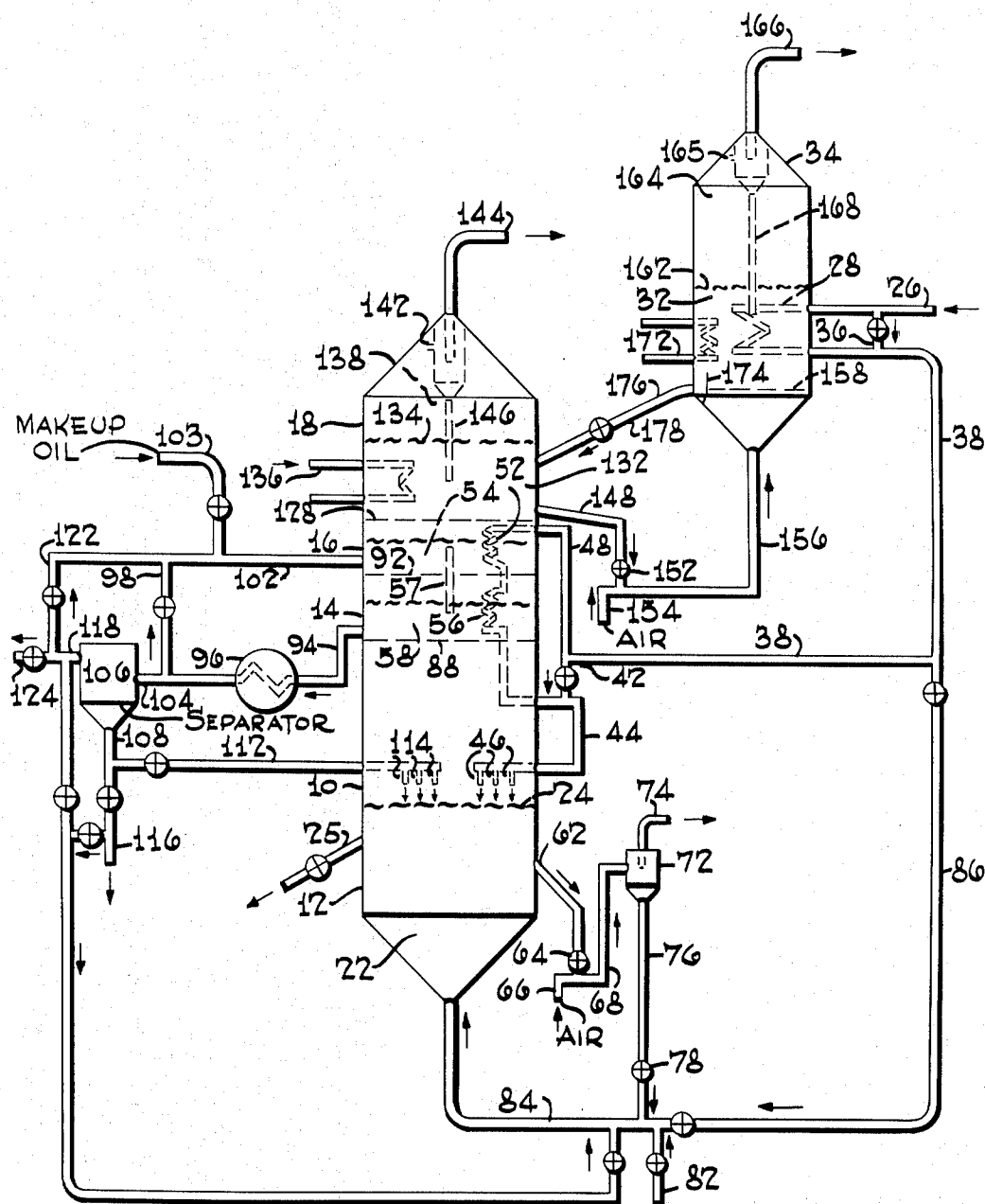


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WITH INERT AND CATALYST PARTICLES
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CONVERSION OF HYDROCARBONS IN TWO STAGES WITH INERT AND CATALYST PARTICLES

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8 Claims. (Cl. 196—49)

This invention relates to a process for the conversion of hydrocarbons and more particularly relates to converting heavy residual petroleum oils to produce gasoline which is treated in an integrated unit.

The conversion of heavy residual petroleum oils to produce gasoline, coke and gas is known. Gasoline from high temperature coking is of high octane number but has an undesirably high gum value and according to the present invention such gasoline is treated in an integral process to reduce gum, improve octane number and otherwise improve product quality.

In the drawing the apparatus shown in the figure is one form adapted to be used in carrying out the present process.

Referring now to the drawing, the reference character 10 designates a vessel having a cracking or coking section 12 in its lower portion, two scrubbing sections 14 and 16 higher up in the vessel and a treating section 18 near the top thereof. The coking section 12 is provided with a dry dense fluidized highly turbulent bed 22 of inert finely divided solid particles which may be sand, coke, pumice, kieselguhr, carborundum, alumina, spent clay catalyst or spent synthetic silica-alumina catalyst or the like, but preferably is petroleum coke. Coke is formed during the coking or conversion of the heavy residual oil in fluidized bed 22 and either deposits on the inert solids or forms additional coke particles. A part of the coke so formed is burned to supply heat for the conversion of the heavy residual oil as will be hereinafter described. The finely divided solid particles preferably have a size between about 30 and 200 standard mesh or finer and the density of the fluidized bed 22 is between about 15 and 45 pounds per cu. ft. The superficial velocity of the gases and vapors passing upwardly through the bed 22 to maintain the particles in dense fluidized condition is about 0.1 to 5.0 feet per second. The fluidized bed 22 has a level indicated at 24. Excess coke is withdrawn from bed 22 through line 25.

The heavy residual petroleum oil to be cracked or converted may have an API gravity of 20° or lower, Conradson carbon between about 5 and 35% wt., and an initial boiling point of about 1000° F. or higher. The feed may include such materials as catalytic or thermal cracked bottoms or cycle oil, visbreaker tar, asphalt, tar from coking, etc. It may also contain fractions boiling lower than 1000° F., if desired. The heavy residual oil is passed through line 26 and for preheating may be passed through coil 28 entirely or partially submerged in dense fluidized bed 32 of retreating catalyst in regeneration zone 34. The residual oil feed may bypass the coil 28 through bypass line 36 and pass through line 38 and valved line 42 to line 44 and nozzles or spray devices 46 arranged above level 24 of coking bed 22 to discharge the residual oil onto the coking bed 22. If desired, the residual oil for additional or initial preheating may be passed from line 38 through line 48 and heating coil 52 partially or completely submerged in the slurry layer 54 in scrubbing zone 16 and then

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through heating coil 56 partially or completely submerged in slurry 58 in lower scrubbing zone 14 in vessel 10. The preheated residuum at a temperature of about 600° F. to 1000° F. is passed through line 44 and into coking bed 22. It will frequently be preferable to introduce part or all of the oil feed at the bottom of bed 22, as by line 84, in order to effect better contacting and give higher conversion. Also a distribution grid may be included at the inlet.

For supplying heat to the coking bed 22 in the coking zone, some of the coke particles or coke-containing particles are withdrawn from the dense fluidized bed 22 through standpipe 62 having a valve 64 at its lower end for controlling the rate of flow of solid particles through standpipe 62. Air or other oxidizing gas is introduced through line 66 and picks up the withdrawn solid particles as a suspension which is passed through transfer line burner 68. In the transfer line burner the velocity of the combustion gases is between about 5 and 75 feet per second and the density of the suspension passing through transfer line burner 68 is about 0.1 to 3 lbs. per cu. ft. The temperature of the solid particles in burner 68 is about 1000° F. or higher. If preferred, the solids leaving line 64 may be heated by contacting them with hot flue gases from an auxiliary burning zone.

The combustion gases and suspended coke and/or other solids are passed to a gas-solids separating device such as a cyclone separator 72, the separated hot combustion gases passing overhead through outlet line 74 and thence through a heat exchanger such as a waste heat boiler (not shown), if desired. The separated heated solid coke or other particles are passed to standpipe 76 having a control valve 78 at its lower end for controlling the rate of withdrawal of solids from the separator 72. The withdrawn heated solids are picked up by steam or other suitable gas introduced through line 82, and the solid particles at a temperature of about 900° to 1800° F. are passed through line 84 as a suspension and into the bottom portion of the coking or conversion zone comprising fluidized coking bed 22. The steam or other gas introduced through line 82 assists in fluidizing the bed 22 of solids in the coking zone in the bottom of vessel 10.

As an alternate some of the residual oil preheated or not may be passed from line 38 through alternate line 86 for admixture with the heated solid particles withdrawn from standpipe 76 and then passage through line 84 to cause conversion of the heavy residual oil by mixing the oil with solid particles heated to a much higher temperature than that which exists in coking bed 22. For example, this line 84 may be operated at say 200° F. higher than reactor temperature and since the contact time is low, cracking will not be excessive. Also, selected feed fractions such as bottoms from catalytic treating or cracking or scrubber slurry from line 124, 116, etc. can be added preferentially to line 84 through line 82. In this form of the invention steam is also added through line 82.

In the coking zone 22 the temperature is maintained at a temperature between about 900° and 1300° F., the pressure is between about atmospheric and 200 lbs. per sq. in. gage and the residence time of the vapors in coking zone 22 is about 4 to 100 seconds. During coking, gas, gasoline, gas oil and higher oils and coke are formed and at high coking temperature the gasoline formed has undesirable high gum but is of high octane number. Also during coking with the temperature as high as these, high boiling hydrocarbons are vaporized so that the vapor products leaving coke bed 22 contain high boiling products which must be separated from the product gasoline. The vapor products leaving coking bed 22 contain entrained coke also. To remove the high boiling constitu-

ents and coke particles from the vapor products leaving the coking bed 22, the vapors may be passed through perforated scrubbing plate 88 on which the slurry 58 is located. The slurry 58 will usually be maintained at a lower temperature than the coking or conversion temperature and the temperature is between 300 and 850° F., preferably 600–800° F. The slurry is maintained at the lower temperature by coil 56 previously referred to as being used for preheating the residual oil feed, if desired. Additional cooling is obtained by cooler liquid flowing down onto scrubbing plate 88 from the upper scrubbing zone 16 via downcomer 57.

The cooling for the slurries in scrubbing zones 14 and 16 will now be further described. The upper slurry 54 of heavy ends or higher boiling constituents on upper scrubbing plate 92 is partly cooled by indirect heat exchange with residual oil feed passing through coil 52 as above described. For maintaining the temperatures of the slurries 58 and 54 on plates 88 and 92 at the desired levels, oil slurry containing heavy ends and coke particles is withdrawn from scrubbing plate 88 through line 94 and passed through cooler 96 and thence through lines 98 and 102 to the slurry 54 on top scrubbing plate 92. While two scrubbing plates 88 and 92 have been shown, it is to be understood that only one such plate may be used. The temperature of scrubbing oil or slurry 54 on top scrubbing plate 92 is maintained between about 300° F. and 800° F., but will generally be less than slurry 58 on plate 88.

Instead of returning all the slurry to top scrubbing plate 92, a part thereof may be passed through line 104 to separator 106 for separating solids from liquid. The separator 106 is preferably a settler or thickener to concentrate the solids in liquid and the more concentrated slurry may be withdrawn from settler 106 through line 108 and returned to the coking bed 22 through line 112 having nozzles or spray members 114 arranged above the level 24 of dense bed 22. Or the concentrated slurry may be withdrawn from the system through line 116 to reject fines from the coking system. In some cases it will be desirable to use cyclones above bed 22 to limit the amount of solids carried up to the scrubbing zone.

The cooled and clarified oil or oil containing less suspended solids than the slurry 54 on plate 88 is withdrawn from the upper portion of settler 106 through line 118 and passed through line 122 and then 102 for return to upper slurry 54 on top scrubbing plate 92. Or some of the clarified oil may be withdrawn from the system through line 124 to offset the oil recovered by condensation from the vapors entering from bed 22. This heavy oil may constitute one of the product streams or it may be recycled to bed 22 via line 84, etc. Extraneous oil such as feed may be added at 103. The slurry temperature in line 102 may be controlled, by adding the cool make-up oil feed through line 103. The latter may contain light components which are stripped out on plates 92 and 88, and are carried up to treating zone 18. In some cases, it will be desirable to operate scrubbing sections 14 and 16 separately and with independent cooling and oil withdrawal systems. Several plates may be used in each section to separate different product fractions.

As the vaporous products at a relatively high temperature or coking bed temperature leave the coking bed and are first scrubbed with residual oil feed from sprays 46 and cooled recycle oil from sprays 114, this removes some of the extremely high boiling materials carried as vapors in the products leaving the coking bed. The vapors at a temperature between about 800° and 1100° F. pass upwardly through perforated scrubbing plate 88 and there intimately contact the oil slurry 58 maintained at a lower temperature to condense higher boiling constituents from the product vapors and also to scrub out any entrained coke particles.

The vapors then leave scrubbing zone 14 at a tempera-

ture of about 300° F. to 800° F. and pass through top scrubbing plate 92 in the scrubbing zone 16 for intimate contact with the oil slurry 54 maintained at a lower temperature than scrubbing zone 14 to condense constituents higher boiling than gasoline so that the vapors leaving upper scrubbing zone 16 are substantially gasoline vapors to be treated in the gasoline treating section 18 which comprises a perforated plate or tray 128 supporting a dry fluidized bed 132 of finely divided clay or other treating catalyst having a level indicated at 134. Instead of a fluid bed a fixed bed of catalyst may be used. The treating catalyst is preferably in finely divided form between about 30 and 200 standard mesh or finer with most of the particles being between about 40 and 150 microns. The velocity of the upflowing vapors through treating zone 18 is selected to maintain the finely divided catalyst particles as a dense fluidized highly turbulent liquid-simulating bed having a density between about 20 and 45 lbs. per cu. ft.

As a treating catalyst, bauxite or clay, spent or used silica alumina synthetic cracking catalyst, silica gel adsorbent, char or activated carbon etc. may be used. Treating may be carried out using catalysts activated with chromium, molybdenum, phosphoric acid, etc. As pointed out above, coke is formed during the coking operation and this coke may be used as a starting product for making a treating catalyst. For example, excess coke may be withdrawn from coking bed 22 through line 25 and ground to the desired size and then treated with steam and/or air at a temperature of about 1600° to 1800° F. to give 50 to 80% yield of activated char or carbon. Similar conditions may be used for revivifying used treating solids.

An indirect heat exchanger 136 may be partially or completely submerged in fluidized bed 132 in the treating zone 18 for maintaining the temperature of the treating fluidized bed 132 between about 500° and 900° F. with a solids hold up on plate 128 to give 1 to 10 parts by weight of oil vapors treated per hour per weight of solid. The heat exchanger 136 is used to add heat or remove some heat of reaction from the treating zone 18. If desired, direct heat exchange may be used in treating zone 18.

Treated vapors leaving dense fluidized bed 132 in treating zone 18 pass to a dilute phase above the dense bed and contain entrained catalyst particles, so the vapors are passed through a gas-solids separating device 142 such as a cyclone separator for separating entrained solids. Separating device 142 is located in the upper portion of vessel 10. The vapors pass overhead through line 144 and are handled as desired to recover treated gasoline which is of improved quality from the standpoint of gum, sulfur, octane number, or lead susceptibility, etc. The separated solids are passed to dip pipe 146 and returned to the dense bed 132 in treating zone 18 below the level 134.

With some treating catalysts such as cracking type catalysts or other inorganic catalysts such as silica or alumina base types the coke which deposits on the catalyst may be removed by burning with air and the heated regenerated solids then returned to the treating zone, any excess heat being transferred to oil feed or product streams or being utilized to produce steam. Carbonaceous type treating agents may be revivified as above stated with steam and/or air under controlled conditions.

The catalyst from the treating zone to be regenerated is withdrawn through line or standpipe 148 having a control valve 152 at its lower end. Air or other regenerating gas introduced through line 154 picks up the withdrawn catalyst and the mixture as a dilute suspension is passed through line 156 to the lower portion of regeneration vessel 34 below distribution grid 158 therein. The velocity of the gases passing upwardly through the regeneration vessel is selected to be between about 0.5 and 5.0 ft. per second to produce dry dense fluidized bed

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32 of solids above referred to. The bed 32 has a level indicated at 162 with a dilute phase 164 thereabove.

The gases leaving the dense bed contain entrained catalyst particles which are mostly removed by passing the gases through a gas-solids separating device 165 arranged in the upper portion of the regeneration vessel 34. The combustion gases pass overhead from line 166 and may be passed through a waste heat boiler or the like to recover heat therefrom. The separated solids are returned through dip pipe 168 to the dense fluidized bed 32 below the level 162 thereof. Any excess heat of regeneration may be removed by a heat exchange coil 172 partially or completely submerged in dense fluidized bed 32. Hot regenerated catalyst passes from the dense fluidized bed 32 into well 174 and thence to standpipe 176 having a control valve 178 at its lower end for controlling the amount of regenerated catalyst passing to the dense fluidized treating bed 132 in treating zone 18.

During regeneration the temperature is maintained between about 900° and 1250° F. and regenerated catalyst at this temperature, or cooled to a lower temperature, is returned via standpipe 176 to treating section 18. Heat from regeneration vessel 34 may also be used in the coking bed 22 using indirect heat exchange as discussed in connection with coil 28. Heat exchange may also be effected by circulating hot catalyst in indirect exchange with coke from bed 22. In some cases the hot catalyst may be contacted directly with the coke and then separated by elutriation, with the catalyst returned to the catalytic section and the coke returned to the coking section.

While the heavy residual oil is shown as being introduced above the bed 22 and into the bottom portion of the bed 22, it may also be introduced directly into the bed 22 at intermediate points.

The slurry on plates 88 and 92 functions as a partial condenser, that is, partial condensation of highest boiling constituents takes place so that the end point of the distillate going to the treating zone 18 is controlled, for example, to the gasoline end point of roughly 400° F., but may extend up to 600° F.

Example

As an example of our invention, its application to the treating of naphtha from a high temperature coking operation is described. Residuum of about 7° API gravity and 20% Conradson carbon is fed to the unit, as described previously. The coking zone is maintained at 1100° F., and without our treating step the 30 vol. per cent yield of C₅/430 naphtha would have high sulphur, poor stability, short breakdown time, and very poor engine cleanliness characteristics. Conjugated diolefins are present to the extent of up to 15% of the total naphtha, and cyclic olefins to about 10-15%.

In our process, the total overhead from the 1100° coker zone is run through a fluidized bed of silica-alumina cracking catalyst maintained in the range of 700° to 775° F., preferably at about 750° F. The temperature of the scrubbing plates is maintained to keep material of a normal boiling point higher than 600° F. from entering the treating bed, and most of it boils below 450° F. In this instance the medium gas oil is removed via the scrubbing oil, although treatment of this fraction also is possible by raising the scrubbing temperature.

The weight of material processed per hour is in the range of 0.1 to 1.0 times the weight of catalyst in the bed, preferably about 0.3 to 0.5. At higher temperatures, higher rates may be used. Some carbon may be deposited, in this case about 1%, and the catalyst is regenerated to maintain activity. Catalyst to material processed weight ratio may range from 0.5 to 20, but in this case a ratio of 2 to 5 is sufficient.

The gasoline resulting from this treatment will have the conjugated diolefins and cyclic olefins reduced to about 1 to 5%, and cleanliness characteristics, stability

and breakdown time will be much improved. A striking demonstration of the improvement obtained is that this naphtha will remain water white or nearly so indefinitely; naphtha directly from the 1100° F. coking bed turns very dark within 24 hours.

In this combination process, coking, partial fractionation and treating steps have been combined with a saving in equipment and with a high level of heat economy. At the same time, a wide range of flexibility in possible operating conditions for each step has been maintained, and operability of the system has not been impaired. Moreover, it provides a combination process wherein the treating catalyst can be kept entirely separate from the coke, so that valuable catalyst is not lost as a result of sticking with coke in the coking zone, nor is the catalyst contaminated by entrainment of coke into the treating zone. In addition, heavier components of the vapor from coking can be excluded from the treating zone where they might tend to result in excessive coke deposits and product degradation.

This invention may also be used to treat catalytically cracked gasoline in which case a bed of catalyst is provided above said coking zone 22 to catalytically crack the overhead vapors from the coking zone and then cracked vapors from the catalytic cracking zone would pass through one or more partial condensation zones as shown in the drawing to remove higher boiling constituents before being passed to treating bed 132. In this case the treating zone 132 would be operated at about 600-850° F. and the catalytic cracking zone at a temperature of about 800-1000° F. As a further modification one or more partial condensation zones may be arranged between the coking zone 22 and the catalytic cracking zone to remove higher boiling constituents unsuitable as catalytic cracking feed stock.

What is claimed is:

1. In a method of producing lower boiling hydrocarbon oils from a heavy residual petroleum oil comprising the steps of coking said residual oil in a coking zone in the presence of a dense fluidized highly turbulent bed of finely divided solid particles in the bottom portion of a contacting zone, said bed being maintained at a temperature in the range of 900° to 1300° F., for a time sufficient to effect cracking and coking of the residual oil; passing the vaporous products upwardly through a bed of treating catalyst to refine said vapors to remove gum-forming materials, said bed being arranged in the top portion of the contacting zone and then removing treated vapors from the top portion, the improvement which comprises passing the vaporous products from the coking step upwardly countercurrently to incoming oil feed and further upwardly through a liquid slurry of oil and some of said solid particles, said slurry comprising a partial condensation zone intermediate to the coking and catalyst beds thereby excluding solid particles and higher boiling constituents from the bed of treating catalyst.

2. A method according to claim 1 wherein said coking zone is maintained at coking temperature by withdrawing coke particles from said coking zone, burning at least a part of the withdrawn coke particles and returning to said coking zone the coke particles heated to a temperature above that in said coking zone.

3. A method according to claim 1 wherein the slurry is cooled by the addition of cool make-up oil feed.

4. A method according to claim 1 wherein the withdrawn slurry containing heavy condensate oil is passed all or in part to said coking zone after it has been mixed with heated solid particles having a higher temperature than exists in said coking zone.

5. A method according to claim 1 wherein the partial condensation zone removes oil heavier than gasoline.

6. A method according to claim 1 wherein the partial condensation zone removes oil heavier than one having a boiling up of about 600° F.

7. A method according to claim 1 wherein said partial

condensation zone comprises a slurry of high boiling hydrocarbons and coke particles through which the vapors resulting from the coking pass to reduce the temperature of the vapors to condense high boiling hydrocarbons and the slurry in the partial condensation zone is maintained at a lower temperature than said coking bed in part by passing heavy residual oil feed in indirect heat exchange with the slurry in said partial condensation zone.

8. The process of claim 1 in which the temperature of the slurry is in the range of 300° to 850° F.

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