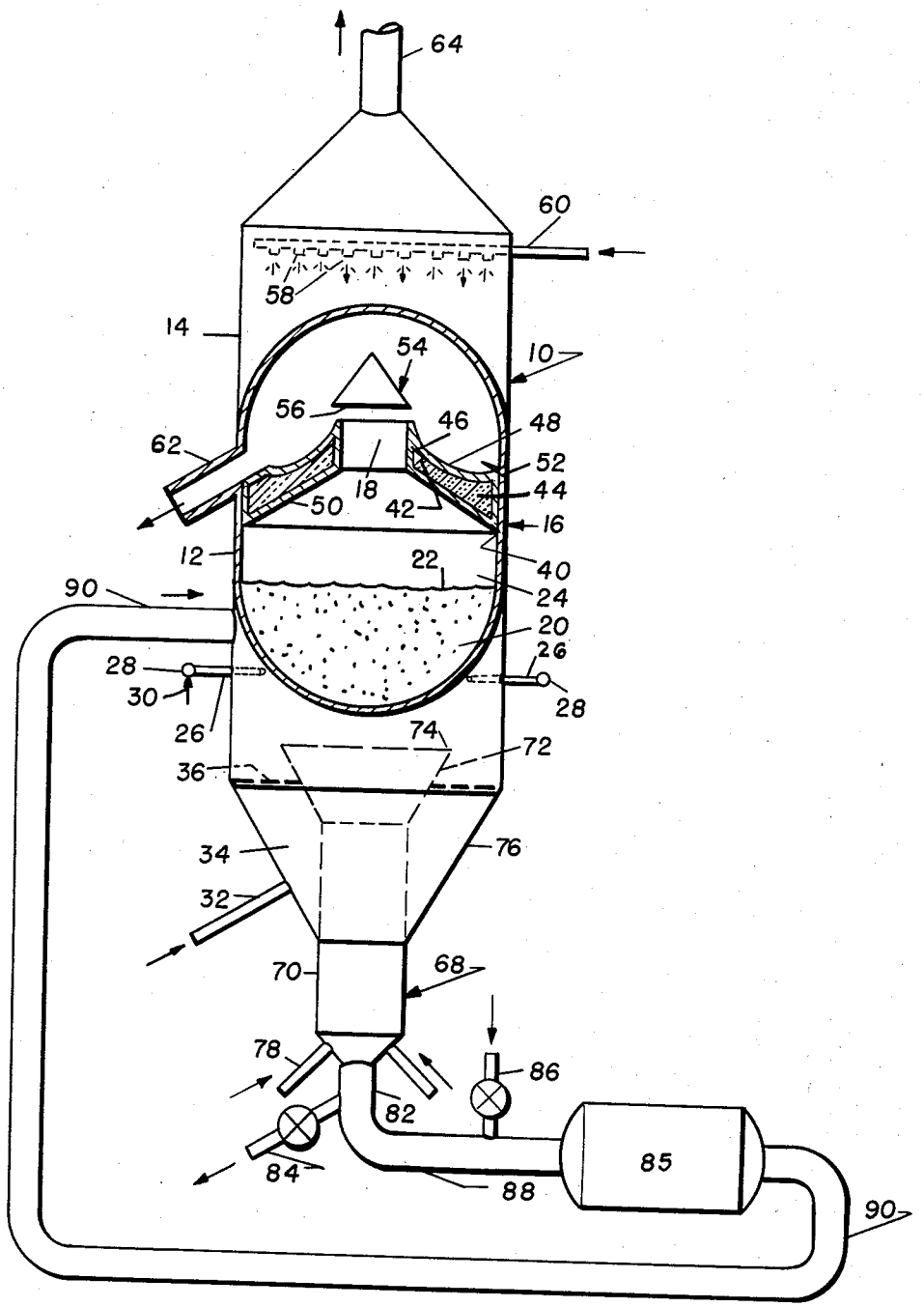
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CONVERSION OF HYDROCARBONS

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CONVERSION OF HYDROCARBONS

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This invention relates to a process and apparatus 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 refractory 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 immediately condensed the condensed liquid stream and the residual gas stream being 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 During coking more coke is formed and some coke may be withdrawn from the process. 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 Some of the stripped coke particles may be withdrawn as produce coke and the rest of the coke particles are passed to a burner where they are maintained in a dense fluidized condition and contacted with air or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 transfer line burner may be used wherein the gas velocity is much greater than in the fluid bed burner. 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 deposition of coke in the overhead system, that is in that part of the process where hot products of coking leave the coking zone or after they leave the coking zone. The hot products of coking leaving the dense fluidized bed in the reactor contain entrained coke particles and in previous processes most of these are removed by passing the products of coking through a separating device such as a cyclone separator or the like for separating solid particles from the hot products of coking. One or more stages of cyclone separators have been used and they may be arranged inside the coking zone at the top thereof or outside the coking zone. Deposition of coke has occurred in the cyclone separator and causes the pressure drop through the cyclone separator to increase to such an extent that shut down of the coking unit has been necessary for cleaning due to this cause.

Deposition of coke also has occurred in the line leading from the cyclone separator. These coke deposits are

believed to be formed through polymerization of unstable reaction products. The natural tendency due to the endothermic reactions taking place is for the temperature to fall steadily as soon as the vaporous reaction products of coking leave the dense solids bed. More cooling takes place in the overhead line after the removal of solid particles by the separator and high boiling materials deposit on the walls and polymerization of the condensed liquid or deposits causes coke deposits due to the high temperature present and because of the unstable character of the condensed liquid.

The problem of coke deposition is avoided in the present process by coking the residual hydrocarbon oil in a fluid dense bed of solids in the lower portion of a vessel and using a scrubber condenser in the upper portion of the same vessel to immediately quench and condense the cracked or coked products. The quenching oil is introduced into the upper portion of the scrubber condenser section of the vessel and is a relatively high boiling hydrocarbon stock such as one of the higher boiling fractions recovered from the cracked or coked products. Other quenching materials may be used. A sufficient amount of cool quench oil is used to condense all the condensable or normally liquid components so that only normally gaseous hydrocarbons pass overhead from the scrubber condenser section. The quenched liquid material is withdrawn from the bottom portion of the scrubber condenser section and further treated to recover desired fractions such as gasoline or motor fuel, gas oil, etc.

In the drawing the figure represents one form of apparatus shown partially in section and adapted for carrying out the present invention but this showing is for purposes of illustration only and the invention is not to be restricted thereto.

Referring now to the drawing, the reference character **10** designates a vertically arranged vessel having a lower coking zone or section **12** and an upper scrubber condenser zone or section **14**. The two zones are separated by a horizontal partition **16** provided with a central opening **18**. The partition will be presently described in greater detail. The coking zone contains a fluidized highly turbulent dense bed **20** of solid finely divided inert particles such as coke or the like and has a level indicated at **22** with a dilute or disperse phase **24** thereabove. The inert solids of the fluidized bed **20** have a particle size between about 12 and 325 mesh preferably between about 35 and 200 mesh and may comprise petroleum coke, or other coke, coke formed in the process, spent cracking catalyst, pumice, sand, kieselguhr, Carborundum, alumina or other refractory materials. Coke is the preferred solid. The other materials may also be used in starting up the process if no coke is available.

The fluidized bed **20** is maintained at a temperature between about 800° and 2000° F. preferably about 900° to 1500° F. When coking to produce motor fuel such as gasoline, temperatures in the lower range of about 800° F. to about 1100° 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. will be used. Temperatures as high as about 1800° F. may be used following by the very rapid quenching provided by the present process.

The oil feed to be converted is introduced into the dense fluidized highly turbulent bed **20** in the coking zone in any suitable manner through one or more feed lines **26** provided with injection nozzles or the like for distributing the oil feed on the hot inert solids. Lines **26** are fed from manifold **28** into which preheated residual oil feed is introduced through line **30**. The oil feed is preferably preheated in any suitable manner to a temerature between about 600° and 850° F. before being

introduced into the coking zone 20. 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. percentage and an initial boiling point between about 850° F. and 1100° F. Steam is preferably introduced at one or more points 32 into conical space 34 below horizontal grid 36, to assist in maintaining the bed in fluidized condition. The bottom portion 38 of vessel 10 has a conical shape. The grid 36 may be omitted if desired. Steam may be added with the oil feed.

The fluidized bed 20 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 20 is between about 1 and 5 feet per second when using finely divided coke of about 12 to 325 mesh and at a superficial velocity of about 1.0 feet per second, the density of the fluidized bed will be about 30 lbs. per cubic foot but may vary between about 10 and 60 lbs. per cu. ft. depending on the gas velocity selected. If it is desired to operate as a transfer line (disperse phase) type reactor followed by rapid quenching to obtain short residence time, the gas velocity will be between about 10 and 60 feet per second.

Vaporous products of coking containing entrained solids leave the bed 20 and pass overhead through opening 18 in partition 16 to scrubber condenser section 14. The partition 16 is shown as being of inverted funnel shape with the lower portion 40 being circular and the same size as the interior of vessel 10. Partition 16 may be of metal or refractory material depending upon the design temperature and is arranged about in the middle of the vessel 10 and is preferably hollow as shown at 42. Partition 16 is suitably supported in vessel 10. Extending up from bottom portion 40, the partition is of conical shape as at 50 which at its top goes into smaller annulus 46. Insulation shown diagrammatically as cross hatching 44 may be packed into the inside of partition 16 the minimized heat exchange between the relatively cool quenched and condensed products and the hot products of coking leaving coking zone 12. Opening 18 is circular and is defined by the annulus 46 of the funnel shaped partition. The upper surface of partition 16 is curved or depressed as at 48 and extends down and out from the top of annulus 46 of opening 18 of the partition to the inner wall of vessel 10 as at 52 to form a trough or the like for receiving liquids formed on quenching and condensing in scrubber condenser section 14.

The opening 18 in partition 16 may be selected of such size that the velocity of the gases and vapors leaving coking zone 20 through opening 18 have a sufficiently high velocity to prevent liquid from the quenching or scrubbing condensation zone 14 from falling or dropping into the coking zone 20. Because of the high velocity of gases passing through opening 18, any coke tending to form here will be scoured off by the particles entrained with the vaporous products leaving coking zone 20. If desired, baffle member 54, which is shown as triangular in vertical cross section, may be arranged a short distance above outlet 18 of partition 16 to prevent liquid from the quenching zone 14 from entering the coking zone 20. The flat side 56 of baffle 54 is arranged in horizontal position above opening 18. Any suitable baffle may be used.

Arranged in the upper portion of scrubber condenser zone 14 of vessel 10 are sprays 58 fed from line 60 for introducing quenching and scrubbing liquid into zone 14. The quenching medium may be any suitable material but it preferably is pitch fed on a high boiling fraction recovered from the coked products and has a boiling range of 1050+° F. The quenching liquid is introduced through line 60 at a temperature between about 300 and 500° °F. and a sufficient amount of quenching liquid is used to condense all the normally liquid components in the products of coking and to immediately stop all secondary undesired reactions. The quenching liquid introduced into zone 14 also acts to scrub out particles entrained with vaporous products of coking leaving coking zone 20.

The scrubbing and condensing liquid introduced through line 60 and nozzles 58 flows down countercurrent to the upflowing vaporous products of coking from said coking zone 12 to condense normally liquid hydrocarbons and to scrub out entrained solids. With the present invention extremely rapid quenching is obtained and this results in improved products. No chance for coking of the overhead equipment by vaporous products of coking is provided because of the short time between coking and quenching. In addition the sprays 58 of quenching and scrubbing condensing zone 14 are arranged to direct quench liquid against the interior wall of vessel 10 and the wall is covered with quenching and scrubbing liquid which removes or washes down heavy polymerizable materials from the products of coking and prevents coking of the inner wall of zone 14.

With the present invention the mechanical gas-solids separating devices such as a cyclone separator are eliminated. This reduces the cost of the equipment and also provides for quick quenching to rapidly reduce the temperature of the vaporous reaction products in a minimum of time to avoid secondary undesired reactions.

Quenched liquid containing scrubbed-out material at a temperature between about 300 and 600° F. collects in the trough 52 on the upper surface of partition 16 as above described and is withdrawn from the trough through line 62. The withdrawn liquid may be passed to a settler to remove scrubber-out solids and then passed to a fractionation system to recover desired fractions such as gasoline or motor fuel, gas oil, etc. Or the liquid withdrawn through line 62 may be passed directly to a fractionation system or the like.

Products leaving overhead from scrubbing condenser or quenching section 14 through line 64 contain only gaseous material such as gaseous hydrocarbons and steam. The overhead products in line 64 have a temperature between about 300 and 600° F.

Returning now to coking section 12 of vessel 10, coke or coked particles are withdrawn downwardly as a dense mixture from solids bed 20 into a stripping zone or vessel 68 which has a lower portion 70 of smaller diameter than vessel 10 and which has an inverted conical top portion or flared out portion 72 which extends above grid 36 and is below level 22 of dense bed 20. The upper end 74 of conical portion 72 terminates a distance from the inner wall of vessel 10 to allow for upward movement of steam or the like introduced below grid 36. The conical portion 72 is parallel to the bottom conical portion 76 of vessel 10 for a distance to form annular space 34 above referred to. Steam or other stripping gas is introduced through one or more lines 78 into the bottom portion of stripping zone 68 to remove volatile hydrocarbons from the coke in the stripping zone and pass them into the dense fluidized bed 20 in the coking zone 12.

When more coke is being produced than is necessary to supply heat to the coking zone 12, it can be withdrawn as product coke from line 82 through line 84. Line 82 conducts stripped coke particles from stripper 68.

Coke particles from line 82 which are to be burned in the burner diagrammatically shown at 85 are mixed with air or other oxygen-containing gas introduced through line 86 and the mixture passed through line 88 to burner 85 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 300° F. higher than that of the particles in the dense bed 20 in the coking zone 12. The temperature in the burner may be between about 800° and 1900° F. The hot coke particles from burner 85

are passed through line **90** in any suitable manner and the hot coke particles are returned through line **90** to dense bed **12** in the coking zone.

During combustion of the coke or other coke-containing particles in burner **85**, the particles are heated to a temperature higher than that in reactor **12** so that when the particles are recirculated to the reactor **12** they will contain sufficient heat to supply the heat of vaporization and cracking of the oil feed introduced into dense bed **20**.

In a specific example about 10,000 barrels per day of residual hydrocarbon oil having an API gravity of 13°, a Conradson carbon of 10 and an initial boiling point of about 950° F. were introduced into dense coking bed **20** through line **30**. The oil was preheated to about 800° F. The temperature of dense bed **12** was 1000° F. and in the burner **85** was 1130° F. About 5 weight percent of steam on the oil fed through line **30** is introduced through lines **30** and **32**. The amount of steam introduced with the feed and through line **32** may be varied between about 0 and 2 weight percent on the oil feed.

The circulating solid in the above example is coke having a particle size between about 12 and 325 standard mesh with the majority of the particles being between about 35 and 200 mesh. The superficial velocity of the gas in the dense bed **20** was about 1.0 ft./sec. and the density of the fluid bed **20** was about 30 lbs./cu. ft.

The overhead products from coking zone **20** passing to quench and condensing zone **14** are quenched to a temperature of about 600° F.

In the above example the quenching and scrubbing oil introduced through line **60** is at a temperature of about 100° F. and it is material of which 17% has a boiling range of 430° to 600° F. and the remaining 83% is 1050° F. + material. About 3 lbs. per lb. of fresh feed of quenching oil are introduced into quenching zone **14**. The overhead gases passing through line **64** are at a temperature of about 600° F. The quenched liquid products containing C_4 and higher boiling hydrocarbons and withdrawn from the quenching zone **14** through line **62** are at a temperature of about 600° F.

The yield obtained from the above example after fractionating will be as follows:

C_3—wt. percent	6.5
C_4—vol. percent	2.7
C_5—430° F. vol. percent	14.8
430–650° F. vol. percent	15.2
650–1050° F. vol. percent	42.6
1050° F.+vol. percent	12.0
Coke wt. percent	14.2

About 20,000 lbs. of coke per hour will be withdrawn as produced coke through line **84**.

The above example is given for purpose of illustration only and the invention is not to be restricted thereto as modifications and changes may be made by those skilled in the art without departing from the spirit of the invention.

Because of the nature of coking, coke particles increase in size during coking and when withdrawing product coke, it is necessary to add finer coke particles to the process as seed coke. Coarse coke from the process may be ground and returned to the process. In the present process the quenched products in line **62** contain coke fines and the bottoms from the settler about referred to (not shown) or from the fractionator (not shown) may be recycled with oil feed through line **30** to supply some of the fines to the system.

What is claimed is:

1. A method of coking heavy residual hydrocarbon which comprises contacting residual oil with a dense, turbulent, bed of fluidized solids in a coking zone in the lower portion of an enlarged unitary treating zone and maintained at coking temperature by recycling hot solids from a burning zone to said coking zone, removing vaporous reaction products containing entrained solids overhead from said dense bed and passing them directly through a restricted opening to increase the velocity of flow to prevent liquid from re-entering said coking zone, without going through a vapor-solid separating means, into a scrubbing-condensing zone in the upper portion of said enlarged treating zone, introducing a high boiling hydrocarbon quenching and condensing medium into the upper portion of said scrubbing-condensing zone to flow counter-currently to the upflowing vaporous reaction products to condense all the normally liquid hydrocarbons and scrub out entrained solids, removing quenched liquids from the bottom portion of said scrubbing-condensing zone and withdrawing substantially only normally gaseous hydrocarbons from the upper portion of said scrubbing-condensing zone.

2. In a method of cracking heavy residual hydrocarbon oils in a cracking zone maintained at cracking temperature and the vaporous products of cracking are quenched and condensed to remove substantially all normally liquid hydrocarbons and it is not necessary to use a gas-solids separating device to remove entrained solids from the vaporous conducts of cracking before quenching, the improvement which comprises providing an enlarged treating zone having a bottom cracking zone comprising a dense, turbulent, fluidized bed of solids maintained at cracking temperature and an upper scrubbing-condensing zone into which a high boiling hydrocarbon scrubbing and condensing liquid is introduced at the top for downward flow counter-current to upflowing vaporous products of cracking containing entrained solids leaving said cracking zone, said cracking zone and said scrubbing-condensing zone being separated by an insulating zone provided with a restricted opening to provide for flow of vaporous cracked products directly from said cracking zone to said scrubbing-condensing zone and to prevent liquid from re-entering the cracking zone where they are immediately quenched to scrub out entrained particles and to condense substantially all the normally liquid hydrocarbons from the cracked products, removing only normally gaseous hydrocarbons overhead from said scrubbing-condensing zone and withdrawing condensed liquid from the bottom portion of said scrubbing condensing zone and from above said insulating zone.

3. The process of claim 1 in which the high boiling hydrocarbon quenching medium introduced into the scrubbing-condensing zone is at a temperature in the range of 300° to 500° F.

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