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HIGH-TEMPERATURE, LOW-CONTACT TIME COKING PROCESS

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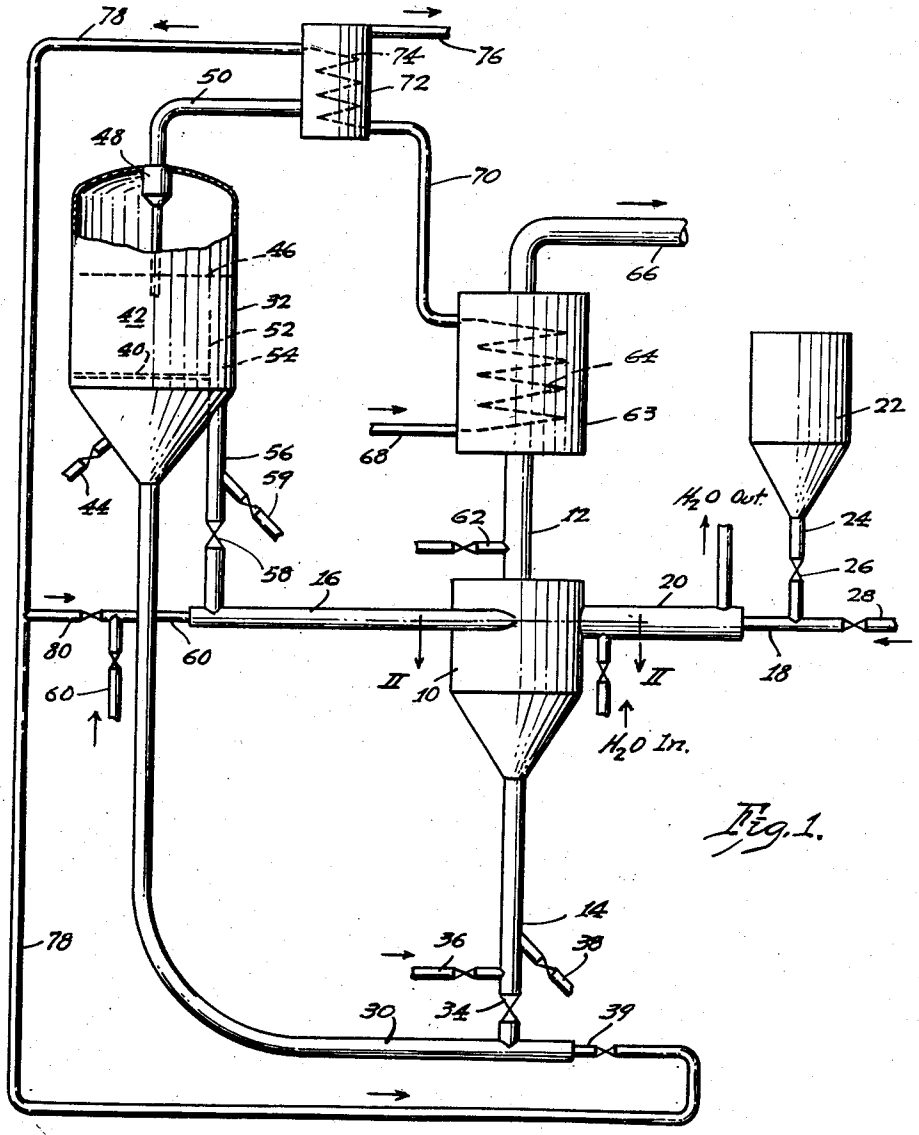


Fig. 1.

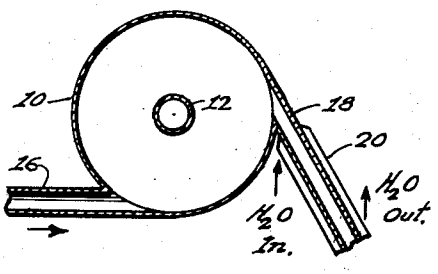


Fig. 2.

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HIGH-TEMPERATURE, LOW-CONTACT TIME COKING PROCESS

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2 Claims. (Cl. 202—14)

This invention relates to a process for the conversion of carbonaceous materials and more particularly to the preparation of volatile hydrocarbons rich in unsaturated hydrocarbons from carbonaceous materials in a coking process.

One method of converting heavy residual oils to more valuable products is the delayed coking process in which the residual oil is heated to a coking temperature, generally in the range of about 900° to 950° F., in heating coils and discharged into a coking drum at about 775° to 850° F. in which it is allowed to remain until coking has been completed. The stream of hot residual oil discharged from the heating coils is switched periodically from one coking drum to another to allow the coke to be removed from one of the drums while another is in use. The distillate products obtained from the delayed coking process are generally of low quality, partly because of the low temperature employed for the conversion of the residual oils. If higher temperatures are employed, excessive coke is formed in the heating coils. The use of several coking drums allows the delayed coking process to be run continuously but increases the cost of the equipment required, which, together with the cost of removing the coke from the coking drum, makes the delayed coking process a relatively expensive process.

A process has been developed for the coking of carbonaceous materials in which the carbonaceous materials are introduced into a fluidized bed of hot coke particles. The carbonaceous materials are converted into volatile products, which are removed from the top of the reactor as gases, and coke which is deposited on the coke particles in the fluidized bed. The fluidized coking process is suitable for use in the coking of carbonizable materials such as asphalts, oil shale, petroleum pitch, tar sands, etc., as well as heavy liquid petroleum oils. The carbonaceous materials can be heated rapidly to a high temperature in the fluidized coking processes; however, volatile products from the coking of the charge stock remain in contact with the hot coke particles for long periods during which time they are further cracked to gases of relatively low value. Moreover, the coke in the fluidized bed, and, hence, the coke in a stream withdrawn therefrom, is of an average composition and contains incompletely carbonized fractions which are susceptible to further cracking to more valuable products.

A difficulty that is encountered in the fluidized coking of heavy carbonaceous materials is the agglomeration of coke particles in the fluidized bed which interferes with fluidization of the bed. Heavy residual oils contain large quantities of hydrocarbon fractions having a high boiling point. The high boiling fractions form a layer of liquid on the coke particles in the fluidized bed and cause adjacent coke particles to stick together. Many of the solid carbonaceous materials which can be used as charge stocks pass through a plastic range as they are heated to coking temperatures in which range they also cause agglomeration of the coke particles.

It has been suggested that heavy carbonaceous materials be coked in a dilute phase of hot coke particles, carried by transfer gas in which there is substantially no backflow of solid particles in a direction opposite the flow of transfer gas. It is difficult to obtain rapid heating of the carbonaceous materials to the desired conversion temperatures to give an optimum yield of desirable reaction products in a dilute phase process. Merely increasing the ratio of the hot transfer gases or coke to the carbonaceous charge stock, or the temperature of the transfer gas or coke, to increase the rate of heating places an additional load on the equipment. An increase in the amount of carrier gas further dilutes the volatile reaction products obtained and makes product recovery more difficult.

This invention resides in a process for converting carbonaceous materials to coke and valuable volatile reaction products rich in olefins or acetylenic compounds in which a stream of hot coke particles is introduced tangentially at a high velocity into a cyclone separator thereby forming a stream of coke particles swirling around the inner surface of the wall of the separator. The carbonaceous material to be converted is introduced through the side of the cyclone separator into the swirling stream of hot coke particles. A temperature in the range of 1400° to 2200° F. is maintained in the separator for the conversion of the carbonaceous material, and the volatile reaction products are rapidly withdrawn from the separator in order that they will remain at the reaction temperature for a short time, in the range of 0.1 to 5.0 seconds. The internal circulation in the cyclone separator, resulting from the many passes of the swirling stream of hot coke particles in the separator, causes an effective ratio of coke to carbonaceous material at the confluence of the coke and carbonaceous material streams much higher than the ratio of coke to carbonaceous material introduced into the separator. The rapid mixing of coke and carbonaceous material and the high effective ratio of coke to carbonaceous material heats the carbonaceous material substantially immediately to conversion temperatures.

Figure 1 is a flow sheet diagrammatically illustrating one system for the conversion of carbonaceous material to coke and volatile products rich in valuable unsaturated hydrocarbons.

Figure 2 is a sectional view taken along section line II—II in Figure 1 illustrating the arrangement of the inlet lines for the introduction of the coke and carbonaceous material into the cyclone separator used as a reactor in this invention.

For purposes of illustration, this invention will be described for the preparation of coke and gases having a high concentration of olefins and/or acetylenic compounds by the conversion of petroleum pitches. This invention is not so limited and can be employed for the conversion of other carbonizable carbonaceous materials such as coal, peat, heavy residual oils, tar sands, oil shale, etc.

Referring to Figure 1 of the drawings, a cyclone separator **10** serves as the reactor in which conversion of the carbonaceous material takes place and is hereafter designated as the reactor. The cyclone reactor **10** is of conventional design and construction for separators with an outlet line **12** for gaseous products extending upwardly from the center of the top of the cyclone reactor **10** and downwardly into the reactor for a short distance below the level of the inlet lines. A dip leg **14** extends from the lower end of the cyclone reactor **10** for the removal of coke particles in the manner hereinafter described.

A coke inlet line **16** opens tangentially into the cyclone reactor **10** near its upper end in the manner illustrated

in Figure 2 of the drawings. The tangential opening of the coke inlet line into the cyclone reactor **10** and the high velocity of the coke particles passing through the line **16** cause the coke particles to swirl inside of the cyclone reactor forming a relatively dense layer of coke particles moving at a high velocity along the inner surface of the walls of the cyclone reactor.

A pitch inlet line **18** also extends through the side wall of the cyclone reactor **10** for discharge of the pitch particles directly into the stream of coke circulating in the cyclone reactor. Pitch inlet line **18** is preferably provided with a water jacket **20**, as illustrated in the drawings, to withdraw heat transferred back from the cyclone reactor **10** through line **18** and prevent melting of the pitch particles prior to entering the cyclone reactor. Water jacket **20** is not required for most carbonaceous materials employed as feed stocks, or even desirable for liquid residual oils.

The petroleum pitch is introduced into the pitch inlet line **18** from a storage hopper **22** having a standpipe **24** extending from its lower end. A slide valve **26** in the standpipe **24** permits control of the rate of feed of the pitch particles into the cyclone reactor. The lower end of the standpipe **24** opens into the pitch inlet line **18**. The pitch particles are transported through inlet line **18** by a transfer gas discharged into the inlet line **18** from a supply line **28**.

The dip leg **14** from the cyclone reactor opens at its lower end into a transfer line **30** for delivery of the coke particles to a heater **32**. A slide valve **34** in the lower end of the dip leg **14** allows control of the rate of withdrawal of the coke particles from the cyclone reactor **10**. A stripping gas, preferably steam, is introduced into the dip leg **14** from a supply line **36** for fluidization of the coke particles in the dip leg **14** and to prevent entrainment of gaseous reaction products from the cyclone reactor into the dip leg. A coke drawoff line **38** extends from the dip leg **14** for withdrawal of coke from the system.

The hot coke particles are carried in the transfer line **30** by a transfer gas, preferably air or flue gas, from a supply line **39** upwardly into the lower end of the heater **32**. The coke particles pass upwardly through a grid **40** extending across the heater **32** and into a fluidized bed **42** of hot coke particles. Additional air for the burning of coke to supply the heat necessary for the conversion of the carbonaceous material is introduced, if required, into the heater **32** through a supply line **44**. Flue gases discharged from the upper surface **46** of the fluidized bed **42** pass through a cyclone separator **48** in the upper part of heater **32** and are discharged through an outlet line **50**.

A baffle **52** extends upwardly through the fluidized bed **42** to form a well **54** through which hot coke particles are withdrawn from the heater. A standpipe **56** extends from the lower end of the well **54** and is connected at its lower end to the coke inlet line **16**. The rate of withdrawal of hot coke particles from the heater **32** is controlled by a valve **58** in the standpipe **56**. Transfer gas for delivery of the hot coke particles to cyclone reactor **10** at a high velocity is supplied through a transfer gas supply line **60**.

In the system illustrated in the drawings for use in this invention heat exchange apparatus is utilized to reduce the heat lost from the system. A heat exchanger **63** provided with suitable heat exchange surface indicated by coils **64** is connected to outlet line **12** from the cyclone reactor **10**. The gaseous reaction products from outlet line **12** pass through heat exchanger **63** to a line **66** for delivery to a product recovery system, not shown.

A transfer gas from a supply line **68** passes through coils **64** in which it is heated by heat exchange with the gaseous reaction products and is then delivered through a line **70** to a second heat exchanger **72** provided with heat exchange surface indicated by coils **74**. Heat exchanger **72** is arranged to pass the flue gases from line **50** in contact with the coils **74** and then through a flue **76** to a stack, not shown.

Hot transfer gases are discharged from coils **74** to a line **78** connected with transfer gas supply line **39**. The hot transfer gas from line **76** can also be employed to transfer coke particles from the heater through line **16** to the cyclone reactor **10**. A connecting line **80** from line **78** to line **60** is provided for this purpose.

In the operation of the process, the hot coke particles having a particle size in the range of about 20 to 80 mesh at a temperature of about 1500° to 2500° F. are transported at high velocities through line **16** and discharged tangentially into cyclone reactor **10**. Conventional transfer gases such as, for example, inert gases, refinery gases (C_2 and lighter), flue gases, and gases containing oxygen can be used. A preferred transfer gas is superheated steam, which facilitates separation of the reaction products. The hot coke particles are delivered into the cyclone reactor at a velocity in the range of 50 to 200 feet per second in a ratio of coke to pitch particles fed into the reactor ranging from 3:1 to 50:1. The coke to pitch ratio and the temperature of the coke particles are adjusted to maintain the heat balance of the system.

Petroleum pitch, preferably having a ring and ball softening point of about 350° F. or higher, in a finely divided form is discharged from the hopper **22** through the standpipe **24** and valve **26** into the pitch inlet line **18**. The pitch has a particle size generally ranging from about 50 to 200 mesh with some fines, normally less than about 5 percent, smaller than 200 mesh. The temperature of the pitch particles delivered into the reactor is not critical but it is desirable to introduce the pitch as a finely divided solid and to avoid partial melting which might cause plugging of the inlet line **18**; hence, the pitch particles are introduced at a temperature ranging from atmospheric temperature up to about 250° F. The pitch is transported through inlet line **18** to the cyclone reactor by carrier gas which may be refinery gases, steam at a temperature below 250° F., or flue gases supplied from line **28**. The pitch particles are introduced into cyclone reactor **10** at a high velocity in the range of 15 to 200 feet per second and preferably from about 50 to 75 feet per second. If the feed is introduced radially into the cyclone reactor, somewhat lower velocities are generally preferred.

The stream of hot coke particles enters the cyclone reactor and swirls along the wall of the reactor, across the entrance of the pitch particles into the reactor. The internal circulation in the cyclone reactor provides a large mass of coke sweeping near the entrance of the pitch inlet line **18** into the cyclone reactor, thereby giving an extremely large surface of coke particles on which the heavy fractions of the pitch not immediately vaporized or cracked are adsorbed. The very thin layer of heavy fractions of pitch adsorbed on the coke particles and the large mass of coke particles as compared with the pitch causes the pitch to be quickly heated to the optimum conversion temperatures maintained in the cyclone reactor **10**. The transfer gases and the gaseous reaction products are quickly separated from the hot coke, removed from the cyclone reactor, and quenched in outlet line **12** before serious degradation of the reaction products occurs.

The temperature within the cyclone reactor **10** ranges from about 1400° to 2200° F., depending upon the reaction products desired. If a high concentration of acetylene is desired in the reaction products, temperatures near the upper limit are preferred. If a high concentration of olefins is desired in the reaction products, the temperature is preferably maintained in the range of about 1400° to 1750° F. The pressure in the cyclone reactor is substantially atmospheric, ranging up to about 75 pounds per square inch gauge.

In order to produce the desired reaction products, it is essential that the time the volatile hydrocarbon vapors liberated in the reactor remain at the high temperatures

be very short to prevent further cracking of olefins to gases of less value. The cyclone reactor quickly separates gases from the solid particles swirling around the wall. In general, the time the gases are in the cyclone reactor will range from about 0.1 to 5.0 seconds and preferably less than about 3 seconds. Gases discharged from the cyclone reactor through line **12** are quenched by the introduction of a suitable quenching medium, such as steam or hydrocarbons, through line **62**.

The coke particles descend in the cyclone reactor to the dip leg **14** in which they form a relatively dense mass of pitch particles. The coke particles remain in the dip leg **14** for a substantial length of time before they are discharged into the transfer line **30**, and, because of the high temperature in the dip leg **14**, the carbonization is substantially completed to form a hard coke suitable for withdrawing directly from the system through line **38**. The stripping gas introduced through line **36** sweeps volatile hydrocarbons formed during completion of the coking from, and aerates the dense mass of coke particles in, the dip leg.

The hot coke particles are carried through transfer line **30** by a transfer gas, preferably an oxygen-containing gas, introduced through supply line **39** into the heater **32** and pass upwardly into the fluidized bed **42** which is maintained at a temperature of 1500° to 2500° F. A portion of the coke is burned to supply the heat necessary to maintain the heat balance of the conversion process. Hot coke particles are withdrawn through well **54** and recirculated to the cyclone reactor **10**. If it is desired to remove coke from the system, the coke particles can be withdrawn from the heater **32**, for example, through a draw-off line **59**, from standpipe **56** rather than from the dip leg **14** through line **38**.

In an example of this invention, coke particles at 1800° F. carried by superheated steam are introduced into the cyclone reactor maintained at a temperature of 1600° F. Finely ground pitch particles are carried by refinery gases at a temperature of 200° F. and are introduced into the cyclone reactor at a rate to give a coke to pitch ratio of approximately 7:1. Volatile reaction products discharged from the cyclone reactor are quenched immediately with steam to give a reaction time of approximately 1 second. Hot coke particles are withdrawn from the bottom of the cyclone reactor through the dip leg and circulated through the heater and returned to the reactor.

The process of this invention can be employed to convert carbonaceous materials other than the petroleum pitches described to coke and gases rich in olefins. Heavy liquid residues of petroleum, or other solid carbonaceous materials such as coal, peat, lignite, and shale can also be employed in the high temperature conversion process. The very high effective coke to carbonaceous material ratio resulting from the internal circulation within the cyclone reactor causes rapid heating of the carbonaceous material to conversion temperatures.

The use of the cyclone separator as a reaction vessel permits rapid removal of gaseous reaction products to avoid cracking of olefins to less valuable gases and also provides efficient disengagement of solids from the gases. In this process, the coke particles can be maintained at a high temperature for substantial periods to complete the coking of the residues adsorbed on the surface of the coke. Moreover, the separate withdrawal of the coke particles and volatile products from the reactor allows the coke to be maintained at high temperatures throughout the system thereby reducing the heat requirements for the conversion processes.

We claim:

1. A process for the conversion of petroleum pitch to coke and unsaturated volatile hydrocarbons comprising introducing tangentially into a cyclone reactor at a velocity of 50 to 200 feet per second coke particles, at a temperature in the range of 1500° F. to 2500° F. and having a particle size in the range of about 20 to 80 mesh, suspended in a transfer gas to form a dense stream of coke particles swirling around the wall of the reactor surrounding a substantially solids free vortex in the center of the reactor, introducing tangentially into the cyclone reactor in the direction of movement of the coke particles and directly into the dense stream of coke particles of cokable carbonaceous solids which pass through a plastic stage as they are heated to coking temperatures suspended in a transfer gas at a temperature below about 250° F., said particles having a particle size in the range of about 50 to 200 mesh, the ratio of the weight of coke charged to the cyclone reactor to the weight of cokable carbonaceous solids charged to the cyclone reactor being in the range of 3:1 to 50:1 adapted to maintain the temperature in the reactor in the range of 1400° F. to 2200° F., the internal circulation of the cokable carbonaceous solids swirling around the wall of the cyclone reactor giving an effective ratio of coke to cokable carbonaceous solids mixed therewith higher than the ratio in which the two materials are charged to the reactor whereby an extremely thin layer of cokable carbonaceous material is deposited on the coke particles and heated rapidly to conversion temperature, rapidly separating volatile reaction products from the coke in the cyclone reactor and quenching the separated volatile reaction products to limit the time the volatile reaction products are at conversion temperatures to 0.1 to 5.0 seconds, passing coke particles separated from the volatile reaction products downwardly through a column maintained at conversion temperatures to complete coking of hydrocarbons thereon, transferring hot coke particles from the column to a heater containing a fluidized bed of hot coke particles, passing an oxygen-containing gas upwardly through the fluidized bed of coke particles to burn a portion of the coke and thereby supply heat for the process, withdrawing coke particles from the system, and recycling hot coke particles from the heat into the cyclone reactor to supply heat for the conversion process.

2. A process as set forth in claim 1 in which the cokable carbonaceous solid is petroleum pitch.

References Cited in the file of this patent

UNITED STATES PATENTS

2,608,526	Rex	Aug. 26, 1952
2,623,011	Wells	Dec. 23, 1952
2,656,308	Pettyjohn	Oct. 20, 1953
2,719,112	Kearly	Sept. 27, 1955
2,739,104	Galbreath et al.	Mar. 20, 1956

FOREIGN PATENTS

288,491	Great Britain	1928

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

February 17, 1959

Patent No. 2,874,092

Harold Beuther et al.

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

Column 6, line 19, for "of cokable" read -- particles of cokable --.

Signed and sealed this 2nd day of June 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents