CONVERSION OF HYDROCARBONS IN THE PRESENCE OF ELECTRODE S

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

The petroleum oil residuum or residual oil which is to be converted according to the present process is a high boiling hydrocarbon oil which cannot be vaporized at ordinary pressures without cracking the high boiling constituents. At present there is a relatively large accumulation of reduced crude or heavy bottoms because lower grade crude oil feedstocks are being processed which leave more residue and because there is a larger demand for motor fuel such as gasoline and other petroleum oil products such as heating oil which means processing more crude oil to leave more residue. Also the tendency is to distill the crude to recover higher boiling feedstocks for catalytic cracking and this leaves higher boiling residual oils...It is known to crack or coke heavy residual petroleum oils in the presence of finely divided inert solid particles maintained as a fluidized bed. Such cracking is difficult to operate at relatively low temperatures except at very low feed rates due to the sticky feed causing loss of fluidity in the bed of solids. In delayed coking, the process is discontinuous and presents a problem of removing coke from the coking vessel. Another known process of coking is one where the residuum is sprayed onto a moving bed of hot coke but this process requires large and expensive equipment and is incapable below about 930°F.

Conversion processes are known wherein the residuum or heavy petroleum residual oil is heated in a coil-and/or soaking drum, under sufficient pressure, to prevent distillation of the gas oil as it is produced but in this type of process the coke remains largely suspended in the oil and the only means available heretofore has been filtration or centrifuging to remove the coke particles, neither of which is desirable. When operating at desirable high conversion the reaction products directly from the conversion zone cannot be fed directly to a distillation zone due to the high content of coke which would result in fouling of the distillation equipment.

The present invention overcomes the objections and shortcomings of prior process by providing an improved distillation zone for the products of conversion leaving the coking zone. The products of conversion or coking are flashed or sprayed into or onto a fluidized bed of heated inert solids, preferably coke particles. The fluidized bed of solids is maintained at a temperature of about 900°F. to 1050°F. to rapidly vaporize the distillable oil leaving the coke particles behind in the fluidized bed. The heated fluidized bed of solids acts as a distillation zone primarily and not as a cracking or conversion zone.

Various modifications of the invention are presented as will appear from the detailed description to be given hereinafter.

In the drawings:

Fig. 1 represents one form of apparatus adapted to carry out the process of the invention;

Fig. 2 represents a modified form in which some of the coke is burned in the distillation zone and heat is supplied to the cracking step by submerging a cracking coil in the fluidized bed in the distillation zone;

Fig. 3 represents a modification where some of the coke is burned in a coil submerged in the fluidized bed in the distillation zone to indirectly supply heat to the distillation zone; and

Fig. 4 represents another modification in which the fluidized solids bed distillation zone is maintained under vacuum.

Referring now to Fig. 1 of the drawings, the reference character 10 designates a line for feeding heavy residual petroleum oil to a preheating coil 12 and a cracking or conversion zone 14 which may be a coil or coil and drum or a drum for cracking the residual oil and to produce coke, gas and distillable oils including gasoline, heating oil and a higher boiling fraction acting as a feed for catalytic cracking. The residual oil may comprise atmospheric or vacuum residual petroleum oil, reduced or whole petroleum crude oil, tar, pitches, shale oil, heavy cycle oil, etc. The residual oil may have a gravity of about 0 to 20° API and a Conradson carbon of about 5 to 30 wt. percent and an initial boiling point above about 800°F. for atmospheric residua or above about 1050°F. for vacuum residua.

The oil is heated in coking zone 14 to a temperature of about 750° to 950° F. and is maintained under a pressure of about 100 to 500 pounds per sq. in. gage with the residence time being about 2 to 240 minutes depending on the temperature selected and the degree of conversion desired. To avoid coke adhering to the internal walls of the coil or drum it is preferred to add finely divided solids preferably coke of a size of about 5 to 250 microns to the oil feed through line 16 to serve as nuclei upon which coke formed during coking is deposited. The added coke particles also act to scour and clean the walls of the coking zone. The amount of solids added through line 16 is about 15 to 100 lbs. per barrel of oil feed, preferably about 30 to 60 lbs. per barrel.

A diluent such as steam or lower boiling petroleum fractions may be added to the residual oil feed through line 18 to aid in vaporization of the residual oil or to improve product distribution in the coking zone and to improve volatility in the fluid distillation zone.

When processing the very heavy vacuum residual oils, it is particularly desirable to add a diluent of lower boiling petroleum fraction such as a heavy naphtha boiling in the range of about 250° to 500° F. This naphtha diluent may be added in amounts of 20 to 120 vol. percent, preferably about 50 to 100 vol. percent of the residual oil to be processed. This naphtha diluent increases the viscosity of the residual oil thus permitting greater turbulence and a more effective scouring action on the vessel walls by the seed coke with the result that fouling of the walls is avoided.

The total products of conversion or coking in the form of a slurry of coke in liquid oil leave coking zone 14 through line 22 and are passed to a fluidized solids distillation zone 24 maintained at a temperature of about 800° to 1050° F. and under a pressure of about 0 to 25 lbs. per sq. in. gage. Substantially all of the cracking or coking has taken place in coking zone 14 so that the distillation zone 24 functions solely as a distillation zone to separate solid coke particles from distillable oils.

A dense fluidized bed 26 of highly turbulent solids is maintained in zone 24 by upflowing gasiform material presently to be described. The gasiform material maintains the bed fluidized having a level indicated at 28 with...
a dilute phase 32 therefore. The density of the fluidized bed when using finely divided coke having a particle size of about 0.00 to 400 standard mesh is about 15 to 40 lbs. per cu. ft. Preferably a gas-solids separating means such as a cyclone separator (not shown) is arranged in the upper part of the distillation zone 24 to remove entrained particles from the vaporous products leaving the distillation zone 24 through outlet line 34 and return them to the dense bed 26.

The total products of coking from line 22 may pass through pressure reducing valve 35 in line 36 where they are flashed or sprayed through a spray nozzle device 38 above level 28 and onto the top of dense fluidized bed 26 in distillation zone 34. Due to the reduction in pressure, some of the coking products are immediately flashed or vaporized and pass overhead through line 34 to a fractionator tower 42 presently to be described. The non-vaporized constituents drop into the fluidized bed 26 and are vaporized and pass overhead through line 34 to leave only the coke particles in the bed 26. Alternatively, the total products of coking may be passed through line 44 into fluidized bed 26 below the level 28 thereof.

For supplying heat to the distillation zone 24, fluidized coke or solid particles containing coke formed during coking and coking vessel 14 are withdrawn from the bottom of distillation zone 24 by means of a standpipe 46 having a valve 48 to control the rate of withdrawal of solids from zone or vessel 24. The withdrawn solids are picked up by air or other oxidizing gas introduced through line 52 and the resulting suspension is passed through line 54 into the lower portion of a burning or reaction vessel 56 provided with a dense fluidized turbulent bed 58 of solids having a level indicated at 62 with a dilute phase 64 thereof. The superficial velocity of the gas-solid material passing upwardly through vessel 56 is selected to be between about 0.5 and 2.5 feet per second to give a density of the bed of about 15 to 30 lbs. per cu. ft. when using 100-400 mesh coke or fines. The heater 56 is maintained at a temperature to heat the solid particles to a temperature of about 1000° F. to 1400° F.

Hot combustion gases pass overhead through a gas-solids separating device such as a cyclone separator 66 for removing entrained solids from the combustion gases and returning them to bed 58 via dip leg 68. The gases pass overhead through line 72 and may be passed through a waste heat boiler or the like to recover heat therefrom. The heated solids are withdrawn from the bottom heater 56 through a standpipe 74 having a control valve 76 and picked up by a gas such as steam introduced through line 78. The resulting suspension is passed through line 82 and returned to the lower portion of the distillation zone 24 where the heated solids supply heat for distillation. Excess coke particles are withdrawn from fluid bed 26 through withdrawal line 84. The amount of steam and gases passing upwardly through bed 26 in distillation zone 24/ is selected so that the superficial velocity of the upflowing gas-solid material is between about 0.5 to 2.5 ft. per sec. to give the density of bed 26 above referred to.

The vaporous products of coking leaving the top of the distillation zone 24 and passing through line 34 are fractionated in fractionating system 42 to separate a light fraction comprising gas and about 430° F. end point gasoline withdrawn through line 86 which is further treated as desired to recover gasoline. From the upper portion of fractionator 42 the overhead gas from line 88 is recovered for use as hot water. The gas from line 89 is recycled to the coking vessel 14, and from line 90 of about 450° to 650° F. boiling range and lower down through line 92 is recovered as a gas oil boiling between about 650° and 1000° F. which is suitable as a stock for catalytic cracking. A bottoms fraction boiling above about 1000° F. is withdrawn from fractionator 42 through line 94 and may be removed from the process through line 96 but is preferably recycled to feed line 10 ahead of preheater 12. The bottoms fraction contains some solids which are carried over into the fractionator 42 through line 34.

Referring now to Fig. 2 of the drawings, the reference character 102 designates a feed line for the heavy residual oil feed into which steam or light petroleum oil diluent may be introduced through line 104, bottoms recycle through line 106 and coke particles to serve as nuclei for coke and for scouring the oil heater 108 introduced through line 112. Steam may be used as the carrying gas for said coke as shown in line 113. The residual oil admixed with other materials passing through preheater 108 is then passed through coil heater 112 most of which is submerged in fluidized solids bed 114 in distillation vessel 116. The dense fluidized, highly turbulent bed 114 has a level indicated at 118 above which is a disperse or dilute phase 122. The oil passing through coil heater 112 is heated to coking temperatures of about 900° F. to 1000° F. and is maintained under a pressure of about 500 to 3000 lbs. per sq. in. gage and the residence time of the oil in heater 112 is about 2 to 5 minutes. The oil in heater 112 receives heat from the dense fluidized bed 114 by indirect heat exchange.

The upper or outlet end of coil heater 112 extends above the level 118 in vessel 116 and at its exit it is directed downwardly and provided with a nozzle member 124 for spraying the liquid products of coking onto the bed 114. Adjacent nozzle member 124 the upper end of coil heater 112 is provided with a pressure release valve 126 to flash the products of coking so that vapors are released and pass upwardly out through outlet line 118 into fractionating system 132 similar to that above described in connection with Fig. 1. The distillation vessel 116 is maintained at a temperature of about 900° to 1050° F. and under a pressure of about 0 to 25 lbs. per sq. in. gage. Vaporized and distilled products pass overhead through line 128 and are preferably first fractionated into a gas-solids separating means such as a cyclone separator (not shown) to separate most of the entrained solids from the outgoing vapors and gases. The distillation vessel is heated by introducing air or oxygen through line 134 into the fluid bed of coke 114 to burn some of the coke. The products of combustion pass out with the conversion products through outlet line 128. These combustion products dilute the dry gas produced in the process; however, this slight degradation in the value of this fuel gas is offset by the great economy of heating the fluidized solids distillation zone by the direct injection of oxidizing gas into the nozzle of fluidizing gas. Excess coke in the form of finely divided solids is withdrawn from the dense bed 114 through line 136. Coke particles in heated condition are withdrawn from the bottom portion of distillation vessel 116 and passed through line 113 for admixture with the residual oil as above described. Instead of using coke from vessel 116, coke particles from an external source may be passed through line 112.

Bottoms withdrawn from fractionating vessel 132 are recycled through line 106 to feed line 102 but may be withdrawn from the process through line 138.

Referring now to Fig. 3 of the drawings, the reference character 152 designates a line for feeding residual oil together with steam or light petroleum oil diluent and added coke particles, if desired, to heating and coking coil 154 substantially completely submerged in the upper portion of a dense fluidized turbulent bed of coke particles 156 in distillation zone 158. The dense bed 156 has a level indicated at 162 with a dilute or disperse phase 164 thereof. The upper portion of coil 154 extends above the level 162 of the dense bed and is then directed downward with the outlet being provided with a spray or nozzle member 166 for spraying the products of coking onto the dense bed 156. The outlet end of coil 154 is provided with a pressure release valve 168 adjacent nozzle member 166. The temperature and pressure conditions in coil 154 are substantially
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the same as in the coking coil of Fig. 2. The distillation zone functions similarly to that described in Figs. 1 and 2 in that coke particles are separated from distillate and gases by the fluidized bed process.

Steam is introduced into the lower portion of distillation vessel 158 through line 172 to assist in maintaining the particles in dense fluidized condition in distillation vessel 158 and to aid in vaporization of the coked products. Arranged and submerged in the lower portion of the fluidized bed 156 in distillation vessel 158 is a coil 174 for supplying heat to the fluidized bed of solids 156 by burning coke particles or coke in the coil. Coke-containing particles are withdrawn from the lower portion of the fluidized bed 156 through standpipe 176 provided with a control valve 178. The withdrawn coke-containing solids are mixed with air or other oxygen containing gas introduced through line 182 and the mixture or suspension, passed through line 184 and coil 174 so that the burning mixture as it passes through coil 174 gives off heat which by indirect heat exchange is transferred to the fluidized solids bed 156. The flue gas from combustion leaves the coil 174 through line 186 and may be passed through a waste heat boiler to recover heat therefrom.

Excess coke may be withdrawn from the fluidized bed 156 of solids via line 183. Vaporous and gaseous products leave overhead through line 192 after having preferably passed through a gas-solids separating device and are introduced into a fractionating system or the like as described in connection with Fig. 1 above.

Referring now to Fig. 4 of the drawings, the residual oil feed is first distilled under a vacuum or subatmospheric pressure to remove some of the vaporizable constituents therefrom and the thus treated residual oil is coked and then distilled under subatmospheric pressure. The residual oil which is of the type above described is passed through line 202 and preheater coil 204 where it is heated to a temperature within the range of about 400°F to 750°F. As above described steam may be added to the residual oil and also coke particles, as nuclei for the coke formed may be added. The heated residual oil under a pressure of about 10 to 100 lbs. per sq. in. is passed through valve line 206 to a distillation tower 208 maintained under a subatmospheric pressure of about 1 to 20 inches of mercury absolute by attaching a vacuum pump (not shown) and condensing system (not shown) to outlet line 212 from distillation tower 208.

Distillable vapors go overhead through line 212 and are condensed and form cracking stock for catalytic or thermal units. The unvaporized residual oil is withdrawn from the bottom of tower 208 through line 214, passed through heating coil 216 by pump 218, under a pressure of about 250 to 3000 lbs per sq. in. sufficient to prevent vaporization of the oil and heated to a temperature of about 800°F to 1000°F. The oil during coking is preferably maintained under the above conditions for about 5 to 60 minutes. Coke particles and steam or a mixture of the two may be added to line 216 by line 219 to prevent or minimize coking of the oil in coil 216. The products of coking are then passed through line 222 having a pressure reducing means 224 into fluidized coke distillation zone 226 having a dense fluidized highly turbulent bed 228 with a level indicated at 229. The fluidized solids bed 230 in distillation vessel 226 is a coil 232 for supplying heat to the fluidized bed of solids 226 by burning coke particles or coke in the coil. Coke-containing particles are withdrawn from the lower portion of the fluidized bed 226 through standpipe 233 provided with a control valve 234. The withdrawn coke-containing solids are mixed with air or other oxygen containing gas introduced through line 236 so that the latter may exert a scrubbing action upon the former. In this manner vaporization of the lighter fractions of the residual feed is aided while the heavier portions of the vapors from line 238 are condensed and the entrained solids and unvaporized liquid particles are scrubbed out. Coke distillation zone 226 is maintained under a subatmospheric pressure of about 1 to 20 inches of mercury absolute.

Steam is supplied through line 242 to fluid bed 228 in the coke distillation zone to maintain the bed in a dense fluidized highly turbulent condition and to aid in heat exchange. The superficial velocity of the steam passing upward through the fluidized bed of solids 228 is between about 0.5 and 5.0 feet per second when the solid particles are of a size between about 100 and 400 mesh or finer.

Heat is supplied to the coke distillation zone to maintain it at a temperature of between about 800°F and 1050°F. by burning coke particles in a coil submerged in the bed 228. Coke particles are withdrawn from the bottom of the fluidized bed 228 and passed to standpipe or barometric leg 244 provided at its lower end with a control valve 246 for controlling the rate of withdrawal of coke from the fluidized bed 228. Air introduced through line 248 picks up the withdrawn coke or coke containing particles and forms a suspension which is passed through line 252 and through coil 254 submerged in the lower portion of the fluidized bed 228 in the distillation zone 226. In this way heat from the burning coke is supplied to the fluidized bed 228 by indirect heat exchange. The hot combustion gases leave coil 254 through outlet line 256 and may be passed through a waste heat boiler, if desired, to recover heat from the hot combustion gases.

Excess coke may be withdrawn from fluidized bed 228 via line 258.

In all the above forms of the invention inert materials such as sand, pumice, kieselguhr, Carborundum, etc., but preferably finely divided petroleum coke is used to form the fluidized bed in the distillation zone and some inert solids in finely divided form may be added in amounts of 15 to 100 lbs. per barrel of feed to keep the interior of the coil or coking equipment clean of coke. During the coking operation coke is formed and excess coke in finely divided form is removed from the process.

The conversion of the residual oil, reduced crude, whole crude, etc., is substantially complete to coke, gas and distillable oil before it enters the distillation zone where the gas oil is rapidly vaporized and leaves the distillation zone after only negligible contact time. Because the conversion of the heavy residual oil is substantially complete in the conversion coil or equipment, the use of a relatively high temperature in the fluidized bed distillation zone does not adversely affect the product quality. The fluidized bed distillation zone functions as a means for distilling the gas oil product from the coke and forms an excellent way of separating coke particles formed during the coking or conversion of the heavy residual oil from distillable gas oil.

A specific example will be given with reference to Fig. 1. A vacuum residuum derived from a mixture of West Texas and South American crude oils and having an API gravity of about 7.4; a Conradson carbon of about 20 wt. percent, a viscosity greater than 1000 seconds Saybolt Furrol at 210°F, and a distillation boiling point at 1050°F. 210°F, 106 volumes of naphtha boiling in the range of about 300°F to 400°F per 100 volumes of residuum. Seed coke having a particle size of 100 to 200 mesh is added in amounts of 55 lbs. per barrel of mixed feed. The mixed feed containing seed coke is introduced into heater 12 and soaker 14 and heated to about 800°F at about 2100 p.s.i.g. pressure. Turbulence is maintained in a soaking zone 14 by means of mechanical agitation. The residence time of the oil in liquid phase in heater 12 and soaker 14 at temperatures above about 775°F is
about 150 minutes. Under these conditions the residual feed is substantially completely converted to coke and distillable products without fouling of the vessel walls. The coked products from soaking zone 24 are introduced into fluid solids distillation zone 24 containing a bed of fluidized coke maintained at about 900°F and 0 psig. Steam amounting to about 10 wt. percent of the oil feed is introduced into distillation zone 24 to maintain the coke in a fluidized condition and to aid in the distillation process. The coked oil feed rate to distillation zone 24 is about 5 weights per hour per weight of coke in zone 24. As the coked oil is sprayed onto the hot fluidized coke in zone 24 it is rapidly vaporized and removed overhead by line 34 without substantial further conversion in zone 24. The coke content of the coked oil entering zone 24 amounts to about 86 lbs. (including the 55 lbs. of seed coke introduced with the feed) per barrel of residuum plus naphtha feed; this coke remains in zone 24 in a dry, finely divided form and becomes a part of the fluidized mass in this zone. The distillate from zone 24 is introduced into a fractionator 42 and fractionated into gas, gasoline, heating oil, gas oil and bottoms. From each barrel of mixed residuum plus naphtha feed the following products are obtained from the distillation zone; (1) about 16.7 lbs. of dry gas, (2) about 24 gal. of gasoline cut boiling below about 430°F. (including the naphtha introduced in the feed as diluent), (3) about 4.8 gallons of heating oil boiling in the range of about 430°F to 650°F, (4) about 7.5 gallons of gas oil boiling in the range of about 650°F to 1000°F, suitable for catalytic cracking feed, and (5) about 1.5 gallons of higher boiling bottoms suitable for fuel oil or for recycling to the process.

What is claimed is:

1. A residual oil conversion process which comprises coking a residual oil in liquid phase in a coil and drum coking zone at a coking temperature in the range of 750°F to 950°F, a pressure in the range of 100 to 3000 psig, and for a time in the range of 2 to 240 minutes while in admixture with 15 to 100 lbs./bbl. of coke particles of a size in the range of 5 to 250 microns and in admixture with 20 to 120 vol. percent of naphtha diluent boiling in the range within the limits of 250°F to 500°F to obtain coke, distillable oils and gas, flashing the total effluent from said coking zone directly into a distillation zone containing a dense turbulent bed of fluidized coke particles maintained at a temperature in the range of about 800°F to 1050°F and a pressure in the range of 0 to 25 psig to obtain said distillable oils in vapors without substantial coking and relatively dry coke, said dry coke becoming a part of said dense turbulent fluidized bed, recovering said vapors overhead from said distillation zone as product, circulating a portion of said dense turbulent bed to a fluid solids heating zone wherein the solids are heated by combustion, and returning heated solids to said distillation zone to supply heat thereto.

2. A process for the conversion of heavy residual petroleum oils containing extremely high boiling constituents, which comprises heating residual oil in a suspended coking coil zone at a coking temperature of about 750°F to 950°F and a pressure of about 100 to 3000 lbs. per sq. in. in liquid phase for about 2 to 240 minutes to convert the residual oil substantially completely to coke, distillable oil and gas, passing the total products of coking to a distillation zone containing a relatively dense bed of finely divided coke particles fluidized by upflowing gases and maintained at a temperature of about 800°F to 1050°F and a pressure of about 0 to 25 lbs. per sq. in. gauge so that the products of coking are flashed and distillable oils are taken overhead without substantial further conversion while the coke particles are separated and collected in the dense fluidized bed.

3. A process according to claim 2 wherein the heating of the residual oil is carried out in a coil submerged in said dense fluidized bed in said distillation zone and heat is supplied to said dense fluidized bed by withdrawing a portion of the coke particles from said dense bed and burning the withdrawn coke particles in a coil submerged in said dense fluidized bed in said distillation zone to supply heat thereto by indirect heat exchange.

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