

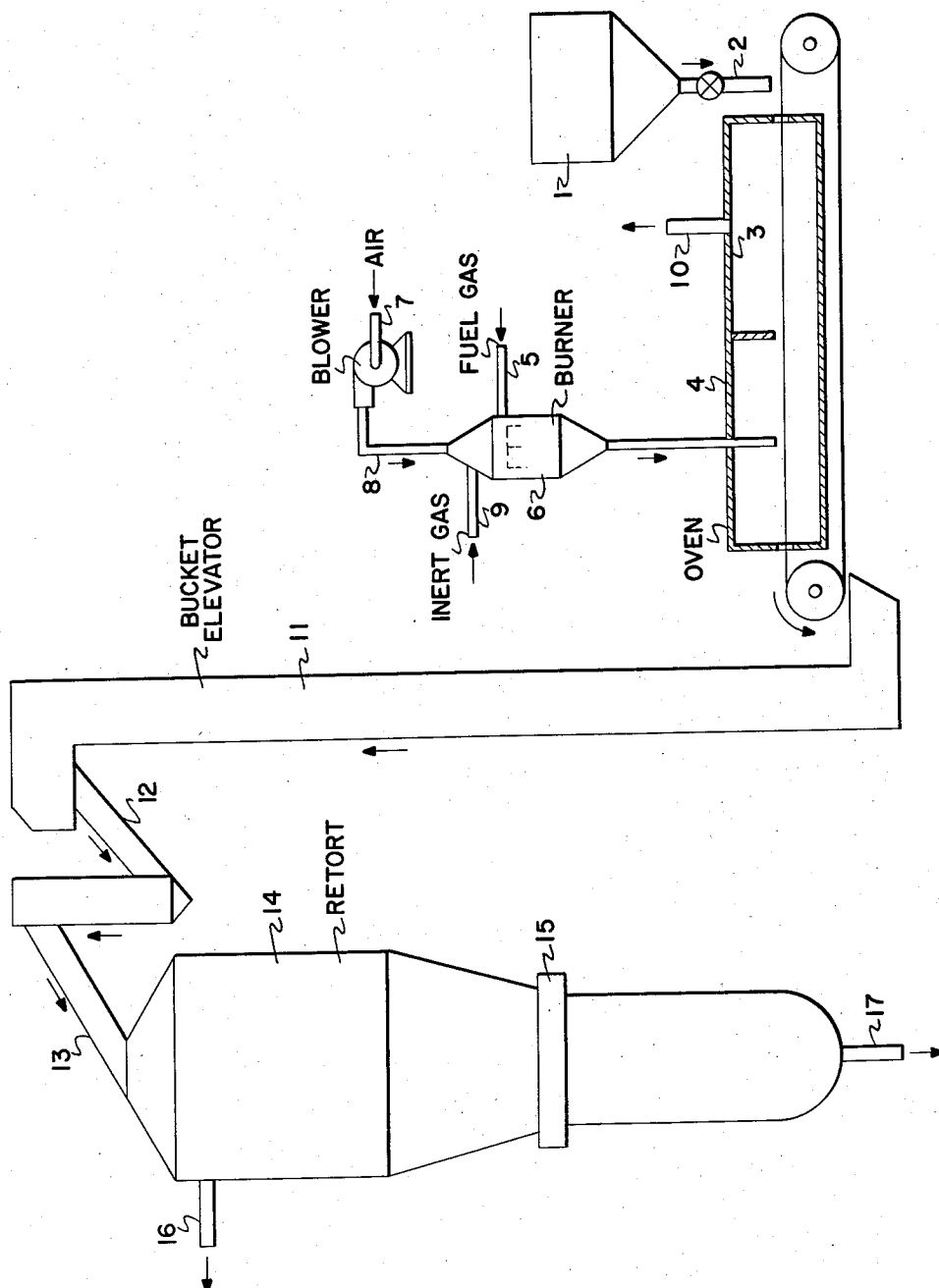
Jan. 20, 1959

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2,869,992

PRELIMINARY HEATING OF FLUID COKE BRIQUETTES

Filed Jan. 2, 1957



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PRELIMINARY HEATING OF FLUID COKE
BRIQUETTES

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Application January 2, 1957, Serial No. 632,207

4 Claims. (Cl. 44-10)

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 in a two-stage process while closely controlling the oxygen content of the treating gases.

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 U. S. Patents 2,725,349 and 2,721,169. 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 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 wt. percent of the coke made in the process. The net coke production, which represents the coke made 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 residue 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

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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 1/4 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 softening point of about 100 to 250° F., heavy ends from the coking operation (coker bottoms), i. e. 1050° F.+ material and mixtures thereof. 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 25 wt. percent based on the coke charge and preferably 5 to 15 wt. percent. The binder can also be admixed with steam in an amount of 1 to 10 wt. percent to produce a finely atomized spray which makes for better mixing with the coke particles. The binder can also be air blown to raise its melting point. The Hawkins coker bottoms, for example, has a softening point of around 120° F. which can be too low. About 3.0 ft.³ of 425° F. air per pound of binder is required.

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. The optimum temperature for binder mixing with the coke is one at which the binder had a viscosity in the range of 1000 to 5000 centipoises, for example 2500 centipoises. The briquetting should be done at a temperature slightly above the softening point of the binder or binders utilized, i. e. conveniently at a temperature in the range of 150° to 200° F., for example 175° F. The mixture is then briquetted by molding in a 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 article "Agglomeration," Chemical Engineering, October 1951, pages 161-165. The mixtures pass directly to the pressing rolls.

These briquettes require heat hardening at a temperature 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 elevated temperatures tend to oxidize the compactions undesirably to form H₂O and CO₂. Several methods have been proposed to overcome these difficulties. Some of them deal with particular ways of conducting a preliminary heat hardening step so as to avoid subsequent deformation in the higher temperature carbonization treatment. Many of the proposed processes are either too costly or give products of less than satisfactory quality.

This invention provides an improved method of thermally and chemically hardening compactions of fluid coke which overcomes these difficulties. The method comprises subjecting the fluid coke briquettes to two-stages of heat treatment. In the first, preliminary or curing stage they are treated with an oxygen-containing gas

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containing 2 to 10 volume percent of oxygen at a temperature in the range of 400° to 1100° F. while in the form of a fixed bed of controlled depth. The rate of flow of the oxygen-containing gas as well as the time are carefully controlled. After this treatment the briquettes are allowed to cool and stand so as to relieve internal stresses. They are then heated while in the form of a downward, moving bed to a temperature in the range of 1400° to 2000° F. by countercurrent contact with hot inert gases. The control features are elaborated upon below, and all of them are necessary in combination in order to achieve the improved results of this invention.

In the first or preliminary stage of heating the briquettes are contacted with gas at a temperature in the range of 400° to 1100° F. while the briquettes are in the form of a "fixed bed." The term "fixed bed" connotes a body of the briquettes supported by direct contact with each other and the retaining walls. Thus the coke particles can be and preferably are treated in the form of a fixed bed while on a moving grate. The bed depth is carefully controlled in order to avoid burning and therefore a depth of about 6 inches to 1 foot are utilized.

The oxygen content of the treating gas is quite important and is kept at 2 to 10 volume percent, preferably 5 volume percent, with the rest inerts such as N₂, CO₂, CO, etc. This operation has been found to be very critical with excessive temperatures or oxygen concentration causing combustion of briquettes and binder while less oxidizing conditions cause the briquettes to melt before sufficient oxidation has occurred to harden the binder by dehydrogenation. The amount of oxygen containing gas utilized is 5 to 5000 s. c. f./cu. ft. of briquettes, preferably 1000. This is the minimum necessary for heat transfer rate and uniformity of treatment. The preliminary heating is conducted for a time interval of 10 to 60 minutes, preferably 30 minutes. The flow of the oxygen-containing gas is frequently reversed, e. g., upflow for one half the indicated time and downflow for the remainder. This is obtained by the use of baffles to reverse the flow of gas through the moving grate.

The thus treated briquettes are then allowed to cool to a temperature in the range of 400° to 700° F. for about 5 to 20 minutes to relieve internal stresses. Experiments showed that briquettes were otherwise too brittle to handle on a conveyor.

The briquettes are then fed to a vertical elongated heat treatment zone conveniently a shaft furnace. They are there heated while in the form of a downward, moving bed to a temperature in the range of 1400° to 2000° F. for a heating time interval of about ½ hour to 5 hours. The requisite temperature is provided by countercurrent

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

Referring now to the flow diagram, coke briquettes prepared as previously explained are sent through hopper 1 and conduit 2 on the moving grate 3 which is conveniently 50 feet long and 4 feet wide. The grate passes through curing oven 4. The briquettes are treated on the grate by hot gas at 900° F. which contains 5 volume percent oxygen. The gas is passed upward through the first half of the grate and downward through the second half. Baffles located above and below the moving grate cause flow reversal as in the shell side of a heat exchanger. This oxygen-containing gas is prepared by controlled combustion of fuel gas such as, e. g. methane, through line 5 in burner 6. Air or other oxygen-containing gas is supplied for the combustion through lines 7 and 8 with inert gas entering the burner through line 9 to dilute the oxygen concentration to 5 volume percent. The treating gas is vented through line 10. The curing gas rate is 1000 s. c. f./cu. ft. of briquettes. The bed depth of the coke briquettes which can be considered a fixed bed as previously described on a moving grate is about 1 foot. The velocity of the grate is maintained such that the preliminary heating is conducted for 30 minutes.

The thus treated briquettes are then discharged into bucket elevator 11. During this transportation they are allowed to stand and cool for 10 minutes to a temperature of 500° F. so as to relieve internal stresses. They are then fed through lines 12 and 13 into a vertical elongated second stage heating zone 14 conveniently a shaft furnace. Hot upwardly flowing flue gas from burner 15 countercurrently contacts the descending cured briquettes which are in the form of a falling, moving bed. The gases are at a superficial velocity of 5 ft./sec. Heating is at the rate of 9° F. per minute so that the briquettes are heated to 1740° F. in 2.3 hours. The tail gas is removed through line 16 and the hot briquettes are withdrawn through line 17.

Scrubbed tail gas can be recycled to the bottom of heating zone 14 to cool the briquettes, pick up heat and improve heat economy.

The advantages of this invention are shown in the following example.

EXAMPLE 1

A number of preliminary heat treating tests were made in which fixed shallow beds of briquettes made with coker bottoms were contacted with oxygen-containing gas at temperatures of 425° F. and 900° F. Minimum strength during heat treatment was measured.

Table I
CRUSHING STRENGTH DURING HEAT TREATMENT

Gas Temp., °F.	O ₂ Content, v. Percent	Crushing Strength (lbs.) After Indicated Time (min.)						
		1	2	3	5	10	30	60
425	21	Fell Apart					0	13
900	0	3.2	0.3	0.6	2.7	30	(No combustion)	
900	5	5.8	0.7	0.4	10	22	(Combustion @ 20 min.)	
900	10	3.5	1.1	0.3	10	38	(Combustion @ 17 min.)	
900	15	2.8	1.1	3.2	12	30	(Combustion @ 10 min.)	
900	21							

contact with hot inert gases, which enter the heat treating 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 preferably no oxygen contacts the briquettes. 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.

These data show that a relatively high temperature, around 900° F., is required to obtain hardening in a short time and to maintain sufficient minimum strength so that a fixed bed of briquettes can be supported.

At 900° F. it is necessary to limit the oxygen concentration to about 5 to 10% so as to avoid combustion.

EXAMPLE 2

The conditions for minimum curing gas consumption at 900° F. with 5% oxygen were next determined in a large heat treating furnace and are shown in Table II.

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Table II

GAS RATES REQUIRED TO HARDEN FIXED BED OF
BRIQUETTES AT 900° F. TO 20 LB. MINIMUM STRENGTH

Bed Depth, in.	Curing Cycle, min. up and down	Gas Flow, s. c. f. m. per cu. ft. of briquettes	Total Curing Gas, s. c. f./ cu. ft. of briquettes
6	6 and 6	140	1,680
6	8 and 8	100	1,600
11	10 and 10	70	1,400
11	12 and 12	50	1,200
11	15 and 15	33	990

It was found possible to achieve minimum gas consumption at 33 s. c. f. m. per cu. ft. of briquettes and 11" bed depth. Lower gas rates and higher bed depth were unsatisfactory because of non-uniform heat hardening.

These examples show that specific conditions can be selected with the specified ranges to minimize treating time and combustion of the briquettes. The briquettes then have sufficient strength to undergo the subsequent heat treating step.

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

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. Other compactions of fluid coke such as pellets or extrusions may also be heat hardened by the process of this invention.

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The advantages of this invention will be apparent to the skilled in the art. Very strong briquettes are prepared in an economical manner with a minimum of deformation, loss of product or combustion.

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. A process for heat hardening briquettes of fluid coke with an agglutinating carbonaceous binder substance at temperatures at which the briquettes normally tend to deform and oxidize which comprises the steps of heating the briquettes while in the form of a fixed bed having a depth in the range of about 6 inches to 1 foot for a time interval in the range of 10 to 60 minutes with an oxygen-containing gas at a temperature of 400° to 1100° F. and having an oxygen content in the range of about 2 to 10 volume percent, the amount of oxygen-containing gas utilized being in the range of about 5 to 5000 s. c. f./cu. ft. briquettes; cooling the thus treated briquettes to a temperature in the range of about 400° to 700° F. for a time interval of 5 to 20 minutes whereby internal stresses are removed and heating the briquettes while in the form of a downward, moving bed to a temperature in the range of 1400° to 2000° F. by countercurrent contact with hot inert gases.

2. The process of claim 1 in which the flow of oxygen containing gas through the fixed bed of briquettes is periodically reversed.

3. The process of claim 2 in which the second heating step is conducted for a time interval in the range of about ½ hour to 5 hours.

4. The process of claim 3 in which the hot inert gases of the second heating step are oxygen free.

References Cited in the file of this patent

UNITED STATES PATENTS

2,164,933	Maurel	July 4, 1939
2,694,038	Findlay	Nov. 9, 1954