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CONVERSION OF HYDROCARBONS

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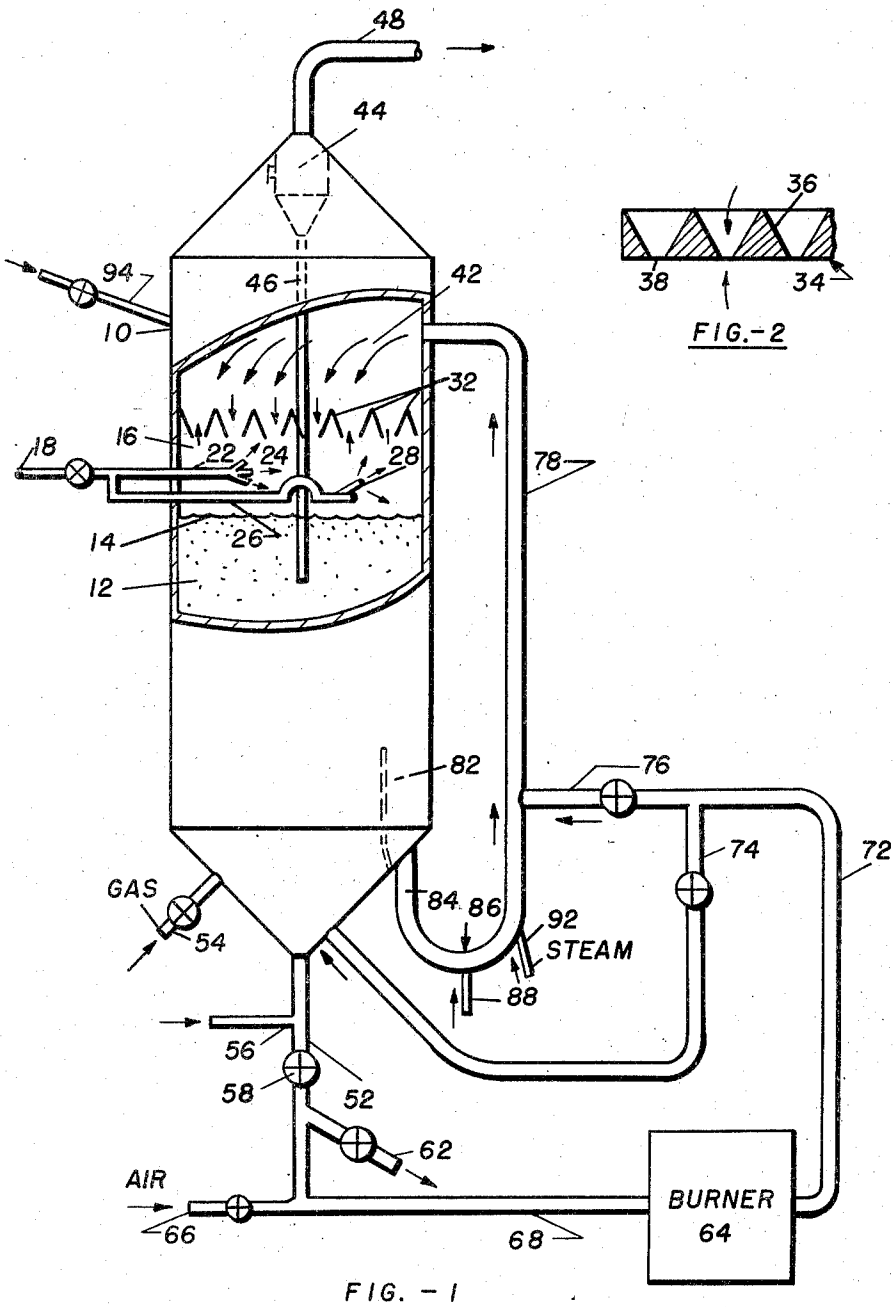


FIG. - 1

FIG. - 2

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CONVERSION OF HYDROCARBONS

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2 Claims. (Cl. 196—55)

This invention relates to a process for treating hydrocarbons and more particularly relates to the cracking or coking of heavy residual oils to produce lower boiling hydrocarbons and coke.

The hydrocarbon residual oil which is to be cracked according to the present process is a high boiling hydrocarbon oil which cannot be vaporized at ordinary pressures without cracking the high boiling constituents. The residual oil may be that produced by distilling crude petroleum oil at ordinary atmospheric pressure or under subatmospheric pressure such as vacuum distillation. The present process may also be used for cracking or coking shale oils, pitches, tars, etc.

Processes are known in the prior art for cracking or coking residual oils in the presence of finely divided inert or substantially inert solids maintained as a fluidized bed.

In the present process a dense fluidized bed of finely divided inert solids such as sand, coke, etc., is used and the preheated residual oil is introduced into the dense fluidized bed of finely divided solids maintained at reaction temperature. Vaporous products of coking are taken overhead and further treated as desired to recover lower boiling hydrocarbon fractions. During coking more coke is formed and some coke may be withdrawn from the process as product coke. Coke particles from the coking zone or reactor are stripped to remove volatile hydrocarbons therefrom. Some of the stripped coke particles may be withdrawn as product coke and the rest of the coke particles are passed to a burner where they may be maintained in a dense fluidized condition and contacted with air or other oxygen-containing gas to burn some of the coke particles and to supply heat to the coke particles. Or a high velocity transfer line burner may be used. The heated coke particles are then returned to the coking zone to supply heat thereto.

One of the problems in the fluid coking of residual or other heavy oil feeds is the distribution of the heavy residual oil feed on the coke or other inert hot particles in the fluid bed in the coking zone.

According to the present invention better mixing of the solids and heavy feed oil is obtained and thus permits operations at a higher oil feed rate than could otherwise be accomplished without causing bogging of the fluid solids bed. According to the present invention there is provided a "semi-disperse" phase of solids above the dense fluidized solids bed level and the feed oil is injected or introduced into this region at a plurality of places. Coke particles are added to the usual dilute or disperse phase above the dense bed level to form the semi-disperse phase and the residual oil feed is distributed onto the hot coke particles falling through this semi-disperse phase.

In the specific form of the invention a baffle or baffles of any suitable design are provided in the coking vessel in the dilute phase and a part of the hot coke from the dense bed and/or a part of the heated coke from the burner are introduced at one or more points above the baffle or baffles so that the hot coke particles "rain down" through the semi-disperse phase where the residual oil is introduced. The openings in the baffles are large enough to permit downward flow of coke particles and upward flow of hot vaporous products of coking or cracking.

In the drawing:

Fig. 1 represents diagrammatically one form of apparatus adapted for carrying out the process of the present invention but the invention is not to be restricted thereto; and

Fig. 2 represents a partial vertical cross-section of one form of baffle which may be used.

Referring now to the drawing, the reference character 10 designates a reactor or coking zone containing a fluidized dense bed 12 of solid finely divided inert particles such as coke or the like. The dense bed 12 has a level indicated at 14 with a less dense phase 16 thereabove as will be presently described. The inert solids of the fluidized bed 12 have a particle size between about 16 and 325 mesh, preferably between about 30 and 150 mesh and may comprise petroleum coke, or other coke, coke formed in the process, spent cracking catalysts, pumice, Kieselguhr, carborundum, alumina or other refractory materials.

The fluidized bed 12 is maintained at a temperature between about 850° and 1600° F. or higher, preferably about 950° to 1300° F. When coking to produce motor fuel such as gasoline, temperatures in the lower range of about 850° F. to about 1100° F., preferably about 950° to about 1050° F., will be used, whereas, when coking at extremely high temperatures to produce chemicals such as unsaturated hydrocarbon gases and aromatic hydrocarbons, temperatures in the higher range of about 1100° F. to about 1600° F., preferably about 1200° to about 1300° F. will be used.

The oil feed to be converted is introduced through feed line 18 into semi-disperse phase 16 above the dense fluidized highly turbulent bed 12 in the reactor. Feed line 18 has one branch 22 provided with nozzles 24 at one side of reactor 10 and another branch 26 provided with nozzles 28 at the other side of the reactor 10 for spraying the oil feed into semi-disperse phase 16 having a density of about 5 to 25 pounds per cubic foot, preferably about 5 to 15 pounds per cubic foot. The semi-disperse phase is formed by hot coke added by recycling coke particles from the dense bed 12 to less dense phase 16. Preferably the recycled coke particles are introduced into the reactor above one or more baffles and the particles fall down through the openings in the baffles into the less dense phase 16. In addition preferably some hot particles from the burner are recycled to the semi-disperse phase 16. The oil feed is preferably preheated in any suitable manner to a temperature between about 500° and 850° F. before being introduced into the reactor 10. The preheating of the heavy oil is done to reduce the viscosity of the oil feed and render it fluid. The oil feed comprises a residual petroleum oil such as tar, pitch, crude residuum, heavy bottoms or other similar hydrocarbon stock having an API gravity between about —10 and 20°, a Conradson carbon between about 5 and 50 wt. percent and an initial boiling point between about 850° and 1100° F. Steam may be introduced at one or more points 54 to assist in maintaining the bed in fluidized condition, or steam may be added with the oil feed in line 18.

The fluidized bed 12 is maintained as such by the upflowing hydrocarbon gases and vapors formed by the coking of the oil feed and by the steam added to the process. The superficial velocity of the gases and vapors passing upwardly through the bed 12 is between about 1 and 5 feet per second when using finely divided coke of about 30 to 150 mesh and at a superficial velocity of

about 1 foot per second, the density of the fluidized bed will be about 40 pounds per cu. ft. but may vary between about 30 and 60 pounds per cubic foot depending on the gas velocity selected and the particle size of the coke.

In the usual operation the dilute phase 16 above the dense bed 12 comprises upwardly rising gases and vapors resulting from the coking operation and the density of this dilute phase is less than about 5 pounds of coke per cubic foot of gas, that is, about 0.01 pound per cubic foot or less. In the present process more coke particles are recycled to the disperse or dilute phase 16 to increase the density thereof and form a semi-dilute or semi-disperse phase in the region 16 above dense bed level 14. Hot solids from the burner to be described hereinafter and from the fluidized dense highly turbulent bed 12 are recycled to disperse phase 16 to form a semi-disperse phase having a higher density than the conventional dilute or disperse phase.

Arranged above the dense bed level 14 is a baffle means 32 which may be of any suitable construction. In one form the baffle means comprises a circular grid or perforated plate 34 shown in Fig. 2 in which funnel-shaped openings 36 are provided with the narrowed portions 38 at the bottom of the grid so that solid particles introduced above the grid 34 fall down through the openings 36 into the dilute phase 16 to increase the density thereof to about 5 to 15 pounds per cubic foot. The narrowed bottom openings 38 are large enough however to permit upward passage of the vaporous reaction products of coking leaving the dense bed 12.

The openings 36 at the top of the grid 34 are so made that there are no flat surfaces on the top of the grid for accumulating solids. For example, the openings may be square on the top surface of the grid so that boundary surfaces between the top of the openings are lines. Other forms may be used having no collecting flat surfaces on the top of the grid or baffle 34. Instead of having a single baffle or grid, a plurality of inverted V-shaped baffle members may be used as diagrammatically shown in Fig. 1. These baffles will be of desired lengths arranged horizontally in spaced relation to provide troughs or elongated openings 38 between the bottom adjacent edges of the inverted V-shaped members. These V-shaped members may be constructed as a unit or are separately supported in the reactor 10 as desired.

The vaporous reaction products from the coking zone 12 pass upwardly through the openings in the baffle or grid 34 and above grid 34 they are passed upwardly countercurrent to the hot coke solids introduced above grid 34 for downward passage therethrough to increase the density of the semi-disperse phase 16. In countercurrently passing the hot solids in region 42 above grid 34 some of the heavy ends of the vaporous reaction products are absorbed by the solid particles and returned to the dense bed 12. This absorption of the heavy ends of the vaporous reaction products can be increased by introducing more of the hot solids from the burner or by steam activating the particles to increase their surface area.

The vaporous reaction products passing up through region 42 above grid 34 contain entrained solids and comprise a dilute or disperse phase, and the reaction products are passed through one or more stages of gas-solids separating devices such as cyclone separators shown at 44 as being arranged inside the reactor 10 but which may be located externally of the vessel 10. The dilute or disperse phase 42 has a density of less than about 5 pounds per cubic foot. Solids are separated from the vapors in separator 44 and the separated solids are returned by dipleg 46 to the dense bed 12. The separated vapors and gases pass overhead through outlet line 48 and may be passed to a scrubbing tower or a fractionator or otherwise treated to recover desired products therefrom.

Returning now to the dense bed 12 in reactor 10, coke or coked particles are withdrawn from the bottom of the dense bed 12 through line 52. Preferably the solids before being withdrawn are stripped with a stripping gas introduced into the bottom of bed 12 through line 54 which also acts to maintain the particles in a fluidized condition. The line or standpipe 52 is provided with one or more fluidized or aerating lines 56. Standpipe 52 is also provided with a slide valve 58 to control the rate of withdrawal of coke particles from dense bed 12.

When more coke is being produced than is necessary to supply heat to the reactor, it can be withdrawn as product coke through line 62 from standpipe 52.

Coke particles from standpipe 52 which are to be burned in the burner diagrammatically shown at 64 are mixed with air or other oxygen-containing gas introduced through line 66 and the mixture passed through line 68 to burner 64 which may be a low velocity dense fluidized burner or a high velocity transfer line burner to burn coke and raise the temperature of the coke particles to a temperature about 50° to 400° F. higher than that of the particles in the dense bed 12 in the coking zone. The temperature in the burner may be between about 1050° F. and about 1300° F. when coking in the lower temperature range for the production of fuels; when coking in the higher temperature range for the production of chemicals the temperature in the burner may be between about 1200° and about 1700° F. The hot coke particles from burner 64 are passed through line 72 in any suitable manner and returned through line 74 to the bottom portion of dense bed 12 in the coking zone. Some of the hot coke particles from line 72 are passed through line 76 to solids recycle line 78 presently to be described. The weight of coke withdrawn from dense bed 12 by standpipe 52 and passed by line 68 to burner 64 and returned to the reaction system by line 72 and lines 74 and/or 76 will be in the range of 1 to 30, preferably 5 to 20, times the weight of residual oil feed introduced by line 18.

To increase the density of the less dense phase 16 normally present above a dense fluidized bed such as bed 12, hot solids are withdrawn from a reservoir 82 in the bottom portion of reactor 10 and from dense bed 12 into a line or standpipe 84 having a U-bend 86 at its lower end which is preferably aerated as at 88. Then the solids are passed up through riser or vertical leg or recycle line 78. The rate of circulation of the solids through recycle line 78 is controlled by the volume of steam or other gas introduced into the bottom portion of riser 78 through line 92.

Hot solids withdrawn from dense bed 12 and passed through riser 78 are introduced into the region 42 above grid 34 for downward passage through openings 36 in grid 34 to increase the density of the suspension in semi-disperse phase 16 below grid 34. To maintain the temperature of the hot solids being recycled to region 42 in reactor 10 some of the hot solids from burner 64 are introduced into recycle line or riser 78 through line 76. If desired, more than one riser or recycle line 78 may be provided to introduce hot solids into the region 42 above grid 32 at more than one point. One such line for introducing hot solids above grid 32 is shown at 94 for introducing solids from a riser similar to riser 78 on the opposite side of the reactor 10.

The weight of coke passed through riser 78 to semi-disperse phase 16 will be in the range of 1 to 30, preferably 5 to 15, times the weight of residual oil feed introduced by line 18. This coke introduced by riser 78 into semi-disperse phase 16 may be all withdrawn from dense bed 12 by line 84; or it may be all withdrawn from burner 64 by line 76; or it may be in part withdrawn from dense bed 12 by line 84 and the remainder withdrawn from burner 64 by line 76. For example, when cracking or coking about 1000 barrels of residual oil per day from line 18, between about 15,000 and 450,000 pounds of coke per hour will be passed by riser 78 into semi-disperse

phase 16; all of this coke may be withdrawn from dense bed 12 by line 84, or all of it may be withdrawn from burner 64 by line 76, or the coke passing through riser 78 may comprise a mixture in any desired proportion of coke withdrawn from dense bed 12 and from burner 64. When all of the coke passing through riser 78 into semi-disperse phase 16 is withdrawn from dense bed 12 the temperature in riser 78 is approximately the same as the temperature of the dense bed 12 and the temperature in the semi-disperse phase 16 is 10° to 100° F. cooler than the temperature of the dense bed 12 due to the cooling effect of the oil feed introduced by line 18. The amount by which the temperature in semi-disperse phase 16 is lowered in comparison to the temperature in dense bed 12 depends upon the ratio of the weight of coke circulated by riser 78 to semi-disperse phase 16 to the weight of oil feed introduced by line 18 and upon the temperature to which the oil feed is pre-heated; the higher the ratio of coke circulation through riser 78 to oil feed and the higher the feed pre-heat temperature, the lower the temperature differential between semi-disperse phase 16 and dense bed 12. When all of the coke passing through riser 78 into semi-disperse phase 16 is withdrawn from burner 64 by line 76 the temperature in riser 78 is approximately the same as the temperature of burner 64 and the temperature in semi-disperse phase 16 is 5° to 100° F. hotter than the temperature of the dense bed 12 due to the cooling effect in dense bed 12 of the endothermic coking reaction occurring therein. On the other hand when the coke passing through riser 78 comprises a mixture of coke withdrawn partly from dense bed 12 and partly from burner 64 the temperature in riser 78 is intermediate between the temperature of dense bed 12 and the temperature of burner 64 and the temperature of semi-disperse phase 16 may be the same as the temperature of dense bed 12 or the temperature of semi-disperse phase 16 may be either below or above the temperature of dense bed 12 depending upon the relative proportions of coke withdrawn from dense bed 12 and burner 64 into riser 78. When coking in the lower temperature range between about 850° and 1100° F. for the production of fuels such as gasoline or gas oils for catalytic cracking feed stocks it is preferred that all or a major portion of the coke passing through riser 78 into semi-disperse phase 16 be withdrawn from dense bed 12 by line 84 and that the temperature in semi-disperse phase 16 be no greater than, and preferably less than, the temperature in dense bed 12 so that vapor phase cracking of the lighter coked products rising from dense bed 12 and passing through semi-disperse phase 16 is avoided and so that the heavier components of the coked products rising from dense bed 12 into the semi-disperse phase 16 are condensed and absorbed on the coke in semi-disperse phase 16 and are returned to dense bed 12 for further coking. On the other hand when coking in the higher temperature range between about 1100° and about 1600° F. for the production of chemicals such as olefins or aromatic hydrocarbons, it is preferred that all or a major portion of the coke passing through riser 78 into semi-disperse phase 16 be withdrawn from burner 64 by line 76 and that the temperature in semi-disperse phase 16 be no less than, and preferably greater than, the temperature in dense bed 12 in order to promote the further vapor phase cracking of the coked products rising from dense bed 12 and passing through semi-disperse phase 16.

By introducing the residual oil feed into the semi-disperse phase 16, a better distribution of the residual oil over the surface of the coke particles is obtained and this permits operations at a higher oil feed rate than could otherwise be accomplished without bogging. In the fluid coking process for any given set of coking conditions and with any given design of coking reactor there is a maximum feed rate or weight per hour of oil feed per weight of coke particles in the reactor (w./hr./w.) beyond which the process becomes inoperable. When this critical feed rate or w./hr./w. is exceeded the coke particles become sensibly wet with the oil feed and agglomerate, first, into large plastic masses and, finally, into large lumps of solid coke which tend to interfere with fluidization and to plug the lines and cause a loss of coke circulation. This condition has been called "bogging." The magnitude of this critical feed rate or w./hr./w. depends upon (1) the nature of the residual oil feed, (2) the coking conditions that are maintained in the reaction zone, and the method employed for introducing the residual oil feed into the coking zone. In general, the higher the API gravity, the lower the initial boiling point, the lower the viscosity, and the lower the Conradson carbon of the residual oil feed the higher the value of the critical feed rate or w./hr./w. Increasing the temperature of the coking reaction zone and increasing the quantity of steam employed for fluidization also permits an increase in the feed rate or w./hr./w. Any means of introducing the oil feed which will result in an improved distribution over the fluidized coke particles and will avoid a localized high concentrations of oil on the coke particles will also permit of an increased feed rate or w./hr./w.; thus introducing the feed at a plurality of points into the dense phase fluidized bed permits a higher feed rate or w./hr./w. than can be achieved when introducing the feed at a single point into the dense phase fluidized bed. When introducing the feed into the semi-disperse phase 16, particularly when introducing the feed into the semi-disperse phase 16 through a plurality of spray nozzles 24 and 28, a maximum degree of dispersion of the oil feed over the surface of the coke particles is attained and as a consequence the permissible feed rate or w./hr./w. when introducing the feed into the reaction zone in this manner is greater than has been achieved under otherwise comparable conditions by introducing the feed oil directly into the dense phase bed 12.

As above pointed out hot coke particles withdrawn from dense bed 12 together with hot coke particles from burner 64 are passed through one or more risers 78 and introduced into the upper portion of reactor 10 above grid or distributor 32 so that the hot coke particles first contact vaporous reaction products leaving the coking bed and act to adsorb any heavy ends of the vaporous reaction products. The hot coke particles then pass down through openings 36 in grid 32 where they pass countercurrent to vaporous products of coking leaving dense bed 12.

The hot coke particles in the semi-disperse phase then contact sprays of residual oil feed introduced through line 18 and sprays 24 and 28. By having troughs 38, the hot coke particles will "rain down" therethrough as elongated streams rather than as a plurality of relatively small single streams from single circular openings. The hot coke particles having the residual oil feed distributed thereon then fall down into the dense fluidized bed 12 where the coking or cracking of the oil is substantially completed.

The temperature in the dilute phase 42 may be between 10° and 100° F. hotter than the temperature in the semi-disperse phase due to heat exchange between the hot coke introduced by riser 78 above grid 32 and the cooler coked vapors passing upward through grid 32 from semi-disperse phase 16 into dilute phase 42. This is of particular advantage since the coked vapors in passing from semi-disperse phase 16 into dilute phase 42 are heated above their dew-point with the result that condensation of liquid and consequent formation of coke deposits on the upper walls of vessel 10, cyclone 44, and outlet line 48 can not occur; thus the increased temperature of dilute phase 42 over that of semi-disperse phase 16 insures the absence of coke deposits on the walls of the reaction system in contact wtih dilute phase 42. The temperature in semi-disperse phase 16 may be in the range of 100° F. cooler than the temperature of dense phase bed 12 to 100° F. hotter than dense bed 12. As hereinbefore described the temperature in semi-disperse

phase **16** will be determined by (1) the ratio of the weight of coke circulated by riser **78** to semi-disperse phase **16** to the weight of oil feed introduced by line **18** into semi-disperse phase **16**, (2) the relative proportions of coke withdrawn from dense bed **12** and from burner **64** into riser **78**, and (3) the degree of preheat of the oil feed introduced by line **18**. The temperature of the preheated residual oil feed introduced through line **18** may be between about 500° and 850° F. From the above it will be seen that substantially all the heat of cracking and coking and the heat of vaporization are supplied by the hot coke particles from the burner **64**.

In a specific example about 100 barrels of oil per day of residual oil having an API gravity of 11°, a Conradson carbon of 17, and an initial boiling point of about 1050° F. and about 14,000 lbs. per day of superheated steam are added to the reactor. The oil feed is fed in by a plurality of nozzles **24** and **28** into the semi-disperse phase **16** which has a density of about 10 lbs./cu. ft. The oil feed passing through line **18** is preheated to about 700° F. to lower the viscosity of the heavy oil feed and to render it fluid. The temperature in the semi-disperse phase **16** is about 990° F. The temperature in the dense bed **12** is about 1000° F. The ratio of the weight of oil feed per hour to the weight of solids in reactor **10** (w./hr./w.) is about 1.25.

For the amount of oil being cracked or coked about 25,000 lbs./hr. of hot coke particles are withdrawn from dense bed **12** through line **84** and passed through riser **78** to dilute phase **42** which is at a temperature of about 1010° F. The hot solids withdrawn through line **84** are at a temperature of about 1000° F. The temperature of the hot solids passing through riser **78** have their temperature increased to about 1020° F. by the introduction of hot coke particles from burner **64** through lines **72** and **76**. The amount of hot coke added by lines **72** and **76** is about 5,000 lbs./hr. The rest of the hot coke particles from burner **64** is passed through line **74** to the dense bed **12** in the reactor and amounts to about 17,000 lbs./hr.

In the present example the bottom openings **38** in a circular grid are about 3 inches in diameter or across, whereas, the top of each funnel shaped opening **36** is about 6 inches across.

The circulating coke particles have a particle size of about 16 to 200 standard mesh with the majority of the particles being between about 30 and 100 mesh. During coking the coke particles increase in size and therefore it is necessary to add fine coke or seed coke having a particle size below about 150 mesh to the reactor **10**. Coarse coke particles may be withdrawn and ground and the ground material returned to the reactor **10**. The superficial velocity of the upflowing gases and vapors in dense bed **12** is about 1 ft./sec. and the density of the fluid bed is about 40 lbs./cu. ft.

The yields obtained are as follows:

C_3, wt. percent	7
C_4, vol. percent	2
C_5: 430° F., vol., percent	13
430–650° F., vol. percent	15
650–1050° F., vol. percent	25
Coke, wt. percent	10

About 85 lbs./hr. of coke is withdrawn as product coke through line **62**. The remainder of the coke produced by the coking reaction is burned in burner **64** to supply heat to the process.

With the present invention it is possible to feed 100 barrels of residual oil feed while getting proper distribution of oil on the coke particles as compared to about 80 barrels of residual oil when feeding the oil to the dense bed **12** directly under otherwise comparable coking conditions in reactor **10**. Thus the present invention provides about a 25% increase in the critical feed rate when coking under the conditions of the example. The increase in the critical feed rate resulting from the introduction of the feed into semi-disperse phase **16** will be between 10% and 50% of the critical feed rate when introducing the feed into dense bed **12**, depending upon the temperature of coking, the velocity in the dense bed, the amount of fluidizing steam, the quality of the feed stock, the particle size of the fluidized coke, and other factors influencing fluidization.

What is claimed is:

1. A process for coking heavy hydrocarbon oils containing extremely high boiling constituents which comprises maintaining a dense fluidized highly turbulent bed of finely divided substantially catalytically inert solids in a cracking zone at cracking temperature, introducing sprays of preheated hydrocarbon oil feed into a mixing zone in the cracking zone above the level of said dense fluidized bed, said mixing zone comprising a suspension of hot solids less dense than said dense bed but more dense than a dilute phase, withdrawing some hot solids from said dense bed and passing the hot solids as a discrete stream to said mixing zone, distributing said discrete stream of solids in said mixing zone to increase the density of the mixture therein and to obtain better distribution of the oil feed on the solids, removing coke-containing solids from said dense fluidized bed and passing them to an extraneous combustion zone to heat the solids to a temperature above that existing in said dense fluidized bed, returning at least part of the heated solids from said combustion zone to said dense fluidized bed to supply heat thereto, supplying another portion of said heated solids to said discrete stream of solids being passed from said dense bed to said mixing zone, passing vaporous reaction products upwardly through said mixing zone and removing them from above said mixing zone.

2. A process according to claim 1 wherein the temperature in said mixing zone is higher than that in said dense fluidized bed.

References Cited in the file of this patent

UNITED STATES PATENTS

2,492,998	Lassiat	Jan. 3, 1950
2,561,420	Schutte	July 24, 1951
2,636,844	Kimberlin et al.	Apr. 28, 1953
2,661,324	Leffer	Dec. 1, 1953
2,684,929	Schutte	July 27, 1954
2,685,559	Voorhies	Aug. 3, 1954
2,733,194	Woerner	Jan. 31, 1956
2,760,915	Bowles	Aug. 28, 1956
2,786,801	McKinley	Mar. 26, 1957