

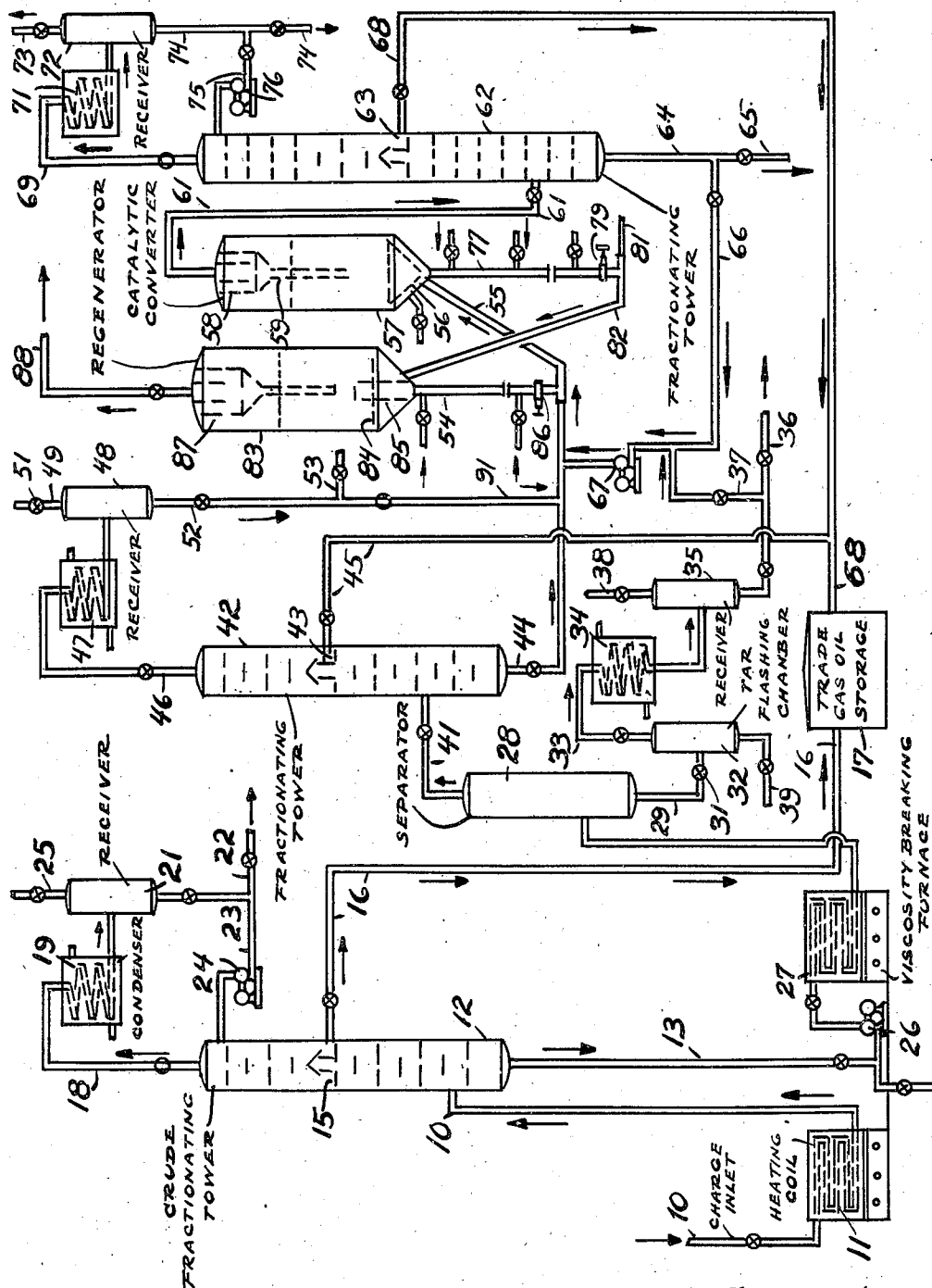
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CONVERSION OF HYDROCARBON OILS

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CONVERSION OF HYDROCARBON OILS

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This invention relates to the conversion of hydrocarbon oils and pertains more particularly to a process for the conversion of high sulfur crude oils or fractions thereof into gasoline and intermediate distillates, such as kerosene, heating oil and Diesel fuel.

It has heretofore been proposed to crack hydrocarbon oils in the presence of an active catalyst to form gasoline. In addition to the production of gasoline, other low boiling distillate fractions, such as kerosene, furnace oil and Diesel fuel, are also formed during the catalytic cracking operation. For convenience, intermediate distillate fractions, including kerosene, furnace oil, Diesel fuel and other oils of similar boiling range, will be hereinafter referred to as "trade gas oil."

While the catalytic cracking process for conversion of heavy oils into gasoline has a number of advantages over the thermal cracking operations previously employed, when the catalytic cracking operation is applied to heavier fractions derived from high sulfur crude oil, the trade gas oil fraction of the catalytic operation usually contains excessive amounts of sulfur which cannot be readily removed without extensive desulfurizing treatment.

For example, a relatively light fraction from a high sulfur-bearing crude comprising 35% to 70% of the original crude, having a mid-boiling point of about 600° F. and containing about 1.2% sulfur, will, when subjected to catalytic cracking treatment, produce a trade gas oil having a sulfur content of about 0.9%, which will normally meet trade specifications for this type of oil. However, if a heavier fraction from the same source of high sulfur crude, having a mid-boiling point of 750° F. and comprising 50% to 80% of the original crude and having a sulfur content of 1.6%, is catalytically cracked under the same conditions, the sulfur content of the trade gas oil produced will be of the order of about 1.4%.

If a still higher boiling fraction of the original crude, having a mid-boiling point above 950° F., for example, comprising 70% to 85% of the crude and having a sulfur content of 1.9%, is catalytically cracked, the trade gas oil obtained from the catalytic cracking operation will contain about 1.6% of sulfur. The trade gas oils produced from the last two cracking operations will contain excessive sulfur which will require further desulfurizing treatment in order to meet the maximum sulfur specifications for this type of oil.

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One of the primary objects of the present invention is to provide a process for the conversion of hydrocarbon oils having a high sulfur content which will retain the advantages realized by catalytic cracking and which will at the same time produce a trade gas oil having a relatively low sulfur content capable of meeting sulfur specifications for this type of oil without further desulfurizing treatment.

It has been found that by subjecting a high-boiling crude oil fraction containing a relatively high percentage of sulfur first to mild thermal cracking treatment and then subjecting the vaporous products from the thermal cracking treatment to catalytic cracking, the gasoline fraction formed from the catalytic cracking operation will be of the same high quality as that obtained by direct catalytic cracking of the original high sulfur oil without preliminary thermal cracking and in addition the trade gas oil distillate will be materially lower in sulfur. Expressed in another way, the preliminary mild thermal cracking treatment prior to the catalytic cracking operation reduces the percentage of sulfur contained in the gasoline and trade gas oil fraction resulting from the catalytic cracking operation subsequently carried out.

Having set forth the general nature and objects the invention will be better understood from the more detailed description hereinafter, in which reference will be made to the accompanying drawing which is a diagrammatic illustration of an apparatus suitable for carrying the invention into effect.

Other objects and advantages of the invention will also be apparent from the more detailed description hereinafter.

Referring to the drawing, the reference character 10 designates a charge line through which a crude oil containing a relatively high percentage of sulfur is introduced into the system. The crude oil is charged through line 10 to a crude still furnace 11 in which the oil is heated to a temperature sufficient to vaporize the lower boiling fractions, such as the gasoline and trade gas oil constituents. The oil during its passage through the heating furnace 11 may be heated, for example, to a temperature of from 600° F. to 800° F.

The oil after passing through the crude still 11 may discharge into a separating and fractionating tower 12 in which the vapors formed during the heating are liberated from unvaporized residue. The unvaporized residue, together with any initial condensate formed in the bottom sec-

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tion of the fractionating tower 12, is removed therefrom through line 13 and treated as hereinafter described.

The crude fractionating tower 12 may be provided with a trap-out tray 15 having a central vapor passage through which vapors liberated in the bottom section of the tower may pass into the upper portion thereof. The temperature of the tower above the trap-out tray 15 may be controlled by suitable reflux medium, cooling elements and the like to condense the constituents boiling in the trade gas oil range, such as constituents boiling between 400° F. and 700° F.

The condensate formed in the upper section of the tower 12 collects in the trap-out tray 15 and is withdrawn therefrom through line 16 and passed to the trade gas oil storage tank 17.

Vapors remaining uncondensed in the upper section of the fractionating tower 12 are removed overhead through line 18 to a condenser 19 in which any gasoline constituents present in the crude oil are condensed. Products from the condenser 19 may then pass to a product receiver 21 in which the virgin gasoline condensed in condenser 19 separates from uncondensed gases. The virgin gasoline is removed from the distillate receiver 21 through line 22. If desired, a portion of the raw gasoline removed from the bottom of the receiver 21 may be passed through line 23 and pump 24 into the upper end of the tower 12 as a reflux medium therefor. Gases separated from the distillate in the receiver 21 may be removed therefrom through line 25.

Residual oil removed from the bottom section of the crude fractionating tower 12 through line 13 is charged to a pump 26 in which it is placed under a pressure ranging, for example, between 100 and 500 pounds per square inch, after which it is charged to a viscosity-breaking furnace 27 in which the oil may be heated to a temperature of from 700° F. to 900° F. and maintained at said temperature for a period sufficient to reduce the viscosity of the oil. The oil during its passage through the viscosity-breaking furnace 27 is subjected to mild cracking treatment to form from 5% to 15% of gasoline. It will be understood that the object of this thermal treatment is not to produce gasoline but to pretreat the oil to form a final trade gas oil having a low sulfur content. The degree of cracking carried out in the viscosity-breaking furnace 27 is controlled to obtain this objective rather than for the production of gasoline. The viscosity-broken products from the furnace 27 pass into a separator 28 in which vapors separate from unvaporized residue.

The unvaporized residue may be withdrawn from the separator 28 through line 29 and passed through a reducing valve 31 into a tar flashing chamber 32 in which further vaporization is obtained. Vapors liberated in the tar flasher 32 pass overhead through line 33 to a condenser 34 and thence into a receiver 35.

Condensate from the tar flashing chamber 32 collecting in the receiver 35 may be withdrawn through line 36 from the process or it may be passed through line 37 and further processed, as hereinafter described. Uncondensed vapors and gases from the product receiver 35 may be vented to a fuel gas line through line 38. Viscosity-broken tar of desired gravity is withdrawn from the tar separator 32 through line 39 as a product of the process. If desired, steam or other stripping gas may be introduced into the tar flasher 32 to aid in vaporizing the oil therein.

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Vaporous products liberated in the separator 28 are removed overhead to a fractionating tower 42 in which the vapors are subjected to fractionation. The fractionating tower 42 may be provided with a trap-out tray 43 for segregating condensate formed in the tower 42 into fractions of different boiling range. The higher boiling condensate formed in the bottom section of the fractionating tower 42 is removed from the bottom thereof through line 44 and subjected to catalytic cracking, as later described.

The temperature of the top section of the fractionating tower 42 may be controlled to condense the trade gas oil fraction of the desired boiling range formed during the viscosity-breaking treatment. The viscosity-broken trade gas oil condensed in the upper section of the tower 42 is collected in the trap-out tray 43 and is withdrawn through line 45 to the trade gas oil storage tank 17.

Vapors remaining uncondensed in the top section of the fractionating tower 42 are removed overhead through line 46 to condenser 47 in which gasoline formed during the viscosity-breaking operation is condensed. Products from the condenser 47 may pass to a receiver 48 in which the gasoline distillate separates from normally gaseous constituents. The normally gaseous constituents are removed from the receiver 48 through line 49 having a release valve 51 for maintaining the desired pressure on the viscosity-breaking and fractionating equipment. The raw gasoline distillate separated in the receiver 48 may be withdrawn from receiver 48 through line 52 and may be removed from the system through line 53 or passed to the catalytic cracking unit, as later described.

The condensate formed in the bottom section of the fractionating tower 42 and withdrawn therefrom through line 44 is intermixed with a finely divided active cracking catalyst discharging through line 54. This catalyst may be any active cracking catalyst, such as, for example, activated clays and synthetic gels comprising silica-alumina, silica-zirconia, boria-alumina, silica-magnesia, or mixtures thereof. The catalytic material discharging through conduit 54 into the oil stream passing through line 44 is preferably at a temperature sufficient to raise the oil to active cracking temperature. The temperature of the catalytic material introduced into the oil stream may range from 1000° F. to 1200° F. The amount of catalytic material so introduced may be controlled to bring the oil to the desired cracking temperature, which in turn may be of the order of from 800° F. to 1000° F. The mixture of oil vapors and finely divided catalyst resulting from the intermixing of the hot catalytic material with the oil passing through line 44 continues through line 55 to a distributing nozzle 56 located in the bottom section of the catalytic converter 57. The upper end of the distributing nozzle 56 is preferably in the form of a perforated grid which uniformly distributes the mixture through the catalytic converter. The velocity of the oil vapors passing upwardly through the catalytic converter 57 is preferably controlled to maintain a relatively dense turbulent mass of catalytic material therein. To this end the velocity may range from 0.5 to 5 feet per second, depending upon the particle size and density of the catalytic material. In most cases, it is preferred to employ catalytic material having a particle size such that from 60% to 80% is capable of passing through a 400-mesh screen. The depth of

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the relatively dense mass of catalytic material maintained in the converter 57 is controlled to maintain the desired contact time to obtain the required conversion.

The cracked vapors containing some entrained finely divided catalytic material after passing through the dense turbulent bed of catalytic material in the converter 57 may pass into a cyclone separator 58 located in the top section of the converter 57. Catalytic material removed from the cracked vapors in the cyclone separator 58 may be returned to the main body of catalytic material through line 59. The cracked vapors after passing through the cyclone separator 58 may continue through line 61 to a fractionating tower 62 in which the products are subjected to fractionation to separate the higher boiling constituents therefrom. The fractionating tower 62 is preferably provided with a trap-out tray 63 for segregating a trade gas oil fraction from the cracked products. Condensate formed in the bottom section of the fractionating tower 62 and forming the heavier constituents boiling above the trade gas oil range is removed from the bottom of the tower 62 through line 64. This product may be withdrawn from the process through line 65 or it may be recycled through line 66 and pump 67 to the oil line 44 and intermixed with oil passing to the converter 57. The temperature of the top section of the fractionating tower 62 is controlled to condense a trade gas oil fraction which collects in the trap-out tray 63 and is removed through line 68. This trade gas oil fraction is passed from line 68 into trade oil storage tank 17 wherein it is blended with virgin trade gas oil and gas oil from the viscosity-breaking operation. Due to the initial viscosity-breaking treatment, the trade gas oil collected in the trap-out tray 63 will have a relatively low sulfur content so that the resulting blend of trade gas oil formed from the process will meet sulfur specifications without further treatment.

Vapors remaining uncondensed in the fractionating tower 62 and comprising catalytically cracked gasoline constituents together with normally gaseous hydrocarbons are removed overhead from the tower 62 through line 69 to a condenser 71 in which the catalytically cracked gasoline is condensed. Products from the condenser 71 may pass to a product receiver 72 in which the catalytically cracked gasoline segregates from normally gaseous constituents. The gaseous constituents formed in the catalytic cracking operation are removed from the receiver 72 through line 73 and the gasoline is removed from the receiver 72 through line 74. If desired, a portion of the gasoline may be returned through line 75 and pump 76 to the upper end of the fractionating tower 62 as a reflux medium therefor.

Returning to the catalytic converter 57, catalytic material contained therein is continuously removed from the bottom thereof through conduit 77. If desired, a stripping gas may be introduced into the bottom section of the converter 57 through line 78 to remove volatile hydrocarbon vapors from the catalytic material. Catalytic material removed from the converter 57 through conduit 77 discharges through a control valve 79 into a stream of air or other oxidizing gas introduced through line 81. The mixture of catalytic material and air then passes through line 82 into the bottom portion of a regenerating chamber 83. The air upon contacting with the catalytic material removed from the converter 57 tends to burn any carbonaceous deposits formed

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on the catalytic material as a result of the cracking operation. This burning of the carbonaceous deposits results in the liberation of heat which increases the temperature of the catalytic material. The bottom of the regenerating chamber 83 may be in the form of an inverted cone, above which may be positioned a perforated grid plate 84 through which the mixture of catalytic material and air discharges into the main body of the regenerating chamber.

The velocity of the regenerating gas passing upwardly through the regenerating chamber 83 is also preferably controlled to maintain a dense turbulent body of catalytic material undergoing regeneration within the regenerating chamber 83. To this end, the velocity of the air or oxidizing gas may be of the order or from 0.5 to 5 feet per second. The catalytic material is retained within the regenerating chamber 83 for a period sufficient to burn the desired amount of carbonaceous deposits therefrom and to heat the catalytic material to the desired temperature for supplying the required heat for the cracking operation, as previously described. In cases where the amount of carbonaceous deposits burned from the catalyst is insufficient to supply the required heat for the cracking operation, additional fuel may be supplied to the regenerator to heat further the catalytic material. The regenerated catalytic material is continuously withdrawn from the regenerator 83 through a conduit 85 projecting upwardly from the bottom of the chamber into the space above the perforated grid plate 84. The conduit 85 discharges into the conduit 54 from which the catalytic material is passed through control valve 86 into the oil stream 44, as previously described.

The spent regenerating gas after passing through the catalytic material in the regenerator 83 continues to a cyclone separator 87 located in the top section of the regenerating chamber for removal of entrained catalytic material carried in the combustion gases. The spent combustion gases are removed from the cyclone separator 87 through line 88 and may be vented to the atmosphere or passed to a Cottrell precipitator or other types of solid-gas separating devices for further purification of the gases.

The conduit 77 employed for removing the spent catalytic material from converter 57 and the conduit 54 for removing the regenerated catalytic material from the regenerator 83 may be in the form of a standpipe in which sufficient pressure is built up on the catalytic material to cause it to circulate through the catalytic converter and regenerating chamber. In order to develop a hydrostatic pressure in the conduits 77 and 54, it is important to maintain the finely divided material in a freely flowing fluidized state during its passage through these conduits. To this end an aerating gas may be introduced at one or more spaced points along the conduits 54 and 77.

While I have described a conventional type of fluid catalyst cracking equipment for carrying out the catalytic cracking operation in which the catalytic material is continuously circulated through the cracking and regenerating zones by hydrostatic pressure developed by means of standpipes, it will be understood that other types of catalytic cracking equipment may be employed for carrying out the present invention.

Referring again to the receiver 35, which collects the overhead products from the tar flasher 32, the liquid condensate collected in this receiver

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may be passed through lines 37 and 46, pump 67 and line 44 to the catalytic converter 57 and subjected to catalytic conversion, as previously described. Also, the gasoline obtained from the viscosity-breaking treatment and collected in receiver 48 may also be passed through line 91 and intermixed with oil from line 44 passing to the catalytic converter 57.

Having described the preferred embodiment of the invention, it will be understood that it embraces such other variations and modifications as come within the spirit and scope thereof.

What is desired to be protected by Letters Patent is:

1. A process for producing trade gas oil of low sulfur content from high sulfur-bearing oil which comprises subjecting all of said high sulfur-bearing oil to mild thermal cracking treatment, fractionating the cracked products to segregate a trade gas oil fraction and a heavier fraction, removing the trade gas oil fraction to storage, subjecting said heavier fraction to further cracking treatment in the presence of an active cracking catalyst, fractionating the cracked products from the last-named cracking treatment to obtain at least a trade gas oil fraction and a heavier fraction and recovering said trade gas oil fraction as a trade gas oil of low sulfur content and removing the same to storage.

2. In the process defined by claim 1, the further improvement which comprises mixing the trade gas oil fraction segregated from the cracked products from the thermal cracking treatment with the trade gas oil fraction segregated from the cracked products from the catalytic cracking treatment to recover a total trade gas oil of low sulfur content.

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3. A process for producing trade gas oils having a low sulfur content from high sulfur-bearing crude oils which comprises initially subjecting said crude oil to distillation and fractionation to segregate a trade gas oil fraction and a heavier residual fraction, removing the trade gas oil fraction to storage, subjecting all of said residual fraction to mild thermal cracking treatment, fractionating the cracked products from said thermal cracking treatment to segregate a trade gas oil fraction and a heavier fraction, removing the trade gas oil fraction to storage, subjecting said heavier fraction to further cracking in the presence of an active cracking catalyst, fractionating the cracked products from the last-named cracking treatment to obtain at least a trade gas oil and a heavier fraction and recovering said trade gas oil fraction as a trade gas oil of low sulfur content and removing the same to storage.

4. In the process defined by claim 3, the further improvement which comprises combining the initial trade gas oil resulting from the distillation and fractionation of the crude with the trade gas oil from the thermal cracking treatment and the trade gas oil from the catalytic cracking treatment to recover a total trade gas oil of low sulfur content.

5. In the process defined by claim 3, the further improvement which comprises combining the gas oil fraction resulting from the thermal cracking treatment with the trade gas oil fraction from the catalytic cracking treatment to recover a total trade gas oil of low sulfur content.

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