

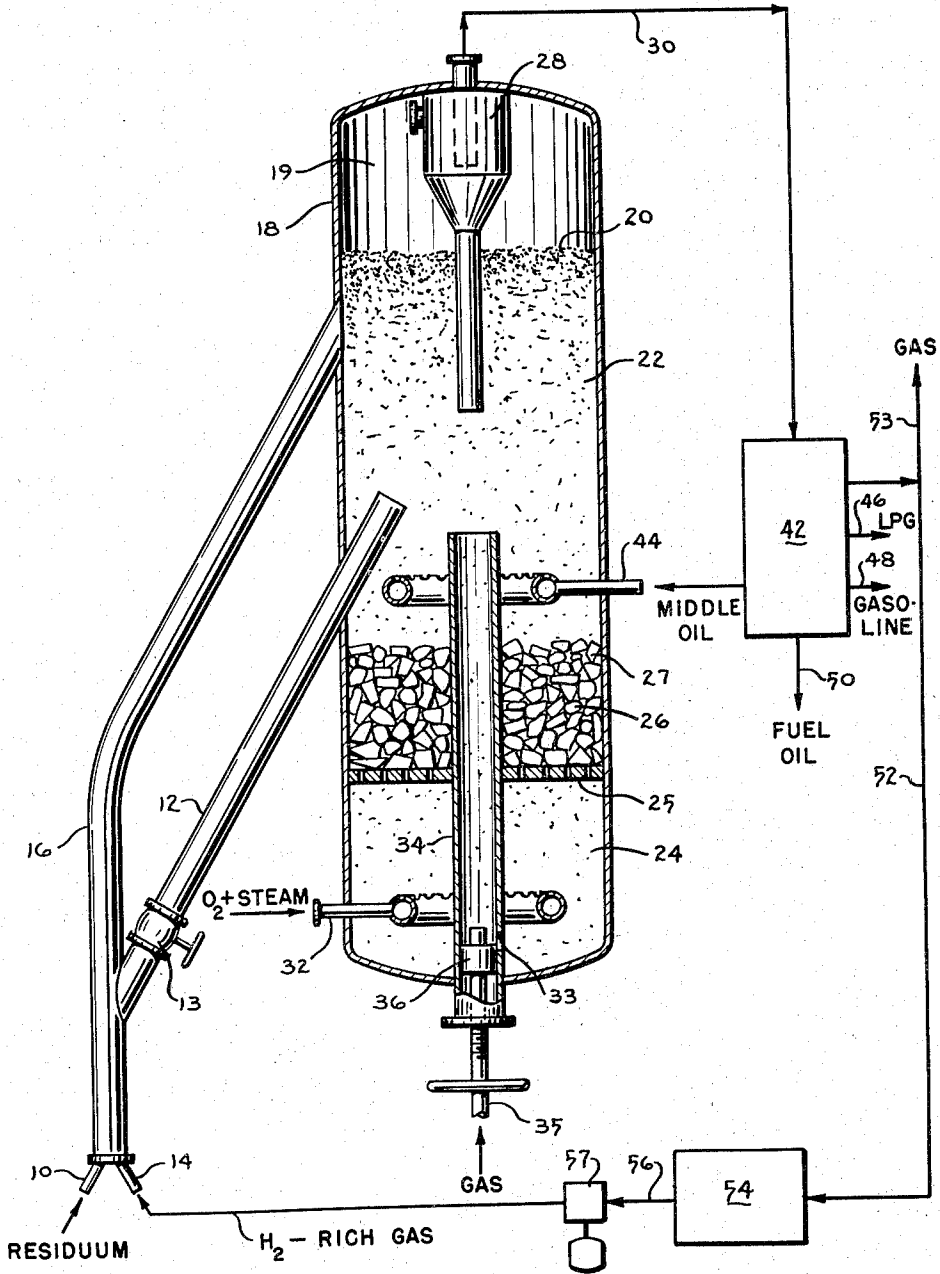
Feb. 24, 1959

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2,875,147

HYDROCARBON CONVERSION PROCESS

Filed Aug. 19, 1953



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1

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HYDROCARBON CONVERSION PROCESS

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Application August 19, 1953, Serial No. 375,133

8 Claims. (Cl. 208—59)

This invention relates to the high-temperature treatment of hydrocarbons and is more particularly concerned with the efficient production of high octane gasoline from heavy hydrocarbon oils.

The invention is particularly applicable to the conversion of heavy charge stocks which cannot be economically treated by conventional processes. It can efficiently convert reduced crudes of high Ramsbottom carbon residue into economic yields of high octane gasoline. It can also be used on heavy crudes which, on coking, would produce a coke salable only for low grade fuel purposes by reason of its sulfur and/or nitrogen and/or metal content. It can be used on lighter oil stocks which contain catalyst poisons such as metals and, therefore, are unsuitable for direct charging to catalytic crackers.

Recently proposed processes suggest converting hydrocarbon oils at elevated pressures and temperatures by contact with a mass of heated contact material in the presence of hydrogen. One such process, described in copending application of Finneran et al., Serial No. 299,114, filed July 16, 1952, discloses contacting the hydrocarbon oil with a fluidized bed of particulate contact material, the particles of which circulate between the conversion zone and a hydrogen-producing regeneration zone. In operating this or similar conversion systems, the compelling necessity for producing hydrogen, achieving heat balance, maintaining good fluidization, etc., imposes limitations on such process variables as temperature, contact time, hydrogen partial pressure, hydrocarbon oil charging rate, etc. These limitations may require operation outside the optimum range of process variables, adversely affecting product yield or quality. In short, the process tends to lack enough flexibility to allow operation within the optimum range of each process variable for different types of oil stocks and rates of charging.

Thus, an object of the invention is to provide a flexible, high-temperature treating process by means of which gasoline of high octane number, high stability and low sulfur content, is produced from low grade, heavy hydrocarbon oils.

Other objects and advantages will be apparent from the description which follows.

In accordance with the invention, hydrocarbon oil is converted in an elongated upflow conversion zone by contact with a hydrogen-containing gas and a particulate contact material or carrier withdrawn from a fluidized bed. The fluidized bed is divided into at least two zones, a reaction zone (hereinafter called the secondary conversion zone) into which the carrier passes after contacting the hydrocarbon oil in the elongated upflow or primary conversion zone, and a regeneration zone wherein a regenerating gas comprising predominantly steam and oxygen reacts at temperatures above about 1600°

2

F. with carbonaceous material deposited on the carrier by the hydrocarbon conversion to form hydrogen-containing regeneration product gases; the regeneration product gases pass up through the bed, fluidizing the carrier particles and aiding the hydrocarbon conversion in the secondary conversion zone.

Circulation of carrier between the fluidized bed and the upflow or primary hydrocarbon conversion zone is largely independent of circulation within the bed between regeneration zone and secondary conversion zone. As one result, the optimum carrier-to-oil ratio (pounds of carrier per pound of charge oil) for the primary hydrocarbon conversion may be set without adverse effect on regeneration conditions, just as regeneration conditions may be set without adverse effect on the primary hydrocarbon conversion. Then again, freeing the primary conversion zone from any dependence upon regeneration conditions imparts additional degrees of flexibility. For example, at any particular carrier-to-oil ratio in the generally employed range of 1:1 to 15:1, the zone of primary conversion may vary, e. g., from a dilute gaseous suspension of carrier as low as 0.5 pound per cubic foot, moving at a linear velocity as high as 40 feet per second, to an upflowing denser suspension as high as 10 pounds per cubic foot transported by gas having a velocity as low as 3 feet per second. Generally, the hydrogen content of the suspending gas is at least 20% by volume. The hydrogen content and total amount of suspending gas used in the primary conversion zone are also freed from dependence on the operating conditions of the regeneration zone. However, the regeneration zone is the preferred original source for the hydrogen. Hydrogen is present in the gaseous effluent from the secondary conversion zone as well as in the pure regeneration product gases. A stream of either of these two gases, after suitable treatment to increase the hydrogen content when desired, will serve well for the suspending gas in the primary conversion zone.

Generally, the primary conversion zone operates in the temperature range of about 800 to 1050° F., preferably 850 to 950° F., with a carrier-to-oil ratio in the preferred range of 2:1 to 10:1 and a carrier-to-gas ratio in the range of about 2 to 6 pounds per cubic foot of suspending gas at conversion pressure and temperature. Total pressure may range from 150 to 1000 p. s. i. g. (pounds per square inch gage); hydrogen partial pressure should be at least 35 p. s. i. (pounds per square inch), the range of 75 to 400 p. s. i. being preferred. Within these ranges, operating conditions in the primary conversion zone are generally selected to achieve maximum production of high octane gasoline consistent with minimum production of coke from the charge oil. To this end, complete conversion of the hydrocarbons into the ultimate products is best not attempted in the primary conversion zone. Rather, an appreciable portion of the conversion is performed in the secondary conversion zone. Contact with freshly regenerated carrier in the secondary conversion zone in the presence of its hydrogen-containing atmosphere is beneficial to the completion of the conversion of the charge oil into valuable hydrocarbon products.

The fluidized bed in the secondary conversion zone is maintained at temperatures ranging from 50 to 200° F. above the temperature in the primary conversion zone by directly returning freshly regenerated carrier particles from the regeneration zone to the secondary conversion zone. Using the hot regeneration product gases to fluidize the carrier in the secondary conversion zone imparts additional heat and, more importantly, provides the hy-

3

drogen-containing atmosphere so beneficial for the completion of the hydrocarbon conversion. The hydrocarbonaceous deposit formed on the carrier particles in the primary conversion zone is converted into volatilized products and a non-volatile carbonaceous residue or coke by the time these particles pass from the secondary conversion zone to the regeneration zone. The secondary conversion zone appears to be particularly beneficial, when operated at a hydrogen partial pressure in the range of 35 to 200 p. s. i., in minimizing the quantity of material that must be removed from the carrier by regeneration.

In the regeneration zone, the coke deposit on the carrier is reacted with regenerating gas consisting essentially of steam and oxygen at a temperature in the range of 1600 to 2500° F., preferably 1700 to 2000° F. The regeneration of the carrier results in the production of a gaseous mixture comprising essentially hydrogen, carbon monoxide, carbon dioxide and excess steam. The regenerating gas contains a preponderance of steam and a minor proportion of high-purity oxygen, the latter more specifically containing at least about 90% by volume of oxygen, preferably at least 95% by volume of oxygen, and obtained, for example, by the liquefaction and rectification of air. Steam-to-oxygen molar ratios in the range of 1.5:1 to 5:1 are generally satisfactory for generating the desired hydrogen. It is frequently preferable to employ a steam-to-oxygen molar ratio of the order of 2:1 to 3:1.

An up-transport zone serves to return hot regenerated carrier to the secondary conversion zone. In the up-transport zone which is fed with carrier particles from the regeneration zone, the carrier particles flow upwardly because of the lower fluid-static head maintained in this zone. The gas velocity in the up-transport zone is generally in the range of about 0.5 to 5 feet per second. The transport gas may be steam or recycled product gas from which, preferably, all hydrocarbons containing more than two carbon atoms have been removed.

The carrier circulation rate is advantageously controlled to ensure that regeneration does not completely consume the coke deposit on the carrier for the reason that regeneration at temperatures above 1600° F. with steam and oxygen activates the carbon left on the carrier. Preferably, the carrier returning through the up-transport zone has about 1 to 3% by weight of activated carbon. In this fashion, the catalytic properties residing in activated carbon may be utilized in the hydrocarbon conversion. For example, lowered production of diolefins may be attained through the catalytic influence of activated carbon, diolefins apparently being readily hydrogenated to more saturated compounds; also, much of the sulfur originally present in the hydrocarbon oil is catalytically converted to hydrogen sulfide. These catalytic properties of activated carbon are effectively brought to bear on the hydrocarbon charge stock through the good gas-solids contact achieved by the dilute phase operation of the upflow or primary conversion zone.

The particular carrier employed in the process of this invention is any solid material that will withstand the desired regeneration conditions, including a temperature above 1600° F., without physically disintegrating or fusing, such as sand, quartz, alumina, magnesia, zircon, beryl or bauxite.

To describe and explain this invention more fully, reference is made to the accompanying drawing which shows diagrammatically a vertical section of a reactor adapted for carrying out the process of the invention.

In the operation of the apparatus illustrated, a heavy hydrocarbon oil, preferably preheated to about 600° F., is supplied by line 10 and brought into contact with hot carrier particles leaving conduit 12. Hydrogen-containing suspending gas from line 14 sends carrier and hydrocarbon oil up through the conduit forming primary conversion zone 16 wherein much of the hydrocarbon oil is

4

converted into volatilized products and a hydrocarbonaceous deposit on the carrier.

Gas, fouled carrier and volatilized products of the conversion pass from primary conversion zone 16 into a cylindrical vessel 18 containing a fluidized bed 20 of carrier particles. Bed 20 is divided into an upper secondary conversion zone 22 and a lower regeneration zone 24 by a packed section 26 which is provided by a perforated plate 25 supporting a mass of packing bodies 27, e. g., Raschig rings. Carrier particles from zone 22 move downwardly through packed section 26 in contact with regeneration product gases flowing upwardly from zone 24. The fouled carrier particles reaching regeneration zone 24 have only a carbonaceous residue of very low hydrogen content. Primary conversion zone 16 discharges suspending gas, carrier and all conversion products directly into the upper portion of zone 22 of fluidized bed 20 but may be arranged to discharge into the gas-solids disengaging space 19 above bed 20. All of the gases and volatilized products from both zone 16 and bed 20 pass through cyclone separator 28 and into line 30.

Zone 22 of fluidized bed 20 together with packed section 26 provides the locus for secondary conversion. In subjacent regeneration zone 24, steam and oxygen supplied by line 32 react with the carbonaceous residue or coke deposit on the carrier to yield regeneration product gases consisting essentially of hydrogen, carbon oxides and excess steam which in fluidizing bed 20 provide the hydrogen-containing atmosphere for secondary conversion. The regeneration incompletely consumes the coke deposit, leaving activated carbon on the carrier particles.

An upright tube 34 open at its bottom to regeneration zone 24 and at its top to zone 22 permits the return of regenerated carrier to zone 22 by means of a gasiform transport medium injected into the base of tube 34 through the tubular stem 35 of adjustable valve 36. The opening 33 in tube 34 may be partially or completely closed by suitable vertical movement of valve 36.

Carrier particles from fluidized bed 20 are passed to primary conversion zone 16 through conduit 12 which is provided with valve 13 to regulate the rate of flow of carrier to zone 16.

The total gasiform effluent passes from reactor 18 by way of separator 28 and line 30 to a conventional recovery plant 42 wherein the effluent is separated into normally gaseous and liquid products. Of the liquid products, a middle distillate, e. g., 400 to 800° F. boiling point range, may be recycled to zone 22 at a level substantially below the level of entry of the fouled carrier from the primary conversion zone, by way of line 44. Liquefied petroleum gas, gasoline and heavy fuel oil fractions are withdrawn from plant 42 through lines 46, 48 and 50, respectively. A residual gas product leaving plant 42 through line 52 contains appreciable proportions of hydrogen, methane, ethane, ethylene and carbon oxides. While a substantial portion of this product gas is discharged through line 53 for utilization as a fuel or chemical raw material, a portion enters hydrogen concentration plant 54 wherein by known methods the hydrogen content of the gas is increased from say 20% by volume to 70% by volume or even higher. For instance, the hydrogen content of the gas may be increased by scrubbing out most of the carbon dioxide, by subjecting the carbon monoxide to the water-gas shift reaction or by effecting partial combustion of the hydrocarbons in the gas with high-purity oxygen. Hydrogen-enriched gas leaves plant 54 through line 56 and is charged to line 14 by compressor 57.

For a further understanding of the practice of this invention, the following specific examples are presented.

Example I

A 25 wt. percent reduced Kuwait crude (8.9° API, 5.3 wt. percent sulfur and 20.2 wt. percent Ramsbottom carbon) is preheated to 500° F. and charged at the rate

5

of 23,000 barrels per day through line 10. This oil is contacted with hot carrier from conduit 12 at the rate of 480 tons per hour and a hydrogen-rich gas from line 14 at the rate of about 2,400,000 S. C. F. H. (standard cubic feet per hour) containing 70% by volume of hydrogen. The resulting suspension passes through primary conversion zone 16 at a temperature of about 850° F. with a velocity of about 10 feet per second. The total pressure is 400 p. s. i. g. and the hydrogen partial pressure is about 260 p. s. i.

Steam and high-purity oxygen (95 vol. percent oxygen) enter regeneration zone 24 through line 32 at the rates of 77,000 and 72,000 pounds per hour, respectively. An additional 25,000 pounds per hour of steam from line 36 transports regenerated carrier up tube 34. The temperature in zone 24 is maintained at 1800° F. and in zone 22 at about 975° F.

From the gasiform effluent removed through line 30 is recovered 20,000 barrels per day of a middle fraction boiling between 400 and 800° F. which is recycled by way of line 44 to zone 22. Also, part of the product gas (comprising chiefly hydrogen, carbon monoxide, carbon dioxide, methane, ethane and ethylene) passes through line 52 to concentration plant 54 where it is scrubbed to remove carbon dioxide, then reheated and shifted in the presence of added steam over an iron-chromium catalyst at a temperature of about 750° F. The resultant mixture is again scrubbed to eliminate carbon dioxide and leave a gas containing about 70 vol. percent hydrogen, 14 vol. percent methane, 7 vol. percent ethane and 4 vol. percent ethylene. The hydrogen-rich gas is compressed and passed through line 56 and line 14 to serve as the suspending gas in primary conversion zone 16.

The ultimate products recovered comprise 13,000 barrels per day of high octane gasoline (91 CFRR clear), 4600 barrels per day of fuel oil meeting ASTM specifications for No. 6 fuel oil, 1700 barrels per day of propane, and about 79,000,000 standard cubic feet per day of fuel gas with a heating value of about 490 B. t. u. per standard cubic foot. The gasoline contains 0.2 wt. percent sulfur and has an oxidation stability corresponding to an ASTM induction time of 7 hours.

Example II

Using substantially the same feed rates of Example I, a second run is made without employing primary conversion zone 16, the Kuwait residuum being charged directly into zone 22 through line 44 along with the recycled middle distillate. Yields approximate those of Example I but the gasoline is not as satisfactory since it contains 0.45 wt. percent sulfur and has an oxidation stability corresponding to only 130 minutes.

Many modifications of the invention will suggest themselves to those skilled in the art. For example, the products issuing from primary conversion zone 16 may be passed directly into a gas-solid separator, the gasiform products removed for treatment per se and only the solids passed into secondary conversion zone 22. Such arrangement simplifies the hydrocarbon product recovery system but necessitates duplication of recovery equipment to handle separately the gasiform effluent from secondary conversion zone 22. Accordingly, all variations conforming to the spirit of the invention are to be considered within the scope of the appended claims.

What is claimed is:

1. A hydrocarbon conversion process which comprises forming with heated particulate carrier a fluidized bed divided into a lower regeneration zone and an upper secondary conversion zone, withdrawing carrier from said secondary conversion zone, contacting a heavy hydrocarbon oil of high Ramsbottom carbon residue with the withdrawn carrier and with a suspending gas containing at least 20% by volume of hydrogen and passing the resulting suspension of said oil and carrier in dilute phase upwardly through an elongated primary conversion zone main-

6

tained at a temperature in the range of about 800 to 1050° F. and a pressure in the range of about 150 to 1000 p. s. i. g. whereby said oil is converted into volatilized products and a hydrocarbonaceous deposit fouling said carrier, passing fouled carrier from said primary conversion zone into said secondary conversion zone and therein converting said hydrocarbonaceous deposit into coke of low hydrogen content by contact with hydrogen-containing regeneration product gases at a temperature about 50 to 200° F. above the temperature of said primary conversion zone, withdrawing said volatilized products for recovery while limiting the contact thereof with said fluidized bed to not more than the upper end portion of said secondary conversion zone, regenerating carrier in said regeneration zone by reacting the coke thereon with steam and oxygen at a temperature in the range of 1600 to 2500° F. to form said regeneration product gases, separating from said regeneration product gases said hydrogen-containing suspending gas, and circulating said carrier in said fluidized bed between said secondary conversion zone and said regeneration zone.

2. The process of claim 1 wherein the carrier, hydrocarbon oil and hydrogen-containing suspending gas traverse said primary conversion zone as a dilute phase suspension containing about 2 to 6 pounds of carrier per cubic foot of suspending gas.

3. The process of claim 1 wherein the hydrogen in said primary conversion zone exerts a partial pressure in the range of about 75 to 400 p. s. i.

4. A process for the conversion of a heavy hydrocarbon oil of high Ramsbottom carbon residue which comprises forming with heated particulate carrier a fluidized bed divided into a lower regeneration zone and an upper secondary conversion zone, withdrawing carrier from said secondary conversion zone, contacting said oil with the withdrawn carrier and with a suspending gas containing at least about 20% by volume of hydrogen and passing the resulting suspension of said oil and carrier in dilute phase upwardly through an elongated primary conversion zone maintained at a temperature in the range of about 850 to 950° F. and a pressure in the range of about 150 to 1000 p. s. i. g. whereby said oil is converted into volatilized products and a hydrocarbonaceous deposit fouling said carrier, passing fouled carrier from said primary conversion zone into the upper portion of said secondary conversion zone, said upper portion being at a temperature about 50 to 200° F. above the temperature of said primary conversion zone and the lower portion of said secondary conversion zone having a vertical gradient of increasing temperature approaching the temperature of said regeneration zone where said lower portion is contiguous to said regeneration zone, withdrawing said volatilized products for recovery while limiting the contact thereof with said fluidized bed to not more than the upper end portion of said secondary conversion zone, converting said hydrocarbonaceous deposit into coke of low hydrogen content by contact with hydrogen-containing regeneration product gases while passing said fouled carrier downwardly through said secondary conversion zone to said regeneration zone, regenerating carrier in said regeneration zone by reacting the coke thereon with steam and oxygen at a temperature in the range of about 1700 to 2000° F. to form said regeneration product gases, separating from said regeneration product gases said suspending gas, and circulating said carrier in said fluidized bed from said upper portion through said lower portion to said regeneration zone and thence to said upper portion.

5. The process of claim 4 wherein the carrier, heavy hydrocarbon oil and suspending gas traverse said primary conversion zone as a suspension having a velocity of at least 3 feet per second and containing not more than 10 pounds of carrier per cubic foot of suspending gas.

6. The process of claim 4 wherein heavy hydrocarbons recovered from the volatilized products are injected into said secondary conversion zone at a level substantially

7

below the level of entry of said fouled carrier from said primary conversion zone.

7. The process of claim 4 wherein the hydrogen in said primary conversion zone exerts a partial pressure in the range of about 75 to 400 p. s. i.

8. The process of claim 7 wherein the hydrogen in said secondary conversion zone exerts a partial pressure in the range of about 35 to 200 p. s. i.

8

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5