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PREPARATION OF FLUID COKE BRIQUETTES

Ralph Burgess Mason, Denham Springs, La., assignor to Esso Research and Engineering Company, a corporation of Delaware

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This invention relates to improvements in the briquetting of fluid coke particles. More particularly it relates to a process of this nature wherein the particles are briquetted utilizing a high melting point binder in conjunction with a volatile hydrocarbon solvent.

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 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 ⅛ inch to 1 inch.

These fluid coke particles have been compacted into briquettes using various carbonaceous binder substances. The particles, as is or ground in part, have been admixed with the binder at elevated temperatures. This mixture is then briquetted 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. All the machines are equipped with steam-heated mixers when briquettes are made with tar binders. The hot mixtures pass directly to the pressing rolls. 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.

The briquettes so made exhibit certain difficulties. For one thing they show preferential oxidation of the binder when exposed to an oxidizing atmosphere at elevated temperature. This results in considerable loss of the coke as fines and dust from the surface. This surface disintegration can result in crumbling of the entire briquette which is very undesirable in many uses of the briquetted material.

This invention provides an improved method of preparing stable briquettes free of these difficulties. The method comprises briefly molding at the indicated elevated pressures the fluid coke particles at atmospheric temperature with a volatile hydrocarbon solvent and a specific high melting point binder. The resulting briquettes are heated at a low temperature to expel the solvent and then at an elevated calcination temperature.

The high melting point binders utilized are quite specific in nature. They are the condensates of the effluent from a fluid coking reactor and have a minimum boiling point in the range of 950° to 1200° F. and preferably a minimum boiling point of 1050° F. This material at temperatures below 150° F. is a hard, non-sticky carbonaceous substance which, upon application of a blow, shatters with conchoidal fracture. It consists of various condensed aromatic nuclei and because of the wide variation in composition does not have a sharp, well defined melting point. Thus, at 350° F. it softens and becomes sticky but is not sufficiently fluid to mix intimately and to wet solid particles such as is required for a binder. The hard, but friable, characteristic permits grinding to a powder at temperatures below 150° F. and the required degree of intimacy between the solid binder and the coke particles is readily achieved by mechanically mixing the pulverized binder with the coke particles. This binder is utilized in an amount of 10 to 20 wt. percent based on the total solid particles. Thus, for example, 20% binder formulations have been prepared which contained 400 parts by weight of fluid coke and 100 parts by weight of pulverized binder. Superior briquettes are obtained utilizing amounts of binder in the upper end of this range. It is significant that briquettes made with this material were superior to those made from other binder materials such as asphalts of about 200° F. melting point or hard pitch from coal tar, one of the better known binders for this purpose.

The addition of a volatile hydrocarbon solvent results in a mixture that can be compacted at room temperature, i. e., 50° to 150° F. This is a distinct advantage in that it eliminates any requirement for hot compaction. The solvents wet the total mass and usually dissolve a portion of the high melting point binder to yield a resultant material of greater cohesive characteristics. The amount and nature of the solvent may vary widely but in general it is preferred to employ an amount less than 10 wt. percent of the total coke plus binder or solids mix. Due to the aromatic nature of the binder, aromatic solvents such as benzene, toluene, Varsol, and naphthas of appreciable aromatic content are preferred. To facilitate solvent removal in subsequent stages of the preparation it is desired that the solvent distills in the range of 150°–600° F. The preferred method of solvent utilization has been given in the foregoing paragraphs. The binder and coke are dry-mixed and the solvent is added to the resultant composite. The mixture is then formed into briquettes by the procedure mentioned previously. The briquettes are then heated to a temperature in the range of 300° to 600° F. for about 0.5 to 2.0 hours so as to expel the solvent material.

The briquettes are then calcined preferably in a non-oxidizing atmosphere at a temperature in the range of 1000° to 3000° F. and preferably 1800° to 2700° F. for about 1 to 4 hours. The best and most oxidation-resistant briquettes are prepared at the higher calcination temperatures but the superiority of the binder and the process permit in many instances use of the lower temperatures. In any event the temperature is increased gradually from the solvent removal stage to calcining temperatures in the range of 1000° to 1800° F. For calcinations in the range of 1800° to 3000° F. it is preferred to calcine first in the temperature range of 1000° to 1800° F. for a period of at least 0.5 hour to avoid the ill effects of rapid heating to elevated temperatures.

This calcination or heat hardening treatment can be carried out by immersing the compactions in fluid bed of coke as taught in copending application, Serial No. 490,424, filed February 24, 1955.

This invention and advantages will be better understood by reference to the following examples.

EXAMPLE 1

A 1050° F.+ boiling coker bottoms, which was prepared in the fluidized solids coking of Elk basin residuum at a temperature of 1000° F. and then in a subsequent distillation of the recycle oil, was ground and passed through a 28 mesh screen. The material was mixed with 35 to 325 mesh coke in a 10/90 ratio. The dry mix was moistened with about 6% by weight Varsol, and was compressed into briquettes at 80° F. and at a pressure of 17,500 p. s. i. g. The Varsol solvent is a petroleum fraction having 55% distilling at 350° F., 90% at 375° F. and a maximum final boiling point of 410° F.

The briquettes were placed in a muffle furnace which was maintained under non-oxidizing conditions and which was heated from ambient temperature to 1200° F. during a period of about one hour. During this heating period the solvent was removed. The furnace contents were then calcined for two hours at 1200° F. in the non-oxidizing atmosphere. The product briquettes were very hard and were remarkably resistant to surface deterioration.

EXAMPLE 2

A still further improvement in oxidation resistance of the briquette was achieved by calcining for 2 hours at 2700° F. in an induction furnace the briquettes calcined at 1200° F. in Example 1. The product briquettes were very hard and remarkably resistant to surface deterioration.

EXAMPLE 3

A similar experiment to the first except for the use of 20% of the 1050° F. bottoms from the coker recycle product was performed. As before, the coke-binder mix which could not be briquetted at room temperature and at temperatures as high as 300° F. was made into a very satisfactory compaction upon moistening with Varsol and compressing as before. The compactions were heated for four hours in a furnace at 350° F. to evaporate the solvent binder and then were calcined for 2 hours at 1200° F. while protected from air. The calcined material was remarkably resistant to preferential oxidation of the binder. This characteristic was further improved by (1) calcining in a separate experiment at 1800° F. in a muffle furnace instead of 1200° F. or (2) by further calcining briquettes calcined at 1200° F. at about 2700° F. in an induction furnace. These advantages with the 20% binder are feasible because of the high softening point of the binder. Under usual conditions with binders of lower melting point and softening point, it is not possible to produce a uniform compaction at this concentration because of distortion prior to or during calcination.

EXAMPLE 4

Briquettes were prepared as in Example 1 but with 10% of hard pitch from coal tar as a binder and with about 5% benzene as the volatile solvent. As previously, the compaction was made at ambient temperature and at about 17,500 p. s. i. g. and then the slovent was removed by heating for four hours at 350° F. The solvent free briquettes were then calcined for two hours at 1200° F. in an inert atmosphere. The resultant briquettes were mechanically strong but were not as oxidation resistant as briquettes prepared as in Example 1 with the coker bottoms as the binder. In this experiment with the pitch binder, as in the experiments described above, compactions in the absence of the solvent could not be made at temperatures as high as 300° F. but with the solvent no difficulty was experienced at the normal laboratory temperature of about 80° F.

EXAMPLE 5

An unsuccessful attempt was made to hot mix a 180°–200° F. M. P. asphalt with fluid coke in a 1/9 ratio (10% binder). Intimate mixing was achieved only upon cooling with Dry Ice and grinding while chilled. The resultant mixture together with water of condensation was compacted at about room temperature with a pressure of 17,500 p. s. i. g. The briquettes after calcination at 1200° F. were mechanically strong but were not as resistant to oxidation as were the briquettes prepared in Example 1. This illustrates the superiority of the binder used in the earlier example. That is, the coker bottoms as a binder provides for a more oxidation resistant briquette and special heating or cooling applications are not required to provide intimate mixing of the coke particles with the binder.

The conditions usually encountered in a fluid coker for fuels are also listed below so as to further illustrate how the "fluid coke" and binder were 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 the skilled in the art. Strong compactions are produced by briquetting at room temperature. Briquettes are made available in which the binder material has the same

oxidation resistance as the coke particles in the agglomerate. Loss of coke and crumbling of the briquettes are avoided. The advantages of making the agglomerates are thus retained. A superior binder material made directly in the same fluid coking process that produces the fluid coke particles is provided. This makes for distinct economy of operation.

The process of this invention also has utility in preparing other compactions such as pellets and extrusions.

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 preparing stable briquettes from fluid coke particles which comprises the steps of molding at elevated pressure and at a temperature in the range of 50° to 150° F. the fluid coke particles with a volatile hydrocarbon solvent and a carbonaceous binder, said binder consisting of a condensate of the effluent from a fluid coking reactor, having a minimum boiling point in the range of 950° to 1200° F., and having been prepared by contacting a heavy hydrocarbon oil feed at a temperature in the range of 850° to 1200° F. with a dense, turbulent, fluidized bed of inert solid particles in a coking zone, removing resultant vapors to a fractionation zone and quenching the vapors to a temperature sufficient to condense the condensate binder, the binder and fluid coke particles having first been admixed prior to the addition of the volatile solvent heating the resulting briquettes to a temperature in the range of 300° to 600° F. to expel the solvent and calcining the thus treated briquettes at a temperature in the range of 1800° to 3000° F.

2. The process of claim 1 in which the binder is utilized in an amount in the range of 10 to 20 weight percent based on the fluid coke and binder.

3. The process of claim 1 in which the binder has a minimum boiling point of about 1050° F. and the calcination is conducted at a temperature in the range of 1800° to 2700° F. for a time interval in the range of 1 to 4 hours.

4. The process of claim 1 in which the calcination is conducted in two heating stages, the first in the range of 1000° to 1800° F. for at least one half hour and the second at a temperature in the range of 1800° to 3000° F.

5. The process of claim 2 in which the hydrocarbon solvent has a boiling point in the range of 150° to 600° F. and is utilized in a maximum amount of about 10 weight percent based on the fluid coke and binder.

6. The process of claim 5 in which the solvent is aromatic in nature.

7. The process of claim 5 in which the solvent is benzene.

References Cited in the file of this patent

UNITED STATES PATENTS

1,635,520	Wetherbee et al.	July 12, 1927
2,556,154	Kern	June 5, 1951
2,560,357	Martin et al.	July 10, 1951
2,709,676	Krebs	May 31, 1955

FOREIGN PATENTS

234,805	Great Britain	May 22, 1925

OTHER REFERENCES

"Residual Oils Fluid Coked to Eliminate Heavy Fuel Problem," Voorhees and Martin. Proceeding of The American Petroleum Institute, 1953, sec. III, refining pages 39–46.