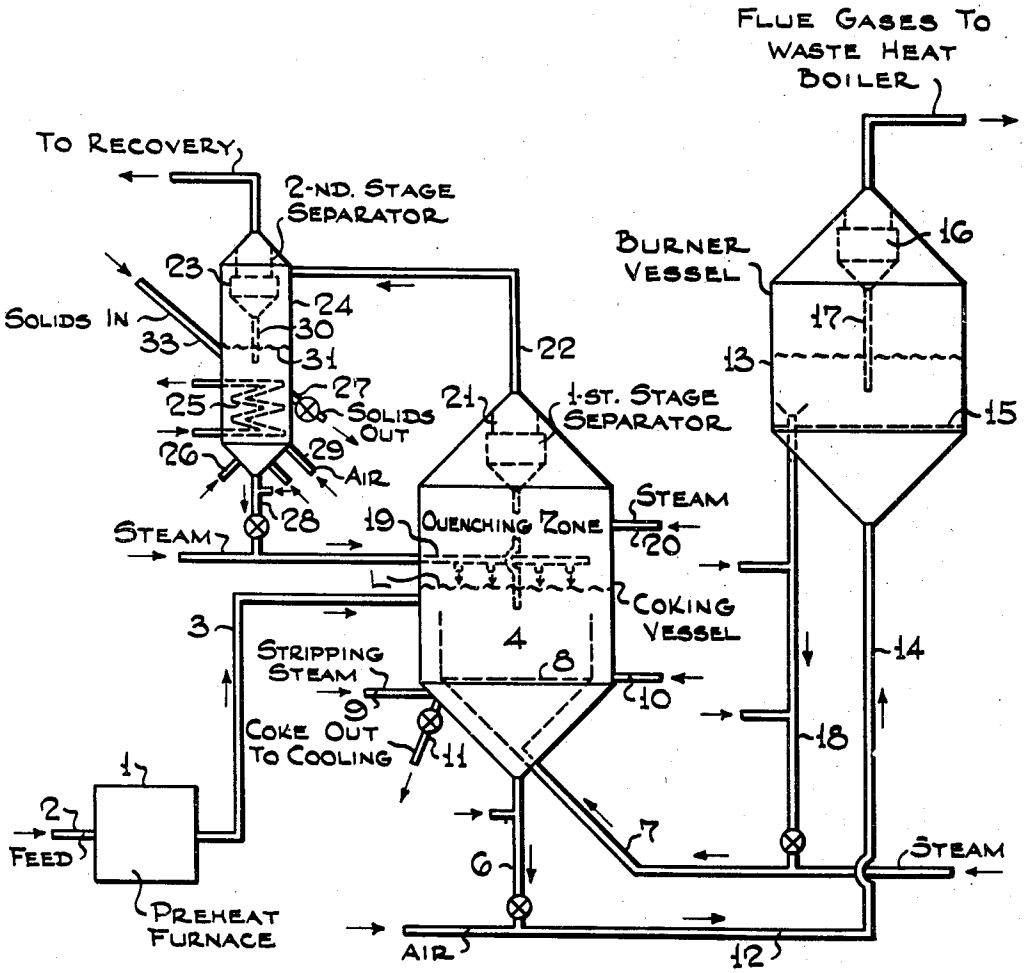
Oct. 18, 1949. W. A. REX ET AL 2,485,315

CONTROLLED SEVERITY FLUID COKING

Filed Dec. 6, 1947



Walter A. Rex
Bruno E. Roethelí Inventors

By J. Cashman Attorney

Patented Oct. 18, 1949 2,485,315

UNITED STATES PATENT OFFICE

2,485,315

CONTROLLED SEVERITY FLUID COKING

Walter A. Rex, Westfield, N. J., and Bruno E. Roetheli, London, England, assignors to Standard Oil Development Company, a corporation of Delaware

Application December 6, 1947, Serial No. 790,075

7 Claims. (Cl. 196—55)

1

The present invention relates to an improved process for conversion of carbonaceous material, such as coal, reduced crudes, asphaltites, oil shales, peat, tar sands, and the like into valuable fuel products. More specifically, the invention relates to a process of controlling the severity of the coking of these materials by the fluid solids technique.

The economic feasibility of a fluid process for coking such materials as reduced crudes and asphaltites, including gilsonite and the like is frequently dependent on the ability to control the temperature level in the reaction zone and the length of time the vapors from coking are subjected to the temperature level of the zone. Thus, in order to produce as a final product a maximum yield of gas oil it may be desirable to operate at relatively low coking temperatures with moderate throughput rates. If a maximum of light distillate product is desired it will be necessary to operate at higher carbonization temperatures, and the ability to control the severity of the coking so as to obtain the desired product distribution and quality becomes essential. Since the carbonaceous heavy liquid, semi-solid, and solid materials suitable for carbonization each require different handling and treatment, the ability to handle different feed stocks in the same equipment and obtain a wide range of products and yields is also desirable. The fluid solids coking technique as described hitherto permits some flexibility in obtaining specific uniform temperature levels in the coking bed, however, it permits only a limited flexibility of contact time and control of severity of vapor treatment, mainly because of the almost complete lack of temperature gradient in the fluidized bed, and because of limitations in vapor velocity imposed by entrainment considerations.

In accordance with the present invention, this major objection inherent in the conventional fluid coking operation, namely the lack of control of severity of heat treatment of coking vapors is overcome by injecting entrainable solids at a temperature level different from that in the fluid bed into the reaction vessel a short distance above the fluid bed. The vapors leaving the bed are thus either cooled below or heated above the temperature of the bed, thus providing for a degree of flexibility in coking severity. The "effective" contact time, i. e. the period of time during which the vapors are exposed to "effective" carbonization temperature, is thus controlled within desired limits by varying the quantity and temperature of the injected solid and to some extent by the height of the modified dilute phase. This solid may be coke from the process, or some other finely divided material such as wood flour, saw dust, coal, partially spent cracking catalyst, etc.,

2

or a combination of these. When it is desired to minimize cracking of the vapors use is made of the vapor quenching embodiment of the invention, and a greater yield of heavier liquid products is obtained from the feed stock, with less material going to coke, light products and gas than if the quenching step were not incorporated in the coking process. The use of the quenching step is thus highly advantageous when processing a stock such as heavy crude residuum to produce feed stock for catalytic cracking.

By the vapor cracking embodiment of the invention, the benefits of high temperature coking vapor treatment are realized, while still obtaining the normal char or coke as the coking product.

In accordance with the invention, reduced crude or other type of carbonaceous material may be given a maximum preheat commensurate with preventing coking in the lines, and is introduced into the coking vessel into a coke bed fluidized by an upwardly flowing gas, such as steam. The coke bed temperature may be maintained by recycling of hot solids from a separate combustion zone if the coking unit is a so-called two vessel system, as in the accompanying figure. Vapors leaving the coke bed are immediately cooled or heated to the desired temperature by the solid which is at a higher or lower temperature level than the fluidized bed, and which has been injected a short distance above the bed into the dilute phase which contains a considerably smaller amount of solid per volume of vapors than the fluid bed. It is preferable that the solids be introduced to the dilute phase in fluidized form and highly essential that they be injected so as to achieve a uniform distribution in the space above the fluid bed. This may be accomplished by introducing the solids through a number of uniformly spaced distributors located in a manifold in the dilute phase above the bed. The solid thus supplied is preferably of finer average particle size and/or of a lower density than the coke in the vessel, and consequently a larger proportion of it is entrained and carried overhead through a first stage gas-solids separator operated under conditions such as to return mainly the larger and denser particles to the coking bed. The use of fines for temperature control has a two-fold advantage, (1) the heat transfer rate and, consequently, the speed of quenching or heating, is high because of the large surface area of the particles and (2) an added heat load is not placed on the coking section, inasmuch as most of the fine solid is carried overhead, and hence mixing of the temperature controlling solids with the fluid bed is minimized. The fine particles, most of which pass through the first stage separator,

the function of the latter being to return entrained coke to the fluid bed, are removed from the vapor stream in the second stage separator, cooled or heated, and may be recycled to the coking vessel.

It is, therefore, the principal object of the present invention to provide a means for controlling the severity of the temperature treatment of the vapors produced from coking carbonaceous solids, semi-solids, and heavy liquids.

It is also the object of the present invention to provide a means whereby the vapors produced by coking carbonaceous materials at elevated temperatures in a fluidized bed can be confined at said elevated temperature for a controllable period of time so as to provide the maximum flexibility in the type of products produced from the coking operation.

Another object of the invention is to provide means for handling different types of feed stock for the coking process in the same equipment and obtain a wire range of products.

Other objects and advantages of the invention will appear hereinafter.

In the accompanying figure there is shown diagrammatically a process by means of which a preferred embodiment of the invention may be carried into effect. The process as indicated in the diagram may be employed either for increasing or decreasing the severity of the heat treatment of the coking vapors. The description that follows immediately is the process of controlling the coking contact time, in which cooled solids are circulated in accordance with the invention. Referring now in detail to the diagram, 1 denotes the preheat furnace to which the carbonaceous material to be coked is first fed from storage through line 2. The feed may be solid, semi-solid, liquid or suspension of a solid in a liquid and may be such material as coal, peat, or semi-solid petroleum fractions or mixtures thereof. If solids, such as coal or asphaltites, they are in a finely divided form, preferably of the order of below 50 mesh or even below 100 mesh, though particles up to about ½ inch size may be employed. The specific example here cited involves a heavy liquid petroleum fraction, but it is to be understood that the invention is not limited thereby. The feed is conveyed through feed line 2 to preheat furnace 1 where it is given the maximum preheat commensurate with preventing coking in the furnace tubes and lines leading to the coking vessel. Preheat furnace 1 is maintained at a temperature ranging from about 500°–900° F., depending upon the charge stock. The hot carbonaceous feed stock is withdrawn from preheat furnace 1 through line 3 and is conveyed in a manner known per se to the coking vessel 4, and is injected therein at a feed inlet.

Coking vessel 4 is in the form of a cylinder fitted at its lower end with a conical base with outlet line 6 for carbonized solids and inlet line 7 for gasiform material such as steam and for hot solids from the combustion zone as will appear more clearly hereinafter. A grid or screen 8 is located in the lower portion of the chamber, as well as gas or steam inlets 9 and 10 for stripping. Line 11 is provided to remove coke and/or ash from the system. In a manner that will be described more fully below, a bed of fluidized hot solids resulting from the coking of the feed stock is maintained in coking vessel 4 by a stream of upwardly flowing steam entering the vessel from line 7 and maintaining the hot coke as a dense, turbulent mass resembling a boiling liquid, and having a well-defined upper level L. The temperature in the fluidized bed is in the range of from about 850° to 1100° F., and the heat required for the coking operation is provided by recirculating hot solids from a combustion zone. The fresh feed inlet is preferably below the top of the fluid bed in coking vessel 4.

Carbonized solids are continuously withdrawn from the fluidized solids bed after first being stripped of adhering vaporization products by steam or inert gas, are conveyed through line 6 and are picked up by a stream of oxidizing gas, such as air, in line 12, and are introduced into the lower conical section of combustion vessel 13 through line 14. This vessel is a conventional fluid solids reactor with a screen or grid 15 for insuring proper distribution of fluidized solids in the reactor, and a dust separator 16 for returning entrained solids to fluidized bed through dip pipe 17. The carbonized solids from the coking vessel 4 are maintained in a fluidized condition in combustion chamber 13 and they are subjected to at least a partial combustion at temperatures of from about 1100° to 1300° F., depending upon the heat requirements of the coking zone. Flue gases from the combustion are withdrawn through dust separator 16 and are passed through a waste heat boiler for steam generation. The separated fines may be returned to the fluid bed by dip pipe 17 or part of it removed from the system.

A stream of hot solids substantially at the temperature of the fluidized bed in combustion vessel 13 is withdrawn from the latter through aerated standpipe 18, further fluidized by steam, and is continuously recycled to the coking chamber 4, which it enters near the bottom through line 7. The solids are maintained as a fluidized bed by the upwardly flowing steam, whose superficial velocity through the bed is determined by the size of the solid carbonaceous particles, and may vary from about 0.3 to 5 feet per second. The heat of coking of the fresh carbonaceous feed stock is thus substantially completely furnished by heat supplied from the combustion chamber 13. As required to maintain the fresh feed-coke balance in the system, coke is withdrawn from the fluid bed in coking vessel 4 through line 11 and removed from the system.

To provide the vapor quenching step of the invention, a stream of steam or inert gas and solid particles, such as coke from the system, coal, sawdust, wood flour, etc., having a particle size of about 200–400 mesh is injected into the coking vessel 4 a short distance above the level L of the fluidized bed and above the fresh feed inlet, through a number of uniformly spaced distributors located in a manifold 19. Vapors resulting from the carbonization and coking of the feed in the coking vessel are immediately cooled after passing upward through the quenching zone provided by the injected cooled particles. To minimize condensation of higher boiling vapors on the surface of the cooled particles, a steam inlet line 20 is provided to furnish a small quantity of extra steam to the vapor space. The quenched vapors and entrained solids are withdrawn through cyclonic solids separator 21, where the coarser and/or higher density carbonization particles are preferentially removed and returned to the fluid coke bed below level L. The vapors and the quenching medium particles are withdrawn overhead from cyclone 21 and are conveyed through line 22 to a secondary more efficient dust separator 23, located at the upper end of vessel 24. This vessel is a fluid reactor equipped with a coil 25,

the purpose of the latter being to cool the fluid solids bed in vessel 24 to the desired temperature for quenching vapors in the coking vessel 4. The latter bed is maintained in a fluid state in vessel 24 by an upwardly flowing gas stream, preferably steam, entering the heat exchanger vessel 24 through line 26. To insure flexibility in the rate of recycle solids cooled by heat exchange and passed to the quenching zone, as will be made clear hereinafter, a solid draw-off line 27 and a fresh solids addition line 33 are provided. The cooling medium circulated through coil 25 may be water, steam, "Dowtherm," or other medium which will serve the purpose of reducing the temperature of the quenching solids to the temperature required for obtaining the desired type and range of distillate from coker 4.

The vapors and quenching solids conveyed at a temperature of between 800°–900° F. or less into cyclone 23 are separated, the former passing overhead to the products recovery system, the solids being conveyed into the body of the heat exchange vessel 24, where they are fluidized by upwardly flowing steam or gas to maintain a fluid bed whose height is adjusted by the rate of solid removal from the bed through line 28, and by the addition or withdrawal of solids through lines 33 and 27 respectively. The cooled solids are withdrawn from the heat exchange vessel 24 through line 28 and are conveyed, by means of the pressure exerted by the pseudo-hydrostatic head of the fluidized solids in the heat exchange zone to the coking vessel, along with fresh make-up as required and as already described. Thus the temperature of the quenching zone in the coking vessel is determined to a large extent by, (*a*) the amount of cooling applied to the solids in the heat exchange zone 24 and, (*b*) the rate of circulation of the cooled solids.

As an exemplifying but not limiting case for processing a crude residuum, the following temperatures and circulation rate may be used to illustrate the coking of 18% East Texas bottoms on the basis of 100 gallons per hour in accordance with the invention:

Feed—17.2° A. P. I. East Texas residuum.

Temperature in fluid bed in coking vessel	°F.	About 1000
Temperature in quenching zone	°F.	About 900
Temperature in second stage separator	°F.	About 890
Temperature of cooled solids from heat exchanger	°F.	About 500
Temperature of preheated feed to coking vessel	°F.	About 850
Temperature of combustion zone	°F.	About 1200
Coke rate to quench zone	lb./min.	About 9
Fluidizing steam to coking vessel	lb./hr.	About 78
Coking vessel top pressure	p. s. i. g.	About 7
Coke circulation rate—burner to coking vessel	lb./min.	About 51

Yields (calc.):

Dry gas	weight per cent	10.9
Total C_4+gasoline	volume per cent	23.8
Gas oil	do	61.2
Coke	weight per cent	9.7

The foregoing illustrative descriptions have dealt with that modification of the present invention in which the severity of coking is decreased by employing the quenching principle of the invention. The operating flexibility of the present invention makes possible increasing the severity of coking by introducing a superheating zone above the fluidized coke bed in coking vessel 4. Such treatment is particularly desirable where coal is being carbonized. When coal is carbonized at moderate temperature levels in the range of 850–1100° F. by the fluid solids technique, a very heavy high boiling tar is produced which is difficult to handle and requires further processing before it can be converted into valuable products. By raising the temperature in the vapor space above the fluid bed a large amount of cracking of tar vapors is accomplished, while the normal low temperature char or coke is obtained as the coking product.

In accordance with the vapor phase cracking modification of the invention, the circulating solids, comprising the vapor cracking phase, may be heated in fluidized heating vessel 24 to a temperature substantially above that obtaining in the coking zone in coking vessel 4. Heating of the circulating solid particles may be accomplished indirectly by passing hot flue gas from the combustion vessel 13 through coil 25, or it may be accomplished directly by injecting a controlled stream of an oxidizing gas, such as air or oxygen, through line 29 and effecting partial combustion of the carbonaceous recirculating solids. If a non-carbonaceous stream of circulating solids, such as partially spent hydrocarbon cracking catalyst is employed, it may be preferable to bleed in some light ends from the process, as C_1 and C_2 gases, and air or oxygen into the circulating solids stream, the combustion of these gases providing the heat requirements of the circulating solids. Carbonaceous feed stock is introduced into coking vessel 4 and carbonization takes place substantially in the manner already disclosed. The vapors from the carbonization ascending above the fluidized coke bed upper level L are passed through a vapor cracking zone, the temperature level of which is substantially above that obtaining in the coking zone. To provide the temperature level of said cracking zone, low density finely divided solids, such as coke, coal, partially spent hydrocarbon cracking catalyst etc., having an average particle size between 200–400 mesh, and heated to the desired temperature level as described above, are injected into the coking vessel 4 a short distance above the fluid bed level L. The products resulting from the cracking of the carbonization vapors as well as entrained solids, are withdrawn into solids separator 21, where the cracked vapors and the bulk of the low density finely divided vapor phase cracking solids are preferentially withdrawn overhead and entrained coke from the coking process returned to the fluid bed below level L. The vapors and solids from separator 21 are conveyed to a secondary more efficient solids separator 23 where vapors are withdrawn overhead to the product recovery system, and solids conveyed through dip pipe 30 to the fluidized bed below level 31 in fluidized heating vessel 24. The fluid bed in heater 24 is maintained, if heating is indirect, by upward flowing steam or, if heating of the solids is direct, by upward flowing air. The latter is advantageous if partially-spent cracking catalyst is employed, which by means of direct heating will be at least partially regenerated. The solids are then recycled to the coking vessel, along with any necessary make-up, as disclosed.

As an alternative or supplementary procedure for supplying heat to the cracking zone above the

fluid bed, highly heated solids from the burner vessel 13 may be conducted in part to the dispersed solids zone above the bed in reactor 4 and the remainder introduced in the regular way at the bottom of the reactor. This would make possible the maintenance of a high temperature in the upper zone of the reactor and a relatively lower temperature in the fluidized bed, and eliminate use of two heaters.

To prevent agglomeration of the finely divided particles by sintering, a combustion supporting fluid such as air, oxygen, or steam may be introduced into the dispersed phase in small amounts along with the finely divided heated solids so that a last boost in temperature of these solids occurs as they are introduced into the dilute phase above the fluidized bed. It is of course desirable to burn other fuel than reaction products in giving the fines the last temperature boost, and so a fuel and a combustion supporting fluid may be introduced together. Thus in the carbonization of coal it may be desirable to heat the gas and vapor products to a temperature of 1800° F. and higher in the zone above the fluidized coking bed, though the temperature in the latter bed may be appreciably below 1800° F. In this instance the combustion supporting fluid may be a mixture, for example, of 25 to 50 parts oxygen and 75 to 50 parts steam.

Although the embodiment of the invention, as disclosed in the diagram, comprises a so-called two vessel fluid coking system, it will be understood that the controlled severity vapor treatment principle of the present invention may be applied to other fluid designs, such as a single vessel system in which the heat for coking is supplied by combustion in the coking vessel itself, or to a so-called high-velocity coking system, where the coking is carried out at extremely short contact time in an elongated dilute phase reactor; or to a single vessel process in which the heat is supplied to the fluid bed by indirect transfer from heated tubes in the bed. It is also to be understood that the invention as here described permits of numerous modifications apparent to those skilled in the art, and which are within the scope of the invention. Thus, additional flexiblity in controlling the severity of treatment of vapors resulting from coking of carbonaceous materials may be attained by employing as quenching or heating solids of the same or even larger particle size than those in the coking and combustion beds. Employing the quenching principle of the first example, higher boiling vapors leaving the coking bed will condense on the surface of these lager particles, causing them to drop into the fluid bed where further cracking of the hydrocarbon, thus returned to the coking zone, will take place, increasing the over-all yield of light products. Particles for this purpose may be obtained by screening product coke, isolating particles of the desired size, and passing such particles to the fluidized heat exchange vessel 24. Other means of classification, such as elutriation may also be employed.

It is also to be understood that the embodiment of the invention contemplates that of solid carbonaceous material is the feed stock, instead of being fluidized prior to its introduction to the preheating and coking zones it may be directly fed without preliminary addition of fluidizing gas, for instance by means of screw conveyors or the like and converted within the coking vessel into a fluidized mass with the aid of gaseous and vaporous substances therein.

The description of the dense phase of the fluidized bed in the coking vessel 4 envisages carbonaceous solids as comprising said bed. However, under some circumstances it may be advantageous for the dense phase to comprise an oxide of a heavy metal, as iron oxide. The advantage of this would lie in that particles entrained from the fluid bed would be substantially less buoyant than the heat content modifying finely divided solids introduced into the coking vessel above upper level. Such finely divided solids may be coke dust, cracking catalyst fines, kaolin, alumina, or other material of lesser buoyancy than the material comprising the dense phase in the coking vessel.

We claim:

1. An improved process for coking heavy hydrocarbon oils which comprises feeding said heavy hydrocarbon oils into a coking zone, maintaining a dense bed of fluidized coke particles in said zone at temperatures suitable for the production of volatile conversion products and coke, and maintaining immediately above said dense bed a dilute phase suspension of said coke particles, permitting said oils and said coke to remain in contact with each other for a sufficient time to permit the desired conversion, withdrawing volatile products through said dilute phase, injecting into said dilute phase in close proximity to said dense phase a stream of quenching solids having a buoyancy such as to be substantially entrained by said volatile products, said quenching solids being at a temperature level substantially below said vapors in sufficient amount to lower their temperature below decomposition temperature levels, withdrawing volatile products and entrained solids from said dilute phase, conveying said entrained solids and volatile products to a first separation zone, returning to said dense bed heavier solid particles, withdrawing from said separation zone volatile products and said buoyant quenching particles, separating said quenching particles from said volatile products in a second separating zone, cooling said solids in a cooling zone, and recycling the thus cooled solids to said dilute phase.

2. The process of claim 1 in which said quenching solids have a density lower than the particles in said fluidized solids bed.

3. The process of claim 1 in which said quenching solids have a particle size smaller than the particle size of the solids comprising said fluidized bed.

4. The process of claim 1 in which said quenching solids have a lower density and a smaller particle size than the particles comprising said fluidized bed.

5. The process of claim 1 in which said finely divided quenching solids comprise coke.

6. The process of claim 1 in which heat is furnished to said fluidized bed by withdrawing a portion of solid carbonaceous material comprising said fluidized bed feeding said material to a combustion zone, forming a fluidized mass of said solid carbonaceous material therein, generating heat in said combustion zone by burning part of the carbonaceous material with an oxidizing gas, withdrawing hot fluidized solid materials from said combustion zone, and feeding said hot fluidized solid materials to said conversion zone to supply at least a portion of the heat required therein.

7. The process of claim 1 in which heat is supplied to said conversion zone by feeding an oxidizing gas to said zone in sufficient quantity to

cause burning of at least a portion of said carbonaceous material.

WALTER A. REX.
BRUNO E. ROETHELI.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,376,191	Roetheli et al.	May 15, 1945

FOREIGN PATENTS

Number	Country	Date
255,159	Great Britain	Apr. 17, 1925