

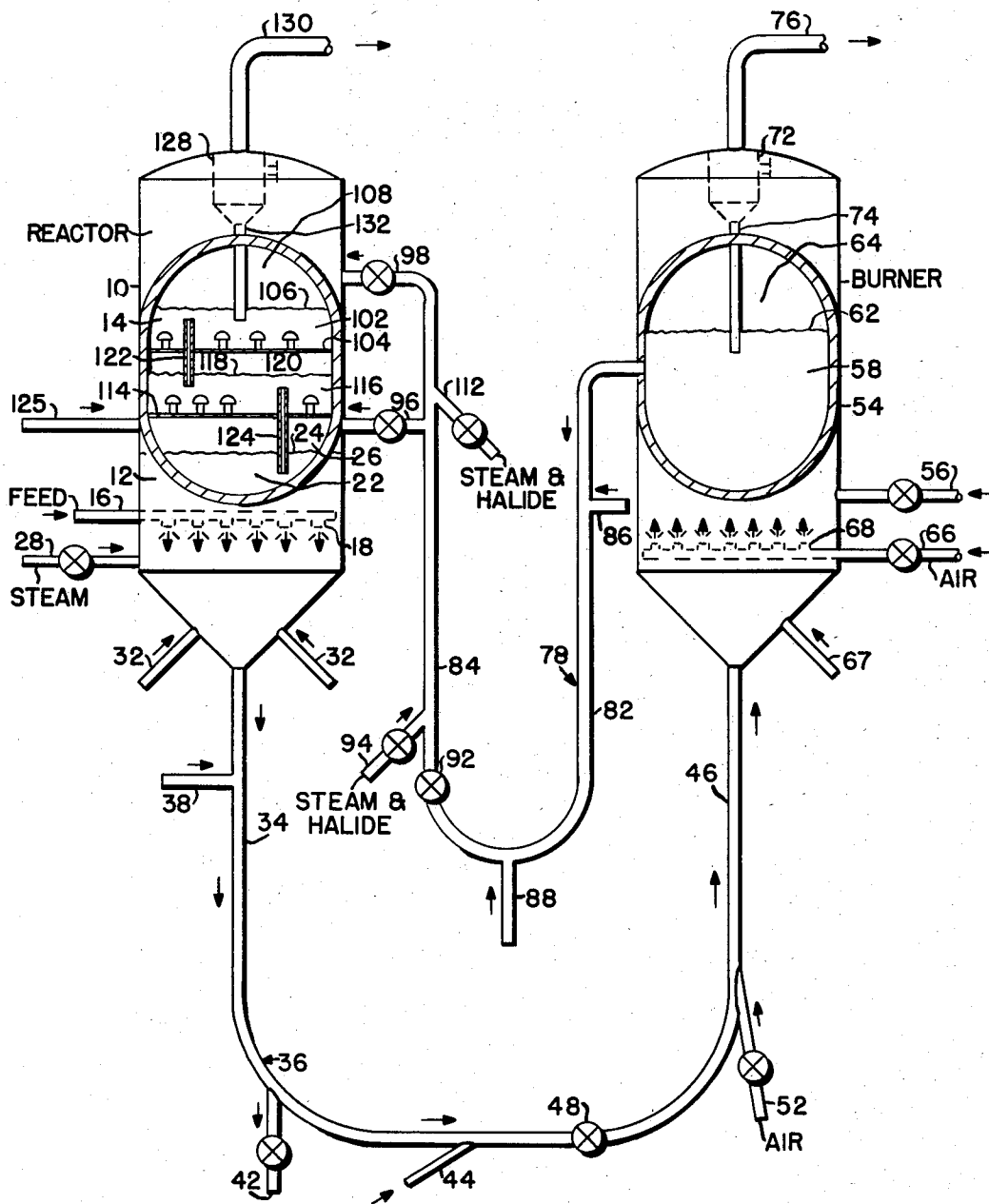
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A. VOORHIES, JR.

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CONVERSION OF HYDROCARBONS

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Alexis Voorhies, Jr. Inventor

By *George J. Silkey* Attorney

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CONVERSION OF HYDROCARBONS

Alexis Voorhies, Jr., Baton Rouge, La., assignor to Esso Research and Engineering Company, a corporation of Delaware

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

The petroleum oil residuum or residual oil which is to be converted or coked 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 crude residual such as that produced by distilling crude petroleum oil at ordinary pressure or under subatmospheric pressure such as vacuum distillation. Other residual oils or similar low grade oils which may be converted are tars, pitches, shale oil, asphalts, or heavy crudes, etc.

The present process is concerned with coking or cracking of heavy or high boiling hydrocarbon oils using a dense fluidized highly turbulent bed of finely divided inert solids which may be coke or other refractory non-catalytic material. Preheated heavy or residual oil is introduced into the fluidized bed of solid maintained at cracking or coking temperature and vaporous products of cracking are taken overhead and further treated as desired to recover lower boiling hydrocarbons. During coking more coke is formed and deposited on the coke or other solid particles of the fluid bed. Some of the coke is withdrawn as a product coke.

The present invention further provides a combination fluidized coking-cracking process in which at least part of the coke particles from the burner vessel are used as cracking catalyst for the overhead products from the coking unit. A two vessel fluidized coking system is used without the necessity of a separate vessel or separate solid catalyst for catalytic cracking. No catalyst regeneration is required. A small amount of halogen-containing catalytic agent or other catalytic agent is added to the coke particles to promote selective catalytic cracking.

In the present process all of the vaporous reaction products from the coking unit are passed overhead to a catalytic cracking section arranged in the same vessel and the catalyst used is hot coke from a burner vessel used to heat up the particles. No separate regeneration of the cracking catalyst is necessary because the catalyst passes from the cracking section to the coking section and then to the burner vessel. During coking additional coke is formed and some of this coke is withdrawn as product coke.

During or after burning, the coke in the burner vessel may have its surface area increased by using higher temperatures and/or using steam to activate the coke particles. Activated coke is a catalyst for cracking hydrocarbons but it produces relatively low octane gasoline. By adding a small amount of hydrogen fluoride or other halogen containing catalytic agent or the like, more selective cracking to higher octane gasolines is produced.

With the present process catalytic cracking is obtained without the necessity of regenerating the cracking catalyst. In the present process the same catalyst is not used over and over again and hence does not become contaminated as do catalysts of the conventional cracking process using

silica-alumina catalysts. The catalytic agent used in the present process is in part expendable and in part continuously made anew.

In the drawing the figure represents one form of apparatus adapted to practice the process of this invention.

Referring now to the drawing the reference character 10 designates a vessel provided with a bottom coking section 12 and a top catalytic cracking section 14. The heavy feed oil to be coked or cracked is introduced into coking section 12 through line 16 which is preferably provided with a plurality of nozzles 18 to distribute the oil in the fluidized bed 22 maintained in the coking section 12. The heavy residual hydrocarbon oil is that produced by distilling crude petroleum oil at ordinary pressure or under subatmospheric pressure such as vacuum distillation. Other residual oil such as pitches, tars, shale oil, etc., may be used as feed stocks. The feed stock is preheated to reduce its viscosity and to make the stock easier to handle.

The fluidized bed of solids 22 has a level indicated at 24 and a dilute or disperse phase 26 thereabove which comprises a less dense suspension of solids in gases. The dense fluidized bed of solids 22 is maintained in a turbulent condition. The finely divided particles in the fluidized bed may be coke or other refractory material such as sand, petroleum coke, coke formed in the process, spent cracking catalysts, pumice, kieselguhr, Carborundum, alumina, etc. The particles in the fluidized bed have a particle size between about 20 and 1000 microns preferably between about 50 and 500 microns.

The fluidized coking bed is maintained at a coking temperature of between about 850° and 1100° F. preferably between about 925 and 1025. Superheated steam may be added with the feed oil in line 16 to assist in vaporizing the feed and/or it may be added through line 28 into the lower portion of coking bed 22. The fluidized solids in bed 22 are maintained as such by the upflowing hydrocarbon vapors and gases formed by coking and also by the upflowing steam. The superficial velocity of the gases and vapors passing upwardly through coking section 12 is between about 0.5 and 5 feet per second and when using finely divided coke of about 35 to 200 mesh and with a superficial velocity of about 3 feet per second, the density of the fluidized bed 22 will be about 40 lbs. per cu. ft., but the density may vary between about 25 and 60 lbs. per cubic foot depending on the gas velocity selected.

The heavy feed oil is a high boiling hydrocarbon oil having an API gravity between about -10 and +20, a Conradson carbon between about 5 and 35 wt. percent and an estimated initial boiling point between about 900° and 1200° F. at atmospheric pressure. The heavy feed oil is preheated to between about 500° and 800° F. in any suitable manner. Steam or other gas may be introduced into the bottom portion of fluidized bed 22 through one or more lines 32 to act as stripping gas to remove volatile hydrocarbons from the coke particles which are to be withdrawn and passed to a burner vessel presently to be described. Or a separate dense phase stripping section may be arranged below coking section 12. Vaporous reaction products of coking pass overhead from the coking zone directly without condensation to the reactor section 14 which will be described hereinafter in greater detail.

Coke particles are withdrawn from the bottom portion of fluidized bed 22 in the coking section 12 and pass into standpipe 34 forming part of U-bend 36. Fluidizing line or lines 38 may be provided for standpipe 34. Excess coke may be withdrawn as product coke through line 42 after suitable quenching or cooling. Fluidizing gas is introduced into the bottom portion of the U-bend by line 44 to maintain the solids fluidized. The vertical leg 46 of the U-bend 36 is provided with a fixed or variable orifice 48. Air or other oxidizing gas is introduced into upflow leg 46 through line 52 above orifice 48. The rate

of circulation of solids is controlled by the amount of gas introduced into leg 46 from line 52. The U-bend and its method of control is similar to that shown in Packie Patent No. 2,589,124 granted March 11, 1952. Additional air may be introduced into burner vessel 54 through line 66 and nozzles 68 to burn coke and to provide fluidizing gas for dense fluidized bed 58. Steam may be introduced into burner 54 by line 67. The action of the steam on the heated coke results in an increase in the surface area of the coke and an enhancement of its catalytic activity.

The solids pass from line 46 to burner vessel 54 where coke is burned to raise the temperature of the solids to about 100° F. to 500° F. higher than the temperature in the reactor section 14 and coking section 12 to supply heat for the cracking and coking reactions. The temperature in the burner vessel may be between about 1100° and 1400° F. If insufficient heat is supplied by burning coke, additional heat may be supplied to the particles by introducing a fuel gas or oil through line 56 into burner vessel 54.

The solids in burner vessel 54 are maintained as a dense fluidized highly turbulent bed 58 having a level indicated at 62 with a dilute or disperse phase 64 thereabove. The superficial velocity of the gas passing upwardly through the dense bed 58 in burner vessel 54 is about 0.5 to 5 ft. per second and the density of the fluidized bed 58 is between about 25 and 60 lbs. per cu. ft. Combustion gases leaving the disperse phase 64 contain entrained solids which are removed by passing the gases through one or more stages of cyclone separators 72, the separated solids being returned to the dense bed 58 by dip leg 74 and the denuded combustion gases passing overhead through line 76 to the atmosphere or to additional gas-solids separation devices, and heat recovery systems, if desired. Instead of a fluid bed burner, a transfer line burner may be used where the superficial velocity of the upflowing gas is between about 20 and 150 feet per second.

During combustion of coke in combustion zone or burner vessel 54, the coke or other particles are heated to a temperature higher than that in coking section 12 and cracking section 14 so that when the particles are recirculated to one or both of these sections, the particles will contain sufficient heat which can be used for cracking and/or coking the hydrocarbons.

Hot coke or other particles are withdrawn from the dense fluidized bed 58 through a second U-bend 78 comprising downflow leg 82 and upflow leg 84. Fluidizing gas is preferably supplied to leg 82 by line or lines 86 and to the bottom of U-bend 78 by line 88 to maintain the particles in fluidized condition. Upflow leg is provided with a fixed or variable orifice 92 similar to that described in connection with U-bend 36 above described. Steam is introduced into upflow leg 84 above orifice 92 through line 94 and the amount of steam introduced determines the rate of circulation of the solids in the unit.

Some of the heated coke particles from leg 84 may be passed by line 96 into the dilute phase 26 above dense fluidized bed 22 in coking section 12 to supply heat to the coking section. Or line 96 may lead directly into dense bed 22. The rest of the heated solids from leg 84 are passed into the upper portion of the cracking section 14 through line 98 and most of the heated solids fall down onto top shallow fluidized bed 102 arranged on a horizontal bubble tray 104 or other perforated tray. Dense bed 102 has a level indicated at 106 and a dilute phase 108 thereabove into which line 98 empties the hot solids from burner vessel 54. Additional steam or other gas is introduced into the upper portion of upflow leg 84 above take-off line 96 by means of line 112. Preferably an expendable catalyst such as hydrogen fluoride, aluminum chloride or other similar volatile halide or mixtures thereof are introduced with the steam or other

gas from line 112 to form with the coke active cracking catalyst for the cracking section 14.

Arranged below tray 104 is another horizontal bubble tray 114 or other perforated tray having thereon a fluidized bed of solids 116 with a level at 118 and a dilute phase 120 thereabove. Tray 104 has downcomer 122 for conducting solids down from tray 104 to lower dense bed 116 and tray 114 has a downcomer 124 for conducting solids down from tray 114 to the dense fluidized bed 22 in coking section 12. The vaporous reaction products of coking from coking section 12 pass upwardly to and through the cracking section 14 without any intermediate treatment, quenching, cooling or the like and the heat of the products from coking is utilized in the cracking section 14. The vaporous reaction products passing upwardly through the cracking section 14 contact the catalyst-coke particles therein to fluidize the particles and at the same time the coker products are cracked. The catalyst-coke particles with the volatile halide catalyst pass downwardly through the cracking section to produce more selective catalytic cracking with higher octane gasoline.

While two bubble trays have been shown in the drawing more or less may be used and the invention is not to be restricted to two trays.

In place of introducing the expendable catalyst such as hydrogen fluoride, boron fluoride, aluminum chloride, or other volatile halide into line 98 by line 112 this may be introduced, either alone or with other gas such as nitrogen or steam, into dilute phase above coking bed 22 by means of line 125. Thus added the expendable catalyst mixes with the vapors from coking bed 22 and passing upward through beds 116 and 102 contacts and activates the coke therein and promotes the cracking of the coked vapors.

The coking section and catalytic cracking sections are arranged one above the other in a single vessel and a compact construction is provided. The present process provides a completely integrated coking and catalytic cracking operation without the necessity for a truly separate catalytic cracking step with its attendant cost of equipment for cracking and regeneration of extraneous conventional cracking catalyst such as synthetic silica-alumina.

The cracked vapors leaving the top of cracking section 14 pass through one or more stages of separation devices, such as one or more cyclone separators 128 and the vapors substantially free of solids are withdrawn through line 130 and may be further treated as desired to recover valuable products such as gasoline gas oil, etc. The separated solids are returned to the top dense bed 102 through dip leg 132.

To produce coke particles having increased surface area the hot coke particles withdrawn from burner vessel 54 through line 78 may be passed through a steam activation zone (not shown) wherein they are treated at a temperature of between about 1200° and 1400° F. for a time of about ¼ to 2 hours to produce coke particles having a surface area above about 100 square meters per gram.

The coke particles issuing from the burner vessel 54 have catalytic activity which increases with the extent of surface area imparted to them in the burner when operated at temperatures above about 1200° F. and in the presence of steam or if the coke particles are given a separate steam treatment as above described.

To produce a desirable type of selective catalytic cracking normally associated with silica-alumina catalysts, it is only necessary to add to the top cracking section 14 of the reactor 10, a small amount of an activating material such as HF, AlCl₃, or other elements or compounds such as boron fluoride, iodine, silicon tetrafluoride, silicon tetrachloride, titanium tetrachloride or mixtures of these which promote selective catalytic cracking in the presence of activated carbon.

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The bubble trays or baffles 104 and 114 prevent admixture between the fluidized coke in the top of the reactor 10 in the cracking section 14 where catalytic cracking occurs and the fluidized coke in the bottom of the reactor in the coking section 12 where coking of heavy residual oils takes place.

In the catalytic cracking section 14 the temperature is between about 850° and 1100° F., the W/Hr./W (weight of oil per hour per weight of solids) may be between 0.4 and 5. If HF is used, about 0.05% to 2% of HF by weight of the oil feed passed through line 16 to coking section 12 is used.

Because the particles grow in size during coking, it is necessary to remove coarse particles and grind them to produce finer seed coke which is returned to the coking zone. Or seed coke from an external source may be supplied to the unit.

For example, a residual oil obtained from the vacuum distillation of mixed South Louisiana crudes, having an API gravity of about 10° to 13°, a Conradson carbon of about 15 to 20 wt. percent, and containing less than about 5 vol. percent boiling below about 1050° F. at atmospheric pressure is preheated to about 750° F., mixed with about 8 wt. percent steam in line 16 and introduced into coking section 12 by nozzles 18. An additional quantity of steam amounting to about 17 wt. percent of the residual oil feed is introduced into coking section 12 by line 28. Coking section 12 has a dense fluidized bed of coke particles produced in the process. The solids to feed oil ratio by weight to the coking section is about 12 to 1. The temperature in the coking section is about 980° to 1020° F. and the temperature in the burner 54 is maintained at about 1125° F. No burner oil is injected into burner vessel 54, the temperature being maintained by combustion of a part of the coke produced in the process.

The circulating coke particles have a particle size of about 16 to 200 standard mesh with most of the particles being between about 35 and 100 mesh. The superficial velocity of the gas in coking section 12 is about 1.5 ft./second and the density of the dense bed 22 is about 50 lbs./cu. ft. The superficial velocity of the gas in the burner 54 is about 2.5 ft./second and the density of the fluidized bed 58 is about 45 lbs./cu. ft.

In coking section 12 the residual feed oil is converted to the extent of about 55 to 65% to coke and hydrocarbons boiling below the boiling range of the feed oil. The vaporous products leaving the coking section 12 have the following composition expressed as percentages of the original feed oil: (1) 35 to 45 vol. percent boiling above 1050° F., (2) 33 to 39 vol. percent of gas oil boiling between 430° and 1050° F., (3) 12 to 17 vol. percent of gasoline components boiling up to 430° F. and including C₄ hydrocarbons, and (4) 4 to 6 wt. percent of C₃ and lighter gases. In addition about 8 to 12 wt. percent of the feed oil is converted to coke in coking section 12.

The cracking section 14 is maintained at a temperature of 990° to 1030° F. The solids to oil ratio by weight in cracking section 14 is about 6 to 1. The solids have a surface area of about 50 sq. meters per gram. HF in an amount about 0.5% by weight of the oil fed to coking zone is introduced with the coke particles going to the catalytic cracking zone.

In cracking section 14 the heavier oils are further converted to lighter fractions and the composition of the vaporous products leaving the cracking section 14 have the following composition expressed as percentages based on the original residual oil feed: (1) 10 to 20 vol. percent boiling above 1050° F., (2) 42 to 46 vol. percent of gas oils boiling in the range of 430 to 1050° F., (3) 27 to 34 vol. percent of gasoline fraction boiling up to 430° F. and (4) 8 to 10 wt. percent of C₃ and lighter gas. In addition the coke produced amounts to about 12 to 16 wt. percent of the residual oil feed. The vaporous products from cracking section 14 containing steam and the added hydrogen fluoride pass overhead through line 130 to fractionating and condensing equipment (not shown).

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The hydrogen fluoride condenses with the steam and forms a separate aqueous layer which may be discarded or, if desired, may be recycled.

If desired, the yield of gasoline fraction may be increased by recycling all or a part or a selected fraction of the gas oil fraction to the cracking section 14. Or if preferred the gas oil product may be further cracked in a separate cracking process employing silica-alumina or other cracking catalyst.

What is claimed is:

1. A method of converting heavy residual hydrocarbon oils to lower boiling hydrocarbons which comprises introducing residual hydrocarbon oil into a dense fluidized bed of coke solids maintained at coking temperature in a coking zone in the lower portion of a vertical vessel, withdrawing coke particles from said coking zone and heating them in a burner, passing a portion of the heated coke particles to the coking zone, passing another portion of the heated coke particles and an activating halogen-containing material to a catalytic cracking section containing at least one fluidized bed of coke solids in the upper portion of said vertical vessel, passing vaporous coker products directly from said coking zone upwardly into said catalytic cracking zone, removing catalytically cracked vapors overhead from said cracking zone, passing solids downwardly from said cracking zone to said coking zone.

2. A method of converting heavy hydrocarbon oils which contain constituents unvaporizable at ordinary pressures without cracking which comprises introducing heavy hydrocarbon oil into a dense fluidized bed of coke in a coking zone in the lower portion of a vertical vessel, said coking zone being maintained at coking conditions, removing coke particles from said coking zone and passing them to a combustion zone where coke is burned with air and the coke particles are heated to a temperature above that in said coking zone, withdrawing heated coke particles from said combustion zone, passing a portion of the heated coke particles to the coking zone, introducing another portion thereof together with an activating halogen-containing catalyst material into the upper portion of a cracking zone to form at least one fluidized bed of solids in the upper part of said vertical vessel, passing vaporous reaction products directly from said coking zone substantially at coking temperature into said cracking zone and passing such vaporous reaction products upwardly countercurrent to downwardly flowing coke particles from said upper fluidized bed of solids and through said upper fluidized bed of solids to crack the products from coking to lower boiling hydrocarbons and removing cracked vaporous products overhead from said cracking zone.

3. A method according to claim 2 wherein the heated coke particles are activated before being passed to said cracking zone.

4. A method of converting heavy hydrocarbon oils which contain constituents unvaporizable at ordinary pressures without cracking which comprises introducing heavy hydrocarbon oil into a dense fluidized bed of coke in a coking zone in the lower portion of a vertical vessel, said coking zone being maintained at coking conditions, removing coke particles from said coking zone and passing them to a combustion zone where coke is burned with air and the coke particles are heated to a temperature above that in said coking zone, withdrawing heated coke particles from said combustion zone, passing a portion of the heated coke particles to the coking zone and introducing another portion thereof into the upper portion of a cracking zone to form at least one fluidized bed of solids in the upper part of said vertical vessel, introducing hydrogen fluoride into said cracking zone, passing solids from said upper fluidized bed of solids downwardly into said coking zone, passing vaporous reaction products directly from said coking zone substantially at coking temperature into said cracking zone and upwardly

countercurrent to downwardly flowing coke particles from said upper fluidized bed and through said upper fluidized bed of solids to crack the products from coking to lower boiling hydrocarbons and removing cracked vaporous products overhead from said cracking zone.

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