

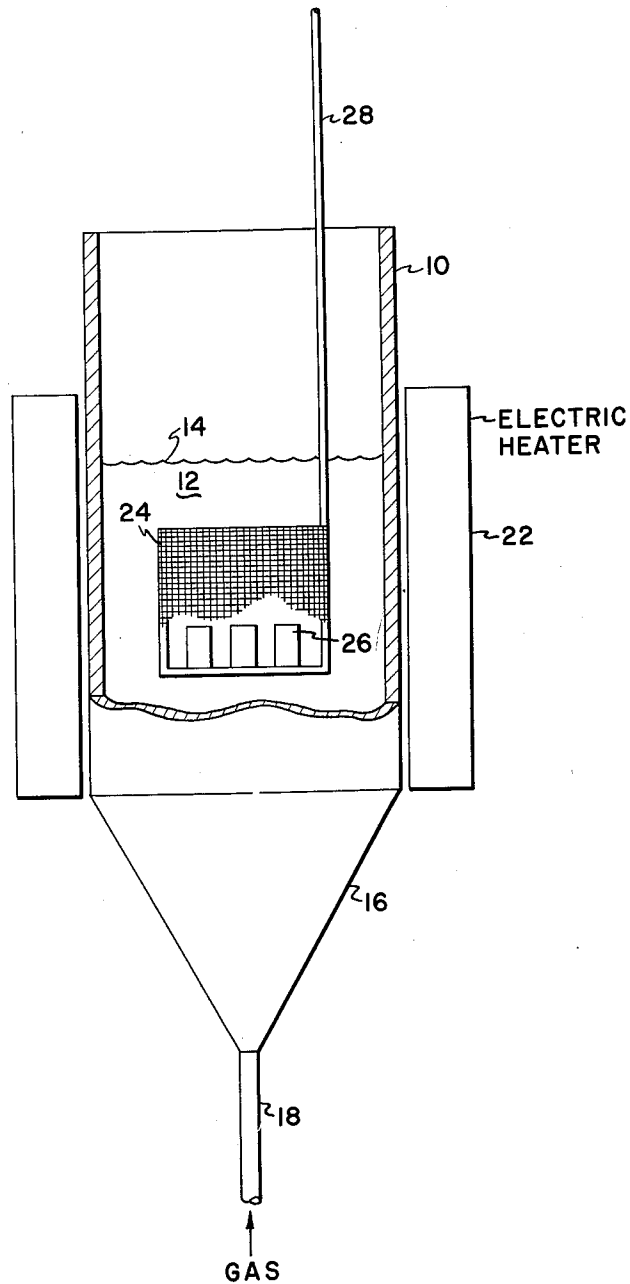
Feb. 6, 1962

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3,020,210

HEAT HARDENING FLUID COKE COMPACTIONS

Filed Feb. 24, 1955



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3,020,210

HEAT HARDENING FLUID COKE COMPACTIONS
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Filed Feb. 24, 1955, Ser. No. 490,424
11 Claims. (Cl. 202—26)

This invention relates to improvements in the thermal heat hardening of fluid coke compactions. More particularly it relates to a process of this nature wherein the compactions are heat hardened by being immersed in a dense turbulent fluidized bed of coke particles.

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 19, 1953, now Patent No. 2,881,130, granted April 7, 1959. 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 makes 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, i.e., about 60-90 wt. percent, are 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 in-

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dustrial 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 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 10 to 15 wt. percent.

The natural fluid coke can be used to make briquettes, but the behavior of briquettes during heating and the strength of the final products are improved by grinding the coke to produce finer particles. If the coke is to be pelletized, 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. 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 became too sticky, even when mixed with coke, to enable them to be ground at normal temperatures. Consequently, artificial cooling is 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 mill with about 25% water. Ice is 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 250° 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," Chemical Engineering October 1951, page 161 on, especially pp. 163-65.

The machines are equipped with steam-heated mixers when coal briquettes are made with tar binders. The hot mixtures of coal and binder pass directly to the pressing rolls.

These compactions require heat hardening at temperatures of above 900° 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 heat treating the compactions by immersing them in a dense, turbulent, fluidized bed of coke particles, preferably fluid coke particles, at a temperature in the range of about 900° F. preferably 1200° to 1800° F. The time of treatment is conventionally in the range of 15 minutes to 2

hours. The fluid coke particles of the bed can be utilized as is, without grinding.

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

The dense, turbulent, fluidized bed of coke can be brought up to temperature by means of external heating and/or partial combustion of the coke. Thus, the coke in the fluid bed can be partially heated by indirect heat exchange and partially burned by a fluidizing gas such as air. Conversely all of the heat can be supplied by burning the coke in an auxiliary burner and recycling the hot coke to the compactions treating zone. Fluidizing gas such as air or nitrogen can be employed depending upon whether combustion of the coke is required to supply the necessary temperature. A superficial fluidizing velocity of the gas in the range of 0.5 to 4 ft./sec. can be employed. Air slides can be utilized to convey the compactions through the bed.

Several stages of fluid bed reactors can be utilized where it is desired to bring compactions slowly up to a temperature as in the case of moisture containing pellets. 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 a mist, bedding them in cold fluid coke or by passing a gas such as cooled combustion gas over them.

Two types of tests are employed to evaluate the physical properties of compactions:

(1) *Tumbling*.—This is used as an indication of abrasion or dusting resistance. The test is carried out in a porcelain jar 7½ 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.

(2) *Drop test*.—This is carried out on the compactions

The effect of baking conditions on the quality of briquettes

Final Temp. of Heating Fluid, ° F.	Time to Reach Final Temp., Min.	Wt. of Baked Briquettes, Percent of Green Briquettes	Wt. of Briquettes After Tumbling, Percent of Green Briquettes	Wt. of Material (Minus 20-Mesh) Abraded From Briquettes in Tumbling, Percent of Green Briquettes	Wt. of Plus 4-Mesh Material After Dropping Tumbled Briquettes, Percent of Green Briquettes	Wt. of Minus 4-Mesh Material Produced in Dropping, Percent of Green Briquettes	Volatile Combustible Matter, Percent of Baked Briquettes
900.....	18	89.4	82.0	7.4	79.5	2.5	-----
900.....	31	89.8	83.3	6.5	79.1	4.2	----- 7.6
1,200.....	49	88.5	81.6	6.9	79.6	2.0	-----
1,500.....	83	82.7	76.5	6.2	75.6	0.9	-----
1,800.....	102	78.4	69.1	9.3	68.4	0.7	-----
1,200.....	15	88.1	83.6	4.6	81.2	2.4	----- 6.4
1,500.....	22	86.0	81.4	4.6	79.4	2.0	----- 4.7
1,800.....	35	82.7	78.5	4.2	78.0	0.5	----- 2.4

recovered from the tumbling test. They are dropped 33½ feet onto a steel plate. The fragments are screened to provide a quantitative measure of degradation.

The FIGURE represents one form of apparatus adapted to carry out the process of the present invention.

Referring now to the drawing, the reference character 10 designates a heater containing a fluidized bed of finely divided solids 12 which are preferably fluid coke particles having a level indicated at 14. The heater or furnace 10 has a conical bottom 16 into the apex of which is introduced a fluidizing gas through line 18 to maintain the coke particles as a dense turbulent fluidized bed by flowing upwardly therethrough. If it is desired to supply additional heat to the fluidized bed 12, the fluidizing gas may be air which is used to partially burn the fluid coke particles in the fluidized bed. The furnace or heater 10 can be heated by any conventional indirect heat exchange means or it may be placed in another furnace. One relatively simple way of heating the heater 10 is by electrical heat and this is diagrammatically shown at 22

and may be a 220 volt Globar furnace using electrical resistance heaters 22.

To heat the formed briquettes a wire basket is provided which is shown at 24 and is partially broken away to show briquettes 26 in the basket. The basket has an open top and has a smaller diameter than the diameter of the heater 10. The wire basket is provided with a handle 28 so that the basket may be submerged in the fluidized bed as shown in the drawing and may be removed from the fluidized bed after the desired heating.

The following example demonstrates the invention.

EXAMPLE

Briquettes were prepared from fluid coke and 10 wt. percent Elk Basin residuum binder by molding at a pressure of about 9000 p.s.i. The mixture which was briquetted in the particular case consisted of:

Constituent:	Parts by weight
Natural fluid coke	45
Ground fluid coke (87% minus 200 mesh)	45
Elk Basin asphalt	10

This mixture, at room temperature, was pressed into briquettes by use of an automatic hydraulic press operating at two tons pressure or about 9000 p.s.i. The green briquettes were about ¾ inch in diameter and one inch tall. They weighed about 9.2 grams each. It was not necessary to dry these briquettes because they contained no water.

These briquettes were then immersed in a dense, turbulent fluidized bed of coke, the coke being predominantly in the normal fluid coke range. The bed was brought up to temperature in a fluid bed reactor by a combination of an electrically heated jacket and partial combustion with the fluidizing air. The heating was carried up to 900° to 1800° F. but the briquettes were immersed when the bed was at 500° F. The baked briquettes were tested by the beforementioned tumbling and drop tests. The results are presented below in the table.

The table shows the heating conditions employed. All of the green briquettes were immersed when the fluid coke under fluidization was at 500° F. The first vertical column shows the temperatures that were attained in the fluidized coke bed when the various specimens were removed. The second vertical column in the table shows the time that was employed to heat from 500° F. to the temperature shown in the first column. The numbers in the fifth and sixth vertical columns reflect the strength of the products obtained by heating under the conditions of time and temperature shown in columns 1 and 2. All of the products are considered satisfactory as far as strength is concerned. That is, the maximum degradation during the tumbling test was 9.3%, as shown in the fifth vertical column and most results were below this figure. A sample of high grade foundry coke, which is an article of commerce, lost 8.2% when subjected to the same tumble test.

The only method that consistently produced briquettes that were considered acceptable was by heating in fluid

coke. Two other general methods were tried. One employed a heated rotating kiln and the other employed blasts of hot gases. Both air and combustion gases were passed through beds of the green agglomerates. The products from these experiments were visibly too poor to warrant formal evaluation of their quality.

The conditions usually encountered in a fluid coker for fuels are also listed below so as to further illustrate how the 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 are apparent to those skilled in the art. Strong compactions are produced by heat hardening the latter in a manner which prevents their normal deformation. In addition a reducing atmosphere is made available during this heat hardening treatment which prevents the excessive oxidation and consequent 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 thermal heat hardening of compactions of fluid coke particles made by a fluidized coking process with an agglutinating hydrocarbon binder substance at heat hardening temperatures at which temperatures the compactions normally tend to deform and oxidize, the improvement which comprises immersing the fluid coke compaction in a dense, turbulent, fluidized bed of coke particles maintained at heat hardening temperature to decompose said binder to a carbonaceous residue to produce adequate strength whereby deformation and excessive oxidation of said compaction are prevented, and withdrawing the thus heat hardened compaction from said fluidized bed.

2. The process of claim 1 in which the heat hardening temperature is in the range of 900° to 1800° F. and the compactions treated contain about 5 to 20 wt. percent binder based on the fluid coke.

3. A process according to claim 1 wherein said heat hardening step is maintained under reducing conditions.

4. The process of claim 1 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 an agglutinating carbonaceous substance in a briquetting press.

6. A process for heat hardening compactions of coke particles made in a fluid coking process with a high boiling agglutinating hydrocarbon binder in an amount of about 5 to 20% based on said fluid coke particles, which comprises heating the compaction at a heat hardening temperature between about 900° F. and 1800° F. for 15 minutes to 2 hours to decompose the binder to a carbonaceous residue and to improve the strength and cohesion of the coke particles by immersing the fluid coke compaction in a hot dense, turbulent fluidized bed of coke particles maintained at heat hardening temperature and removing the heated compaction from said fluidized bed.

7. A process according to claim 6 wherein the compaction being treated is a briquette prepared by subjecting the mixture of said fluid coke particles and agglutinating binder to a pressure of between about 2100 and 9600 p.s.i.

8. A process according to claim 6 wherein at least part of said fluid coke particles are subjected to grinding before being heat hardened.

9. A process according to claim 6 wherein at least part of said fluid coke particles are subjected to grinding before being mixed with said agglutinating binder.

10. A process according to claim 6 wherein said heat hardening step is maintained under reducing conditions.

11. A process according to claim 6 wherein the coke particles of said dense turbulent fluidized bed comprise fluid coke particles.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,020,210

February 6, 1962

Frank M. Stephens, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the sheet of drawing, bottom of the sheet, name of first inventor, for "Frank M. Stevens, Jr." read -- Frank M. Stephens, Jr. --.

Signed and sealed this 5th day of June 1962.

SEAL)
ttest:

RNEST W. SWIDER
ttesting Officer

DAVID L. LADD
Commissioner of Patents