec., e. g. .5 ft./sec. This is sufficient to fluidize the coke particles but not the compactions. The fluidizing gas may be admitted in two portions via lines 6a and 6b so as to secure some aeration of the compactions. A portion of the fluid coke is withdrawn from an upper portion of the vessel through line 7 and sent to a separate heating vessel 8 where it is heated to a temperature in the range of 1000° to 1800° F., e. g. 1500° F. This heating can be done by combustion with air, heat exchange with an inert material such as shot, in a fluid bed heater, a transfer line heater or other means known in the art. The reheated solids are returned to a lower portion of vessel 2 through line 9. Countercurrent contact with the compactions is thereby obtained. The heat hardened compactions are withdrawn through line 10 responsive to slide valve 11. The cooling of the briquettes can be accomplished by a wide variety of methods, such as by the use of water quench in the form of mist, bedding them in cold fluid coke or by passing a gas such as cooled combustion gas over them. Vapors are withdrawn through line 12.

Referring now to Figure 2 heat treating vessel 102 is a multistage elongated vertical vessel. Vessel 102 consists of a tower containing a plurality of bubble plates or other gas pervious materials which permit build up of the fluid coke in the form of dense, turbulent, fluidized beds. Downcomers 104 are used but they have no weirs which would trap the briquettes on the trays. The bub-

ble plates 103 preferably can be sloped slightly from the horizontal, e. g. 1° to 4° to permit easier flow of the compactions. Air slides can be used at this point. The compactions enter an upper portion of the treating vessel through line 101. They build up during the course of their downward flow through the heat treating vessel into a series of shallow moving beds of one or two layers thick on each of the plates 103. They flow from the uppermost stages to the next lower stage, etc. The bed temperature can be 1000°–1800° F. at the bottom, e. g. 1200° F., and 200°–800° F., e. g. 600° F. at the top, controlled by circulation rate to heater. Hot solids can be added to the intermediate beds to flatten the temperature gradient. The fluid coke at a temperature of 1500° F. is sent through line 109 to a lower portion of treating vessel 102 and is built up into a series of dense, turbulent beds on the plates 103 and is in countercurrent flow to the compactions. The fines flow through the perforated plates. The shallow beds of the compactions are thus contained in the fluid beds of the coke particles. Fluidizing gas to give a velocity of .1 to 3 ft./sec., e. g. .5 ft./sec. enters through line 106. Exit gases including fluidizing gas and evolved volatiles such as H₂, CH₄, and H₂O are vented through cyclone 110 and line 111 with solid particles being returned through dipleg 112. Fluid coke is withdrawn from an upper portion of the vessel through line 107 and sent to heater 108 wherein it is reheated as discussed for Figure 1. Hot coke particles can be injected into various points of the vessel 102 for selective purposes such as to regulate temperature gradient. Time in the beds should be such as to give the required drying and baking, so that the briquettes are sufficiently hardened before passing to the lower zones. The heat hardened coke compactions are withdrawn through line 113 and can be quenched as stated previously.

The fines also flow down through downcomers along with descending compactions. This fines circulation is held to a moderate value by having a relatively small downcomer and high tray pressure drop. No weirs on downcomers, so compactions flow freely. The flow of fines up through compactions tends to lift them so they move easily. Fines of high density can be used so that compactions will have more tendency to float, e. g. calcined fines can be employed.

Data demonstrate that heating briquettes in fluid coke consistently gave superior results from those obtained in other heating methods such as utilizing a rotary kiln or using hot flue gas. The countercurrent contacting of the compactions with fluidized coke particles can also be applied to rotary kiln operations.

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.

Conditions in fluid coker reactor

	Broad Range	Preferred Range
Temperature, °F.	850–1,200	900–1,000
Pressure, Atmospheres	1–10	1.5–2
Superficial Velocity of Fluidizing Gas, ft./sec.	0.2–10	0.5–4
Coke Circulation (Solids/Oil Ratio)	2–30	7–15

The advantages of this invention will be apparent to the skilled in the art. Strong compactions are produced by heat hardening in a manner which prevents normal deformation. In addition a reducing atmosphere is made available during this heat hardening treatment which prevents the excessive oxidation and consequent weakening and yield degradation of the compactions.

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 compactions of fluid coke

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with an agglutinating carbonaceous binder substance at heat hardening temperatures at which temperatures the compactions normally tend to deform and oxidize, the improvement which comprises the steps of countercurrently contacting the fluid coke compactions flowing downwardly in the form of a moving bed with fluidized finer coke particles at heat hardening temperature in a vertical elongated heat treating zone, the compactions being fed to an upper portion of the treating zone; withdrawing a portion of the coke particles from an upper portion of the treating zone; circulating them through an extraneous heating zone wherein their temperatures are elevated; returning them to a lower portion of the treating zone to supply heat thereto and withdrawing the heat hardened compactions from the lower portion of the treating zone.

2. The process of claim 1 in which the coke particles are in the form of a dense, turbulent, fluidized bed.

3. The process of claim 2 in which the heat hardening temperature is in the range of 1000° to 1800° F., the treating time is in the range of 15 minutes to 2 hours, and the compactions treated contain about 5 to 20 weight percent binder based on the fluid coke.

4. The process of claim 2 in which the coke particles in the dense, turbulent, fluidized bed are fluid coke particles.

5. The process of claim 4 in which the compactions being treated are briquettes prepared by molding fluid coke with the binder under pressure.

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6. In the heat hardening of compactions of fluid coke with an agglutinating carbonaceous binder substance at heat hardening temperatures at which temperatures the compactions normally tend to deform and oxidize, the improvement which comprises the steps of feeding the fluid coke compactions to an upper portion of an elongated vertical treating zone; passing the compactions downwardly through the treating zone wherein they are treated countercurrently at heat hardening temperature in a plurality of superposed, shallow beds contained in dense, turbulent fluidized beds of finer coke particles; withdrawing a portion of the coke particles from an upper portion of the treating zone; circulating them through an extraneous heating zone wherein their temperatures are elevated; returning them to the lower portion of the treating zone to supply heat thereto and withdrawing the compactions from the lower portion of the treating zone.

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