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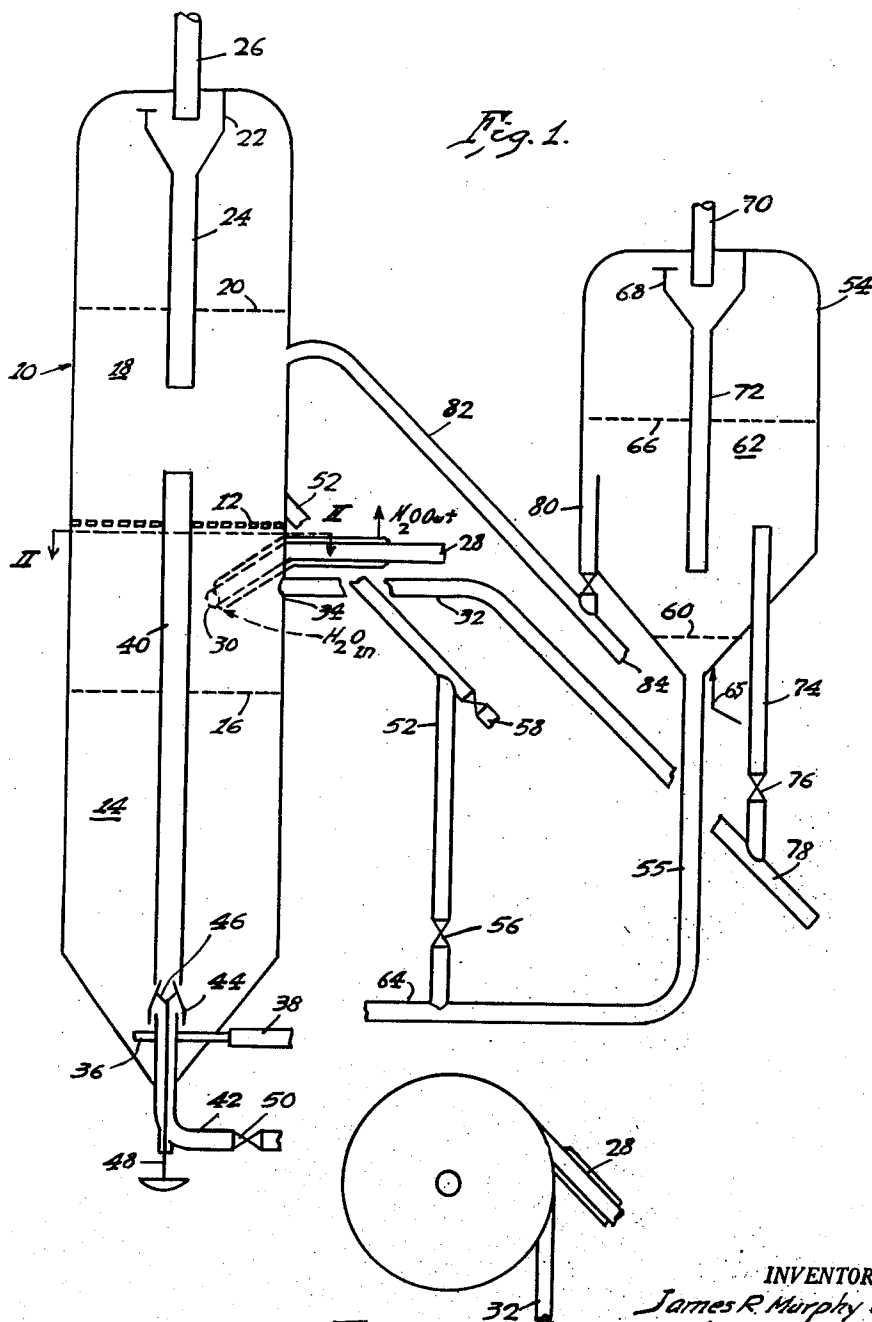


Fig. 2.

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FLUIDIZED COKING OF SOLID CARBONACEOUS MATERIALS

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8 Claims. (Cl. 202—14)

This invention relates to a process for the conversion of solid carbonaceous materials and more particularly to a fluidized coking process employing solid carbonaceous materials as charge stocks.

In most instances, solid carbonaceous materials such as coal, lignite, oil shale, tar sands and pitches are of relatively low value as compared with more volatile normally gaseous or liquid products which can be derived from them. In the past the solid carbonaceous materials were generally converted to coke and volatile materials in batch operations in which the carbonaceous material was heated in a coking chamber to liberate volatile components which were withdrawn during the heating and form coke which was removed at the end of the treatment.

More recently the fluidized technique of handling finely divided solids has been suggested for the conversion of solid carbonaceous materials to coke and volatile gases and liquids in a continuous process. In the fluidized processes the heat required for the conversion is generally supplied by hot coke particles introduced into the reactor. A fluidized bed of hot coke particles is maintained in a dense phase, hindered settling condition in the reactor by an ascending fluidizing gas. The fluidized bed resembles a boiling liquid in some aspects being extremely turbulent and having a well defined upper surface or level of the dense phase. The solid carbonaceous material is charged directly to the fluidized bed in a continuous stream, and a continuous stream of coke and volatile products is withdrawn from the reactor.

Several difficulties are encountered in fluidized coking of solid carbonaceous materials. Most of those materials pass through a sticky plastic stage as they are heated. Heat transferred back through the feed line may be sufficient to partially melt and then coke some of the charge stock to plug the feed line. Particles of the carbonaceous material also may adhere to the inner surface of the reactor and gradually build up large coke deposits in the reactor. Moreover high local concentrations of the charge stock in the fluidized bed causes agglomeration of the coke particles, which interferes with fluidization.

This invention resides in a high temperature fluidized process for the coking of solid carbonaceous materials in which the solid carbonaceous materials and hot coke particles are fed tangentially into a reactor above the dense-phase level of a first fluidized bed of coke particles. The volatile components liberated from the carbonaceous charge stock pass through a second fluidized bed of hot coke particles. Coke particles are withdrawn from the first fluidized bed and transferred to the second fluidized bed in which coking is completed.

The process of this invention can be used to convert coal, lignite, oil shale, tar sand, pitch and the like to coke and normally liquid and gaseous products. For convenience, the invention will be described for the conversion of petroleum pitch. Petroleum pitches are dark, brittle solids which have high softening points of the order of 300° F. or higher, preferably about 350° F., as determined by the ring and ball test. The petroleum

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pitches can be prepared, for example, by extremely deep vacuum reduction, combined with visbreaking, of petroleum crude oils.

Figure 1 of the drawings is a diagrammatic illustration of a system suitable for carrying out a preferred embodiment of this invention.

Figure 2 is a horizontal sectional view of the reactor taken along section II—II in Figure 1.

Referring to Figure 1 of the drawings, the reaction vessel, indicated generally by reference numeral 10, is a vertical cylindrical vessel closed at its upper and lower ends. A grid 12 extends horizontally across the reaction vessel near its center to divide the reaction vessel into a lower section and an upper section. A first, or lower, fluidized bed 14 of coke particles having a dense-phase level indicated by reference numeral 16 is maintained in the lower section of the reaction vessel below the grid 12. Above the grid 12 is a second, or upper, fluidized bed 18 of coke particles having a dense-phase level indicated by reference numeral 20.

A separator 22 is mounted in the upper end of reaction vessel 10 to separate coke particles carried by gaseous reaction products passing upwardly from the dense-phase level 20 of fluidized bed 18. The coke particles are returned from the separator 22 through a dip leg 24 to the fluidized bed 18. The gaseous reaction products are discharged from the separator 22 and reaction vessel 10 through outlet line 26 for delivery to product recovery apparatus, not shown.

The pitch particles in a finely divided state in which substantially all of the particles have a diameter in the range of 10 to 200 microns are introduced tangentially into the reaction vessel through a water jacketed feed line 28, which opens into the reaction vessel at inlet 30 above the upper surface 16 of the lower fluidized bed 14. The pitch particles are transported by a carried gas moving at a velocity of from about 10 to 70 feet per second, and preferably at about 20 to 30 feet per second, through feed line 28 into the reactor. Suitable carrier gases are, for example, carbon dioxide, nitrogen, refinery gases (Ca and lighter), flue gas, methane and hydrogen. Steam at a temperature low enough to avoid softening the pitch, generally below about 300° F., can also be used. The pitch is preferably introduced into the reactor at a temperature ranging from atmospheric temperature up to about 150° F. The density of the pitch stream ranges from about 0.05 to 5 pounds per cubic foot. The pitch particles are directed slightly downwardly, as well as tangentially, toward the surface of the fluidized bed 14 by the carrier gases in the apparatus shown in the drawing.

Hot coke particles are introduced tangentially into the reaction vessel 10 through a coke inlet line 32. The line 32 discharges into the reaction vessel 10 at the opening 34 in a position to direct the hot coke particles tangentially into the reaction vessel whereby they travel across the opening 30 of the pitch feed line 28. In the embodiment of the invention illustrated in the drawings, opening 34 is slightly higher than opening 30.

The coke particles range in size from about 50 to 1000 microns, preferably from 100 to 500 microns, and at a temperature in the range of about 1000° to 1800° F. The coke particles are carried by a suitable carrier gas, for example, steam or inert gases, in a dilute phase having a density in the range of 0.2 to 8.0 pounds per cubic foot, into the reaction vessel at a velocity in the range of 15 to 70 feet per second, and preferably 20 to 30 feet per second. A mixture of coke and pitch particles is thereby delivered in a dispersed stream downwardly onto the dense-phase level 16 of the fluidized bed.

The coke and pitch are charged to the reaction vessel at relative rates to produce a coke to pitch ratio in the

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range of 5:1 to 40:1. It is preferred that the velocity of the coke particles as they are introduced be slightly higher than the velocity of the pitch particles so that at the point where the two streams meet, the velocities will essentially be the same to insure good mixing without disruption of the smooth flow of either stream. In starting the unit, the coke stream is introduced into reaction vessel 10 before pitch is charged to the reaction vessel, to form a layer of coke particles moving around the inner surface of the reaction vessel and prevent caking on the walls thereof when the flow of pitch is commenced. The rapid mixing of the coke and pitch at the opening 30 and the relatively large coke to pitch ratio rapidly heat the pitch to conversion temperatures.

The fluidized bed 14 consists of coke particles suspended by upwardly moving fluidizing gases in a dense phase, turbulent, hindered settling condition. The dense phase in the fluidized bed 14 has a density of about 10 to 50 pounds per cubic feet. The fluidizing gases are introduced through a distributor 36 at the bottom of the fluidized bed 14 connected with a gas supply line 38. The superficial velocity of the upwardly moving fluidizing gases is about 0.5 to 5 feet per second. The temperature of the fluidized bed 14 is maintained in the range of 900° to 1600° F. and more desirably from 1100° to 1400° F. to cause a coking reaction resulting in favorable product distribution.

The volatile components of the pitch are quickly vaporized on introduction into the reaction vessel and pass upwardly through grid 12 into the fluidized bed of coke particles 18. The less refractory components of the unvaporized portions of the pitch are cracked in the fluidized bed 14 to produce volatile constituents which pass upwardly through grid 12 to the upper fluidized bed 18. The remaining heavy, refractory components of the pitch are absorbed by the coke and held at reaction temperatures in the fluidized beds 14 and 18 for a period sufficient to form coke. The residence time of the coke in the two fluidized beds ranges from about 5 to 30 minutes. The relative times in the two beds will depend upon the charge stock and the temperatures of the fluidized beds. The large surface area of the coke allows the heavy refractory components to adhere thereon in a very thin film whereby the coke remains in a substantially dry, readily fluidized condition.

The coke particles are transferred from the fluidized bed 14 to the fluidized bed 18 through a vertical transfer line 40. A transfer gas is introduced from a supply line 42 into the lower end of the transfer line 40 to effect the movement of the coke particles in a dilute phase. The density of the density of the dilute phase in transfer line 40 is in the range of 0.5 to 10 pounds per cubic foot. The rate of transfer of coke particles from the fluidized bed 14 to the fluidized bed 18 is controlled by a valve 44 which controls the opening at the bottom of transfer line 40. Valve 44 is connected by means of a spider 46 to a valve stem 48 which extends downwardly below the line 42. The rate of introduction of the transfer gas, which ordinarily is a substantially inert gas such as carbon dioxide, refinery gas, flue gas, nitrogen, methane, hydrogen or steam, but can be an oxygen-containing gas when it is desired to supply heat to the coke particles delivered to the bed 18, is controlled by a valve 50 in line 42.

The temperature in the fluidized bed 18 is usually substantially the same as the fluidized bed 14. Fluidized bed 18 provides additional time for the gases liberated from the pitch in the lower section of the reaction vessel to remain in contact with the hot coke particles and to be cracked to more valuable products. In addition, the coke delivered through transfer line 40 is maintained at a high temperature in the fluidized bed 18 for sufficient time to complete the conversion to a hard, dry coke. Gaseous reaction products pass through separator 22 and line 26 to product recovery apparatus.

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Typical yields from the fluidized coking process are gas, 5 to 40 percent by weight; gasoline, 15 to 40 percent by weight; gas oil, 20 to 80 percent by weight; and coke, 10 to 30 percent by weight. The heat required to maintain the fluidized beds in the reaction vessel 10 at the desired temperature is supplied by circulating coke particles from the fluidized bed 18 through a heater 54 and back into the fluidized bed 14. For this purpose, a standpipe 52 extends downwardly from the fluidized bed 18 to a transfer line 55. The rate of transfer is controlled by a valve 56 in standpipe 52. A coke discharge line 58 for withdrawal of coke from the system opens off the standpipe 52. The coke is carried through transfer line 55 and a grid 60 into a fluidized bed 62 of coke particles in heater 54 by an oxygen-containing gas supplied through line 64.

The temperature in the fluidized bed 62 is in the range of 1000 to 1800° F. thereby igniting the coke particles when they come in contact with the oxygen-containing gas present in the fluidized bed. If desired, additional oxygen-containing gas can be introduced directly into the heater 54 through a suitable supply line 65. The heat of combustion of the coke raises the temperature of the coke particles entering the heater 54 to the temperature of fluidized bed 62. Flue gases discharged from the upper dense-phase level 66 of the fluidized bed 62 pass through a separator 68 supported in the upper end of the heater and are discharged through an outlet line 70 connected with a suitable stack, not shown. Coke particles entrained by the gases discharged from the dense-phase level 66 of bed 62 are removed in separator 68 and returned to the bed 62 through a dip leg 72.

Hot coke particles are discharged from the heater 54 through a line 74 into the coke inlet line 32 for delivery to the reaction vessel 10. A valve 76 in line 74 permits control of the rate of flow of the coke particles from the heater. A carrier gas introduced through a supply line 78 transports the hot coke through inlet line 32 and injects it tangentially into the reaction vessel 10.

In some instances, it is desirable to supply additional heat to the upper fluidized bed 18 to overcome heat losses and maintain that bed at the same temperature as, or at a higher temperature than, the lower bed 14. For this purpose, a drawoff line 80 extends downwardly from the fluidized bed 62 in the heater 54. A hot coke transfer line 82 extends from the lower end of drawoff line 80 into the reaction vessel 10 above the grid 12. A transfer gas introduced into the lower end of hot coke transfer line 82 from a supply line 84 carries the hot coke particles into the fluidized bed 18.

In a specific example described for the purpose of illustrating this invention, a pitch having a ring and ball melting point of 350° F. is introduced at a temperature of 130° F. into the lower fluidized bed 14 which is maintained at a temperature of 1200° F. Hot coke particles at a temperature of 1350° to 1400° F. are introduced into the reaction vessel in a ratio of 15 parts by weight of coke to 1 part of pitch. Coke particles are transferred to the second fluidized bed by steam through transfer line 40. The second fluidized bed is maintained at 1200° F. The average residence of the time of the coke in the fluidized beds 14 and 18 is 15 minutes. The space velocity of the pitch is approximately 0.3 wt./hr./wt. coke.

This invention permits introduction of the pitch into the fluidized bed without plugging of the pitch feed line. The greater density and larger average particle size of the coke allows varying portions of the coke particles to move, through their greater centrifugal action provided by the tangential introduction, across the stream of pitch particles so that a thorough mixing of the pitch and coke particles is obtained. This mixing occurs in a relatively free space, and, thereby, eliminates coking of walls in the confined spaces of transfer lines which often occurs in conventional apparatus when high coke formers, such as pitch, are mixed with inert solids. Furthermore, the greater centrifugal action of the coke particles forms a

sufficiently high concentration of coke particles in the regions next to the vessel walls to provide a scouring action and prevent coke build-up on the walls of the vessel above the bed. The difficulties commonly encountered by agglomeration of the fluidized bed are avoided by the thorough mixing of the pitch with a large volume of coke before the pitch enters the fluidized bed, the relatively high degree of turbulence within the fluidized bed, and the very large area of the coke particles which causes the heavier components of the pitch to adhere to the coke particles in an extremely thin film. The high temperature of the fluidized beds and the extended time at the conversion temperatures made possible by passing the reaction products from the lower fluidized bed to the upper fluidized bed gives a severe cracking and favorable distribution of products from the coking process. The pitch discharged from the system by withdrawal from the upper fluidized bed is a hard coke, not contaminated with substantial quantities of incompletely coked pitch.

The apparatus and process herein described allows extremely flexible control of the conversion process by varying the total or relative depths and the temperatures of the two fluidized beds. This method of control may take several different aspects. When operating at high temperatures, the upper bed should be shallow to prevent too severe cracking of the more volatile compounds from the lower bed if high yields of gasoline are desired. If high yields of olefinic gases are desired, the upper bed should be deeper to provide more severe cracking of the more volatile compounds.

At low-temperature conditions, the upper bed should be shallow when producing gas oil for catalytic cracking in order to prevent undue cracking of the gas oil. If, however, it is desired to produce gasoline by coking, the upper coke bed should be deeper to convert the gas oil by increasing the contact time. These methods of control can be applied without altering the total inventory of coke in the unit, thereby maintaining the same overall holding time for the coke to allow for the production of a hard, dry material.

We claim:

1. A process for converting a charge stock of a solid carbonaceous material into more volatile hydrocarbons and coke, comprising introducing a stream of finely divided particles of charge stock suspended in a carrier gas tangentially into a first reaction zone containing a first fluidized bed of coke particles above the surface of the fluidized bed, said fluidized bed comprising coke particles between about 50 and 1000 microns in diameter at a temperature of 900° to 1600° F. maintained in a turbulent, dense, fluidized condition by ascending fluidizing gases, passing vapors discharged from the first reaction zone to a second reaction zone containing a second fluidized bed of coke particles maintained at a temperature of 900° to 1600° F., delivering coke particles from the first fluidized bed to the second fluidized bed, discharging gaseous reaction products from the second reaction zone, discharging a stream of coke particles from the second reaction zone, withdrawing a second stream of coke particles from the second fluidized bed and transferring them into a heater, passing an oxygen-containing gas in contact with the coke particles in the heater to burn a portion of the coke and thereby heat the particles, and withdrawing hot coke particles from the fluidized bed in the heater and introducing them tangentially into the first reaction zone into the stream of particles of charge stock discharged into the first reaction zone above the surface of the first fluidized bed.

2. A process as set forth in claim 1 in which the charge stock is petroleum pitch.

3. A process for converting a charge stock of a solid carbonaceous material into more volatile hydrocarbons and coke, comprising introducing a stream of finely divided particles of the charge stock carried at a high velocity by a carrier gas tangentially into a first reaction zone above the surface of a lower fluidized bed of coke particles, said

lower fluidized bed being maintained at a temperature of 900° to 1600° F., passing vapors liberated from the charge stock in the first reaction zone upwardly through a grid, located above the point of introduction of the charge stock particles, into an upper fluidized bed of coke particles maintained at a temperature of 900° to 1600° F. in a second reaction zone, withdrawing coke particles from the lower fluidized bed and transferring them to the upper fluidized bed for contact with the vapors liberated in the lower fluidized bed, withdrawing a stream of coke particles from the second reaction zone and discharging them from the system, discharging a stream of gaseous reaction products from the second reaction zone, delivering a stream of coke particles from the upper fluidized bed into a bed of coke particles fluidized by ascending oxygen-containing gases in a heater, the temperature of the fluidized bed in the heater being about 1000° to 1800° F., and withdrawing hot coke particles from the heater and introducing them tangentially into the first reaction zone into the stream of charge stock particles entering that reaction zone above the surface of the lower fluidized bed.

4. A process for converting a charge stock of a solid carbonaceous material into more volatile hydrocarbons and coke, comprising introducing a stream of finely divided particles of charge stock carried at a high velocity by a carrier gas tangentially into a first reaction zone above the surface of a lower fluidized bed of coke particles, said lower fluidized bed being maintained at a temperature of 900° to 1600° F., passing vapors liberated from the charge stock in the first reaction zone upwardly through a grid above the point of introduction of the charge stock particles into an upper fluidized bed of coke particles maintained at a temperature of 900° to 1600° F. in a second reaction zone, withdrawing coke particles from the lower fluidized bed and transferring them to the upper fluidized bed for contact with the vapors liberated in the lower fluidized bed, discharging a stream of coke particles from the second reaction zone, discharging a stream of gaseous reaction products from the second reaction zone, withdrawing a stream of coke particles from the upper fluidized bed and delivering them into a bed of coke particles fluidized by ascending oxygen-containing gases in a heater, the temperature of the fluidized bed in the heater being about 1000° to 1800° F., withdrawing hot coke particles from the heater and introducing them tangentially into the first reaction zone into the stream of charge stock particles discharged into that reaction zone above the surface of the lower fluidized bed, and withdrawing a second stream of hot coke particles from the heater and delivering them to the upper fluidized bed.

5. A process for converting a charge stock of a solid carbonaceous material into more volatile hydrocarbons and coke, comprising introducing a stream of finely divided particles of charge stock carried in a dilute phase by a carrier gas tangentially into a first reaction zone above the surface of a lower fluidized bed of coke particles, said lower fluidized bed being maintained at a temperature of 900° to 1600° F., passing vapors liberated from the charge stock in the first reaction zone upwardly through a grid above the point of introduction of the charge stock particles into an upper fluidized bed of coke particles maintained at a temperature of 900° to 1600° F. in a second reaction zone, introducing coke particles from the lower fluidized bed into a transfer line extending to the upper fluidized bed, introducing an oxygen-containing transfer gas into the transfer line to deliver hot coke particles to the upper fluidized bed, discharging a stream of gaseous reaction products from the second reaction zone, withdrawing a stream of coke particles from the upper fluidized bed and delivering them into a bed of coke particles fluidized by ascending oxygen-containing gases in a heater, the temperature of the fluidized bed in the heater being about 1000° to 1800° F., and withdrawing hot coke particles from the heater and introducing them tangentially into the first reaction zone into the stream of

charge stock particles discharged into that reaction zone above the surface of the lower fluidized bed.

6. A process for converting a charge stock of a solid carbonaceous material into more volatile hydrocarbons and coke, comprising introducing a stream of finely divided particles of charge stock carried at a high velocity by a carrier gas tangentially into a first reaction zone above the surface of a lower fluidized bed of coke particles, said lower fluidized bed being maintained at a temperature of 900° to 1600° F., passing vapors liberated from the charge stock in the first reaction zone upwardly through a grid above the point of introduction of the charge stock particles into an upper fluidized bed of coke particles maintained at a temperature of 900° to 1600° F. in a second reaction zone withdrawing coke particles from the lower fluidized bed and transferring them to the upper fluidized bed for contact with the vapors liberated in the lower fluidized bed, withdrawing a stream of coke particles from the second reaction zone and discharging them from the system, discharging a stream of gaseous reaction products from the second reaction zone, withdrawing a stream of coke particles from the upper fluidized bed and delivering them into a bed of coke particles fluidized by ascending oxygen-containing gases in a heater, the temperature of the fluidized bed in the heater being about 1000° to 1800° F., withdrawing hot coke particles from the heater and introducing them tangentially into the first reaction zone into the stream of charge stock particles discharged into that reaction zone above the surface of the lower fluidized bed, and adding heat to the upper fluidized bed by the introduction of hot coke particles thereto.

7. A process for converting a charge stock of a solid carbonaceous material into more volatile hydrocarbons and coke, comprising introducing a stream of finely divided particles of charge stock tangentially at a high velocity into a first reaction zone above the upper surface of a first fluidized bed of coke particles, the coke particles ranging in size from 100 to 500 microns and the temperature of the first fluidized bed being 1100° to 1400° F., introducing a fluidizing gas into the lower portion of the first fluidized bed to maintain a dense, turbulent, fluidized bed, passing vapors from the first reaction zone upwardly through a second fluidized bed in a second reaction zone maintained at a temperature of about 1100° to 1400° F., withdrawing coke particles from the first

fluidized bed and transferring them to the second fluidized bed, whereby the average length of time of the hot coke particles in the reaction zones is about 5 to 30 minutes, withdrawing a first stream of coke particles from the second fluidized bed and discharging them from the system, discharging gaseous reaction products from the second reaction zone, withdrawing coke particles from the second fluidized bed and delivering them to a fluidized bed of coke particles in a heater, passing an oxygen-containing gas through the fluidized bed of coke particles in the heater to maintain the temperature of the bed at about 1200° to 1500° F., and withdrawing a stream of hot coke particles from the heater and introducing them tangentially at high velocity into the first reaction zone to mix with the charge stock particles above the fluidized bed, the ratio of the coke to the charge stock introduced into the first reaction zone ranging from about 5:1 to 40:1.

8. Apparatus for the conversion of a charge stock of a solid carbonaceous material pitch in the presence of fluidized coke particles comprising a vertical substantially cylindrical reaction vessel, a horizontal grid in the reaction vessel extending thereacross to divide the reaction vessel into an upper reaction zone and a lower reaction zone, a charge stock inlet line opening tangentially into the reaction vessel below the grid, a coke inlet line opening tangentially into the reaction vessel below the grid, said coke inlet line being positioned to direct the coke across the opening of the charge stock inlet line, a transfer line extending from the lower reaction zone to the upper reaction zone for the transfer of fluidized coke particles from the lower reaction zone to the upper reaction zone, a transfer gas inlet line opening into the lower end of the transfer line, a gas outlet at the upper end of the upper reaction zone, and a coke withdrawal line extending from the reaction vessel above the grid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,577,632	Roetheli	Dec. 4, 1951
2,624,697	Clouse	Jan. 6, 1953
2,656,308	Pettyjohn	Oct. 20, 1953
2,719,112	Kearby	Sept. 27, 1955
2,739,104	Galbreath	Mar. 20, 1956