

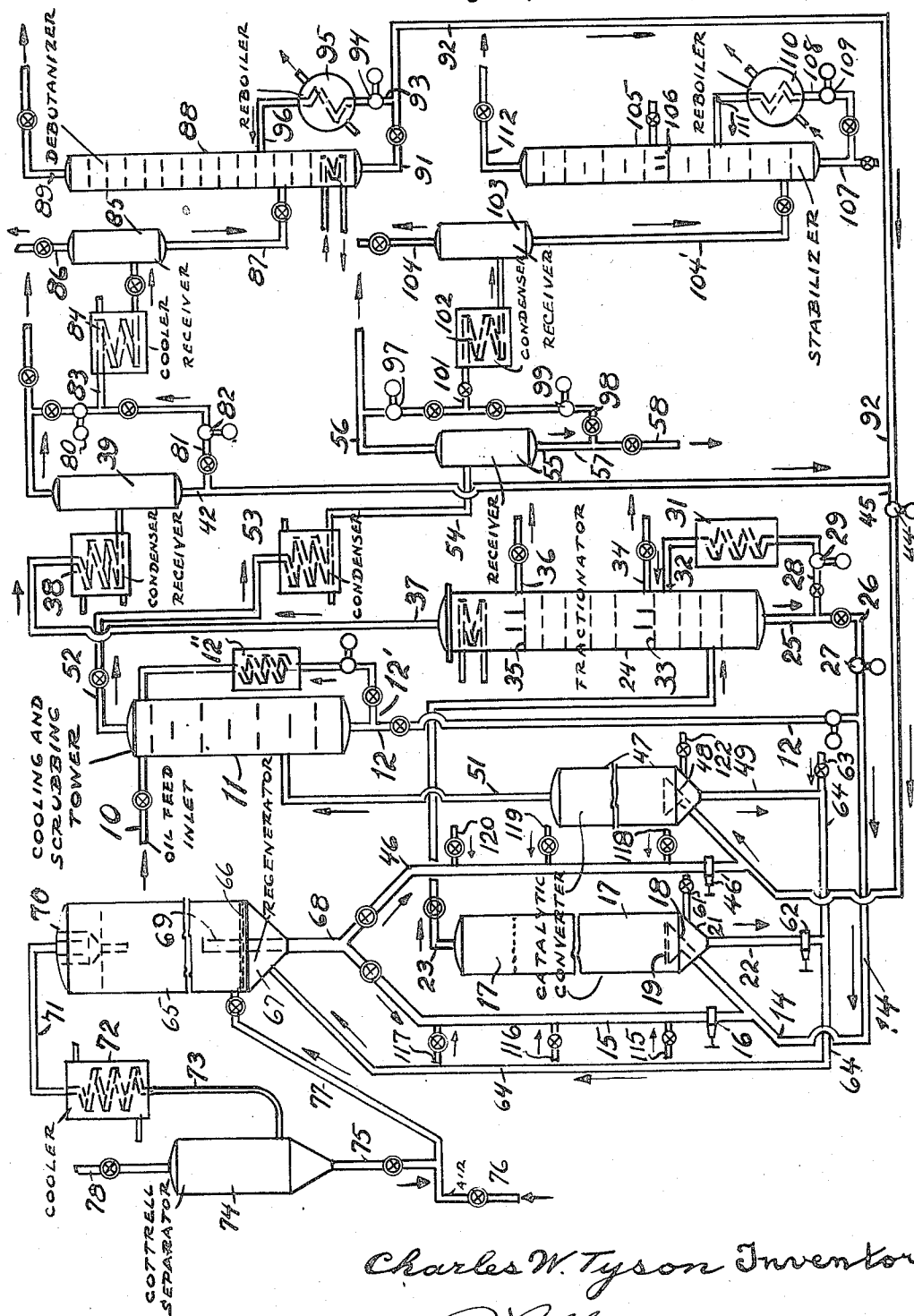
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CATALYTIC CRACKING AND REFINING OF HYDROCARBON OILS

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CATALYTIC CRACKING AND REFINING OF
HYDROCARBON OILS

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1

This invention relates to the catalytic conversion of hydrocarbon oils and is directed more particularly to a continuous process for cracking oils in which the cracking is carried out in the presence of a finely divided powdered catalyst.

While the invention in some of its broader aspects has a more general application, it is particularly adapted to a two-stage cracking process wherein the petroleum oil is first cracked to form a naphtha fraction, and the naphtha fraction or a selective cut therefrom is then subjected to treating to improve the quality thereof.

It has been proposed heretofore to crack higher boiling hydrocarbons in the presence of finely divided catalyst to form lower boiling hydrocarbons in the motor fuel boiling range. According to the general procedure followed, when employing this general type of process, the oil to be cracked is first passed through a cracking zone containing the finely divided cracking catalyst at a controlled velocity to maintain a dense turbulent mass of catalytic material within the cracking zone. Following the cracking treatment, the cracked products are separated from the finely divided catalytic material and thereafter fractionated to condense the insufficiently cracked constituents therefrom. The initial condensate formed during the latter fractionation contains the entrained catalytic material present in the cracked vapors so that the resulting distillate product resulting from the fractionation is virtually free of entrained solids and no additional purification treatment is necessary to remove solids therefrom.

More recently it has been discovered that the quality of the gasoline, and particularly the aviation fraction, may be materially improved with respect to its acid heat, lead response and other properties by further treating of the motor fuel or a selective fraction thereof resulting from this initial cracking operation. However, the vapors resulting from the treating or reforming of the motor fuel constituents are relatively free of constituents boiling above the end point of the desired product. Consequently, catalytic material entrained in the cracked vapors from the cracking of the naphtha will normally appear in the final motor fuel product and will therefore require further separation to remove the entrained catalytic material.

One of the primary objects of the present invention is to provide a method of removing entrained finely divided catalytic material from vapors resulting from the treating or reforming of low-boiling distillates, such as naphtha, which

2

contain little if any constituents boiling above the end point of the final product.

It has also been proposed heretofore, when cracking in the presence of finely divided catalysts, to supply a large proportion of the heat required for the process by circulating the catalytic material through a regenerating zone in which the catalytic material is heated to a temperature substantially above the desired cracking temperature and then transferring the hot, regenerated catalyst back to the cracking zone. During the regeneration treatment, the catalyst is heated by burning carbonaceous deposits formed on the catalytic material during the cracking operation. This method of operating materially reduces the capital investment for a cracking unit of given capacity by eliminating the furnaces for preheating the oil and also by eliminating the cooling tubes which might otherwise be necessary for removing heat liberated during regeneration. The process also reduces the operating costs by utilizing a low-grade fuel formed during the cracking process to supply the heat required for the operation.

However, when operating in this manner, it is usually necessary to limit the temperature to which the catalyst is heated during regeneration in order to avoid permanently impairing the activity of the catalytic material. In many cases, the maximum permissible temperature to which the catalytic material may be heated without impairing its activity is not greatly in excess of the temperature desired for carrying out the cracking process. For example, in most of the active catalysts employed at the present time it is desirable to maintain the regeneration temperature below the maximum of 1150° F. or 1200° F., whereas in many cases it is desirable to carry out the cracking process at temperatures of the order of from 900° F. to 1050° F. Since the temperature to which the catalyst may be heated during regeneration is not greatly in excess of that required for the cracking process, it is necessary to circulate large quantities of catalytic material continuously through the cracking and regeneration zones in order to supply the heat required for the cracking operation. For this reason it is important to provide some means of preheating the oil to the maximum permissible temperature without requiring the use of external heating coils or other extraneous devices which would further increase the cost of the cracking equipment.

Another important object of the present invention is to provide an improved method wherein

3

the fresh oil may be preheated to a higher temperature by heat exchange with products from the process before mixing with the hot regenerated catalytic material.

A further object of the invention is to provide a method of preheating the fresh oil from the process and at the same time remove entrained catalytic material from the cracked gasoline vapors.

Other more detailed objects and advantages of the invention will be apparent from the detailed description hereinafter in which reference will be made to the accompanying drawing which is a diagrammatic illustration of an apparatus forming a part of the present invention and capable of carrying out the process forming another part thereof.

In accordance with the broader phases of the present invention, the oil to be cracked is first passed in direct contact with hot cracked products resulting from the cracking or reforming of low-boiling gasoline or naphtha fractions which contain little if any constituents within the boiling range of the oil to be cracked. The fresh charging oil passing in countercurrent contact with the hot cracked vapors cools the cracked vapors, removes entrained catalytic material contained therein, and at the same time preheats the oil for the cracking process.

Referring particularly to the drawing, the reference character 10 designates a charge line through which the oil to be cracked is introduced into the system. This oil may be a clean condensate stock, such as a gas oil, or it may be a residual oil, such as a topped or reduced crude. In some cases it may be a total crude which contains little if any gasoline constituents.

The oil introduced through line 10 is passed into the top of a combined scrubbing and cooling tower 11 through which cracked vapors resulting from the cracking of low-boiling hydrocarbon distillates, such as naphtha, are passed as hereinafter described. The scrubbing and cooling tower 11 may be provided with suitable baffles for effecting more intimate contact between the cracked vapors and the fresh charging oil or it may be a conventional bubble tower capable of efficient fractionation. The fresh charging oil passing in countercurrent contact with the cracked vapors is preheated by the direct contact therewith. The tower 11 may contain a body of fresh oil through which the vaporous products pass before being removed therefrom. The temperature of the oil in the base of the tower may be regulated by pumping a portion of the oil collected in the base of the tower through line 12' to cooler 12'' and returning it to the top of the tower. For example, the cracked vapors introduced into the scrubbing tower may be at a temperature of the order of from 700° F. to 1000° F. and the fresh oil introduced therein may be preheated to a temperature of from 400° F. to 700° F.

To avoid intermixing of the fresh feed with the cracked vapors, the vapors should boil substantially outside the boiling range of the feed and the mixing temperature should be substantially above the dew point of the vapors. Under such conditions, the fresh feed after contacting with the cracked vapors will be substantially free of cracked products and the cracked products will be substantially free of feed constituents.

The fresh charging oil after passing through the combined scrubbing and cooling tower 11 is removed from the bottom thereof through line 12 and continues through line 14 into which is

4

discharged at a hot, finely divided cracking catalyst from vertical conduit 15. The conduit 15 is provided with a feed valve 16 for regulating the amount of catalytic material so introduced. The catalytic material introduced into the oil stream passing through line 14 may be any suitable cracking catalyst, such as naturally active or activated clays and synthetic gels comprising silica-alumina, silica-magnesia, silica-zirconia, and boric oxide alumina. This catalytic material may consist solely of active catalytic components, or the catalytic components may be diluted with relatively inert material, such as sand, diatomaceous earth, clays, or the like, which have little if any catalytic activity but which may serve as a heat carrier for transferring heat from the regeneration zone into the cracking zone, as later described. This catalytic material preferably has a particle size ranging, for example, between 0.1 and 100 microns. The temperature of the catalytic material introduced into the oil stream passing through line 14 should be substantially above the temperature desired for the cracking operation and the amount of catalytic material introduced should be sufficient to heat the oil from the initial preheat temperature before described to the final desired cracking temperature and to supply the necessary heat for the cracking reaction. The temperature of the catalytic material introduced into the oil stream is substantially the temperature maintained during regeneration of the catalytic material which, in turn, may be of the order of from 1000° F. to 1200° F., and preferably about 1150° F.

The cracking process may be carried out at a temperature ranging from 750° F. to 1000° F. The amount of catalytic material necessary to heat the oil from its initial preheating temperature to the desired reaction temperature may be of the order of from 5 to 40 parts of catalytic material per part of oil by weight.

In many cases this relatively large amount of catalytic material necessary to supply the necessary heat may result in undesirable side or chain reactions. For this reason, it may be of advantage in many cases to dilute the catalytic material with relatively inert material, as previously described.

The oil upon contact with the hot regenerated catalytic material is vaporized and heated to the desired reaction temperature. The resulting mixture of catalytic material and oil vapors then continues through line 14 to a catalytic converter 17. This mixture preferably discharges into the converter 17 through a centrally located discharge nozzle 18 positioned in the bottom section of the reactor. The nozzle 18 is also preferably spaced from the outer wall of the reaction chamber and is provided with a perforated grid plate 19 for distributing the mixture of oil vapors and catalytic material over substantially the full cross-sectional area of the converter. The space between the outer wall and the nozzle 18 forms an annular passage through which catalytic material to be regenerated may pass into a stripping or settling section 21 positioned below the inlet nozzle 18.

The velocity of the oil vapors passing upwardly through the converter 17 after issuing from the nozzle 18 is preferably controlled so as to permit the finely divided catalytic material to settle into a relatively dense mass which is maintained in a turbulent condition similar to a boiling liquid by the upward passage of the oil vapors through the mass. The velocity of the oil vapors passing

5

upwardly through the converter 17 may, for example, be of the order of from 0.2 to 5.0 feet per second.

Spent catalytic material after being retained within the converter 17 for the desired length of time is withdrawn therefrom through an outlet conduit 22 positioned at the bottom of the converter. The rate of withdrawal of the catalytic material from the converter is preferably controlled to maintain the relatively dense mass of catalytic material at a level substantially below the top of the converter, such as from 5 to 15 feet or more. By permitting a relatively free space above the dense mass of catalytic material, the amount of entrained powder passing overhead with the cracked products issuing from the top of the reactor may be materially reduced.

The height of the dense mass of catalytic material maintained within the converter 17 is regulated to obtain the desired contact time between the cracked vapors and catalytic material within the converter. This contact time may be of the order of from 5 to 50 seconds, depending upon the nature of the catalyst, the temperature, the characteristics of the oil treated, degree of conversion desired, and other factors.

The cracked vapors containing a small amount of entrained catalytic material are removed from the top of the converter 17 through line 23. The amount of entrained powder contained in the cracked vapors will depend upon the size and density of the catalyst particles, the velocity of the oil vapors passing through the catalyst mass within the converter, the amount of free space provided above the level of the dense catalytic mass within the converter, and other factors. However, under properly controlled conditions, the amount of such entrained material may be reduced to such a point that it can be readily removed from the bottom section of the fractionating tower. However, if desired, additional separating equipment, such as cyclones, may be located in the top section of the catalytic converter or in the transfer line 23.

The cracked vapors removed from the converter 17 through line 23 pass into the bottom section of a product fractionator 24 in which the cracked products are fractionated to condense insufficiently cracked constituents as reflux condensate. The initial condensate formed in the fractionating tower 24 will contain the entrained catalytic material carried overhead from the converter through line 23. This initial condensate may be removed from the bottom of the fractionating tower through line 25 and may be passed through line 26 and pump 27 and combined with fresh feed passing through lines 12 and 14.

The cracked vapors passing into the fractionating tower 24 are normally at a temperature substantially above the dew point. As a result, it is necessary to provide means for cooling the cracked vapors to below its dew point in order to condense the insufficiently cracked constituents. To accomplish this cooling, a portion of the initial condensate removed from the bottom of the tower 24 through line 25 may be passed through line 28 and pump 29 to a cooling coil 31 and thereafter returned to the fractionating tower through line 32 at a point above the point of entry of the cracked vapors. This recycling and cooling of the initial condensate from the bottom of the fractionating tower may serve as a scrubbing medium for removing entrained solids from the cracked vapors and also for cooling the cracked vapors to the dew point.

6

The fractionating tower 24 may be provided with one or more trap-out trays 33 for segregating the cycle oil into various fractions, such as heating oil, kerosene, or the like. This cycle oil may be withdrawn from the trap-out tray through line 34 and may be subjected to cracking or may be withdrawn from the system as a final product of the process.

The top temperature of the fractionating tower 24 may be controlled to take overhead the total gasoline and lighter constituents, or it may be maintained at a lower temperature to condense a heavy naphtha fraction. In the latter case, the naphtha fraction may be collected in separate trap-out tray 35 which may be withdrawn therefrom through line 36.

Vapors remaining uncondensed after passage through the fractionating tower 24 and which may comprise the total gasoline constituents boiling below 400° F. or a selective lower boiling fraction just mentioned are removed overhead from the fractionating tower 24 through line 37 and passed to a condenser 38 wherein they are cooled to a temperature sufficient to condense the normally liquid constituents contained in the vapors. Products from the condenser 38 may then pass to a low-pressure product receiver 39 in which the liquid condensed in the condenser 38 is segregated from the uncondensed gases and vapors.

The cracking process is preferably carried out at a relatively low pressure, such as from substantially atmospheric to 3 or 4 atmospheres. Under such conditions, the receiver 39 will also be under a pressure below the cracking pressure. As a result, the bulk of the butane-butene constituents will remain in vapor form after passage through condenser 38, and substantial amounts of pentane-pentene constituents may also be in vapor form.

Vapors and gases separated from liquid distillate in receiver 39 are withdrawn overhead through line 41. The liquid distillate separated from the gases from receiver 39 is removed therefrom through line 42. The liquid distillate withdrawn from receiver 39 through line 42 may be directly subjected to further treatment to reduce the amount of olefins contained therein. To this end, the liquid distillate from line 42 may continue through line 43, pump 44 into line 45 into which finely divided catalytic material discharges through conduit 46 having a feed valve 46'.

As illustrated, the catalytic material discharging from conduit 46 into line 45 carrying the liquid distillate from receiver 39 is of the same composition as that employed in the initial catalytic cracking process and is obtained from the same regenerator later to be described. The amount of hot regenerated catalytic material introduced into the distillate stream in line 45 should be sufficient to heat the distillate to the desired retreating or reforming temperature, which may be of the order of from 500° F. to 1000° F.

The purpose of the second treatment as just mentioned is to reduce the acid heat of the product by increasing the amount of saturated constituents contained therein. This results in a substantial improvement in the lead response and reduces the amount of lead required for a final product of given octane. For example, an aviation fuel of 100 octane with the addition of 1 cc. of tetraethyl lead per gallon may be obtained by the retreating of this distillate under the conditions above mentioned. This improvement in acid heat and lead response is obtained by re-

duction in the olefin content of the distillate fraction. The exact reason for the reduction in the amount of olefins by retreating of the distillate formed in the initial cracking operation is not fully understood but may be attributed to the polymerization of the olefin constituents or to the transfer of hydrogen from the more saturated constituents or alkylation of the olefins. The olefins contained in the distillate receiver 42 are largely concentrated in the lower molecular weight hydrocarbons, such as in the butane-butene, pentane-pentene, and hexane-hexene components. In view of this, the top temperature of the fractionating tower 24 may be controlled as previously described to condense all of the constituents boiling above hexane-hexene, or the liquid distillate in the tower 38 may be subjected to further fractionation to segregate a light naphtha fraction consisting largely of constituents below hexane-hexene and this latter fraction may be subjected to treatment rather than the total naphtha fraction. Furthermore, in some cases it may be desirable to include in the fraction which is subjected to further treatment some higher boiling hydrocarbons. For example, the fraction passing through line 45 may be a fraction having an end point above 400° F. To this end, the top temperature of the fractionating tower 24 may be controlled to take overhead not only the 400° F. end point constituents but also constituents boiling, for example, up to 500° F. Furthermore, it may be desirable in some cases to segregate a light naphtha such as a fraction containing principally hexane-hexene constituents and lower boiling hydrocarbons and also a fraction having constituents boiling between 300° F. and 400° F.; in other words, a fraction in which a center cut boiling between 170° F. and 300° F. has been removed. It has been further found, for instance, that the fraction of the cracked distillate resulting from the catalytic cracking treatment previously described having a boiling range between 200° F. and 300° F. consists principally of aromatic constituents which are not improved by subsequent catalytic treatment. Consequently, it may be of advantage to remove this fraction from the distillate prior to subjecting it to the second catalytic treatment.

The hot regenerated catalytic material discharging from conduit 46 into the distillate stream through line 45 vaporizes and heats the distillate to the desired reaction temperature. The resulting mixture continues through line 45 into a second catalytic converter 47 through an inlet nozzle 48. The second catalytic converter may be of the same general construction as that previously described with reference to the cracking converter 17 so that no further detailed description is necessary. This converter may be materially smaller than the cracking converter 17 since the distillate charged into the converter comprises only a fraction of the total feed charged into the cracking converter 17. The oil vapors passing through the second converter 47 are likewise preferably controlled to maintain a dense catalytic mass therein which is kept in a violently agitated state by the upward passage of the vapors therethrough. The catalytic material after being retained within the second converter 47 for the desired period is withdrawn from the bottom thereof through conduit 49. The catalytic material is removed from the converter 47 at a rate such as to maintain the level of the dense mass within the converter 47 at a substantial

distance below the vapor outlet communicating with the top of the converter, as previously described in connection with converter 17, so as to reduce the amount of powdered material entrained in the vapors removed from the converter. The oil vapors are retained in the second converter 47 for a period sufficient to obtain the desired improvement in the quality of the product. The contact time of the oil vapors with the catalyst in the converter 47 may, for example, range between 2 and 50 seconds. The treated vapors after passing through the second converter 47 are removed therefrom through line 51 and are passed into the cooling and scrubbing tower 11 previously described through which they pass upwardly in countercurrent contact with the fresh charging oil. This direct contact between the fresh charging oil and the cracked vapors from the converter 47 serves to cool the cracked vapors and preheat the oil. In addition, the fresh heavier charging oil serves to remove any entrained powdered catalyst contained in the cracked vapors removed from the converter 47. If desired, cyclones or other suitable separators may be provided either in line 51 or in the top section of the converter 47 for further removal of entrained powder from the cracked vapors prior to introduction into the scrubbing tower 11. However, under properly controlled conditions the amount of entrainment carried overhead through line 51 from the converter 47 will be sufficiently small so as to permit complete removal therefrom by the scrubbing oil introduced into scrubbing tower 11 through line 10.

Since the treated vapors passing into the scrubbing tower 11 are vapors resulting from the cracking of the low boiling constituents having a boiling range below the boiling range of the fresh feed passing to the cracking operation, the oil vapors removed from the scrubbing tower 11 will be substantially free of fresh oil constituents and the fresh oil constituents removed from the scrubbing tower 11 will be substantially free of cracked products. To this end, it is important, however, that the charge passing into the scrubbing tower 11 be substantially free of virgin gasoline or constituents boiling within the boiling range of the feed passing to the converter 47.

The cracked vapors after passing upwardly through the chamber 11 in contact with the fresh oil are removed from the scrubbing tower through line 52 and may pass directly to a condenser 53 in which the vapors are condensed to liquefy normally liquid constituents of the cracked vapors. The products from the condenser 53 may be then passed through line 54 to a product receiver 55 in which the liquid distillate formed in the condenser 53 separates from uncondensed gases and vapors.

The retreatment carried out in the converter 47 is also preferably under relatively low pressure such as from substantially atmospheric to from 3 to 4 atmospheres and the receiver 55 is also preferably at a pressure somewhat lower than that maintained in the converter 47. As a result of the relatively low pressure maintained in the receiver 55, the bulk of the butane-butene, and even substantial amounts of pentane-pentene constituents, will remain uncondensed after passage through the condenser 53 unless subnormal temperature is maintained therein. As a result, the vapors liberated from the liquid distillate in receiver 55 will contain the bulk of the butane-butene constituents and substantial amounts of the pentane-pentene constituents. The vapors

and gases separated in the receiver 55 are removed therefrom through line 56 and the liquid distillate is removed therefrom through line 57. This latter product may be withdrawn through line 58 as a final product of the process or it may be remixed with compressed vapors from the receiver 55 through line 56, as later described.

Returning to the catalytic cracking converter 17, the catalytic material after being retained in the main body of the reactor 17 for the desired period discharges through the annular space between the inlet nozzle 18 and the outer wall of the reactor into the bottom section 21 into which may be discharged an inert stripping gas through line 61. This stripping gas may serve to remove any volatile hydrocarbons contained in the catalytic material which is to be withdrawn from the converter 17 through conduit 22. The spent catalytic material containing carbonaceous deposits resulting from the cracking treatment discharges from the bottom section 21 of the converter 17 into the conduit 22 as previously described and is fed through a control valve 62 into a stream of air passing through line 63 which serves as a carrier for transporting the catalyst through line 64 into the regenerator 65. The regenerator 65 may be provided with an inverted cone-shaped bottom having a grid 66 positioned above the cone. The mixture of air and catalyst to be regenerated may be introduced in the bottom section 67 of the regenerator 65 below the perforated grid 66 so that the grid serves to distribute the mixture of regenerating air and catalytic material throughout the full cross-sectional area of the regenerator 65. The catalytic material and air pass upwardly through the grid line 66 into the body of the regenerator 65.

The velocity of the regenerating air passing upwardly through the regenerator 65 is preferably controlled so that the catalytic material tends to settle into a relatively dense mass which is maintained in a state of continuous agitation by the upward passage of the regenerating gas therethrough. The density of this mass maintained in the regenerator and also that maintained in the catalytic converters in practical operations may be between 5 and 30 pounds per cubic foot, depending upon the type of catalyst, size of the particles, and other factors.

The air upon contacting with the spent catalytic material, which is at substantially the temperature of the cracking treatment, serves to burn off the carbonaceous material contained on the catalyst. This burning treatment results in heating the catalytic material during the regeneration as previously described. However, it is necessary to avoid heating the catalytic material in the regenerating zone to such a temperature which would impair the activity thereof.

The amount of fuel, in the form of carbonaceous deposits, contained on the catalyst may in many cases be more or less than that required for carrying out the cracking operation. Where the amount of carbonaceous deposits formed during the cracking operation is insufficient to supply the required heat for the cracking and re cracking operations, additional heat may be provided by further heating the catalytic material prior to returning it to the cracking zone. This may be accomplished by adding extraneous fuel to the regenerator or by further heating of the catalytic material passing to or from the regenerator.

Where the amount of fuel, in the form of carbonaceous deposits formed during the cracking operation as previously described, is greater than that required for carrying out the cracking process, some additional means may be necessary for removing the excess heat liberated during the regeneration treatment. However, a considerable flexibility in the amount of heat required to be carried into the oil stream by the hot regenerated catalyst may be obtained by regulating the preheating temperature of the oil prior to mixing with the catalytic material. For example, in cases where the operation results in the formation of excessive quantities of carbonaceous deposits, a portion or all of the fresh charge may be by-passed around the scrubbing tower 11 in which the charge is normally preheated by cracked vapors from the converter 47. The pump back circuit previously described consisting of line 12' and exchanger 12'' may be used in this case to remove the excess heat from the tower. By regulating the preheating temperature of the fresh feed mixing with the cracking catalyst, it is possible in practical operations, in most cases at least, to supply the bulk of the heat required for the process by burning of the carbonaceous deposits from the catalytic material during the regeneration treatment.

The catalytic material after being heated to the desired degree within the regeneration chamber 65 may be withdrawn therefrom through a conduit 68 positioned in the bottom of the regenerator 65 and having a vertical extension 69 projecting upwardly through the grid plate 66 into the main body of the regenerator 65. The catalytic material from the regenerator 65 continuously flows downwardly through the extension 69 into the conduit 68 from which it may be passed into the vertical conduits 15 and 46 for return to the catalytic converters 17 and 47, respectively. The catalytic material is preferably withdrawn from the regenerator which will maintain the level of the dense catalytic mass within the regenerator materially below the top of the regenerator so as to maintain a relatively free space thereabove. The regenerating gas after passing through the main body of the finely divided catalytic material in the regenerator may be passed into a suitable separator such as a cyclone separator 70 located in the top of the regenerator for further separation of entrained powder therefrom. The regenerating gas after passing through the cyclone separator 70 may then continue through outlet line 71 to a cooler 72 in which the regenerating gas may be cooled from the regeneration temperature to a temperature of the order of from 300° F. to 600° F. Products from the cooler 72 may be then passed through line 73 into a suitable separator such as a Cottrell 74 for further separation of the entrained powder therefrom. The catalytic powder separated in the Cottrell 74 may discharge through line 75 into an air stream passing through line 76 and may be returned through line 77 to the regenerator 65. Regenerating gas after passing through the Cottrell 74 may be vented to the atmosphere through stack 78 or it may be scrubbed with a cooling liquid such as oil or water for further purification before being vented to the atmosphere.

Returning again to the low-pressure receiver 39 receiving the products overhead from the fractionator 24, as previously mentioned, this receiver operates at relatively low pressure so that the overhead gases removed from the receiver contain a considerable amount of low-molecular

weight, normally liquid constituents, such as butane-butene, propane-propene, and pentane-pentene constituents. To recover these valuable constituents from the gases, the gaseous products from the receiver 39 may be compressed in a compressor 80 to a pressure of from 100 to 300 pounds per square inch and afterwards mixed with a portion or all of the liquid distillate from the receiver 39. To this end, liquid distillate from the receiver 39 may be passed through lines 42 and 81 and pump 82 and then admixed with the compressed gases in line 83. The mixture from line 83 may be passed into a cooling coil 84 while under a pressure of from 100 to 300 pounds, as previously described. Under these higher pressure conditions, the low-molecular weight, normally liquid components from the initial gases withdrawn from the receiver 39 may be combined with the liquid distillate. Products from the condenser 84 may be then passed to a high-pressure receiver 85 in which the liquid separates from the gaseous constituents. The distillate collected in receiver 85 under such conditions will contain the bulk of the lower molecular weight, normally liquid products previously mentioned, and the gaseous products separated in the high-pressure receiver 85 will contain a materially lower concentration of the lower molecular weight, normally liquid hydrocarbons. The gases separated from the distillate in the high-pressure receiver 85 may be removed through line 86 and passed to a suitable fractionating and absorption equipment for separation of this gas into the desired components, such as propane-propene, ethane-ethene, and the like.

The liquid distillate separated in the high-pressure receiver 85 may be passed through line 87 to a debutanizing tower 88 in which the distillate may be subjected to pressure distillation to vaporize the butane-butene constituents and lower boiling hydrocarbons. The vapors formed in the debutanizing tower 88 and remaining uncondensed therein may be removed overhead through line 89. Liquid remaining unvaporized in the debutanizing tower 88 may be removed therefrom through line 91. This debutanized product may then be passed through line 92 to line 45 and pump 44 to the second-stage catalytic converter 47. Under such conditions, the feed to the converter 47 may comprise a mixture of the raw distillate from the low-pressure receiver 39 and the debutanized distillate from the debutanizing tower 88, or all of the raw distillate from receiver 39 may be first debutanized before being subjected to further catalytic treatment. In order to supply the required heat for distilling the lower boiling hydrocarbons from the distillate in debutanizing tower 88, a portion of the distillate removed from the bottom thereof may be passed through line 93, pump 94 and reboiler 95 wherein it is heated to a temperature sufficient to supply the required heat for the distilling treatment. The heated distillate after passing through the reboiler 95 may be then returned to the debutanizing tower 88 through line 96 at a point above the discharge of the distillate discharging through line 87.

Returning again to the low-pressure receiver 55 which collects the liquid distillate from the second-stage catalytic treatment, the products from this receiver may be treated as previously described to segregate the lower boiling constituents. For example, the overhead gases and vapors from the receiver 55 containing substantial amounts of the lower molecular weight liquid hydrocarbons may be compressed in compressor

97 to a pressure of from 100 to 300 pounds per square inch and thereafter mixed with the raw liquid distillate from the bottom of receiver 55. This distillate may, for example, pass through line 98 and pump 99 and thereafter combined with the compressed vapors in line 101. The resulting mixture may then be cooled in condenser 102 and thereafter passed to the high-pressure receiver 103. The gaseous products consisting principally of hydrogen and low-molecular weight hydrocarbons, such as propane-propene, and lower boiling hydrocarbons may be removed from the high-pressure receiver 103 through line 104 and passed to suitable fractionation and absorption equipment for separation of the desired components therefrom. The liquid distillate in receiver 103 which contains the major portion of the butane-butene and higher boiling constituents is removed from the high-pressure receiver 103 through line 104 and passed to a stabilizing tower 105 in which the products may be distilled and fractionated to produce a product of the desired volatility. In cases where the liquid distillate treated in the second catalytic converter 47 comprises a 400° F. end point product or higher, the stabilizing tower 105 may contain a trap-out tray 106 for segregating an aviation gasoline distillate from the higher boiling constituents. The higher boiling fraction is removed from the bottom of the stabilizing tower 105 through line 107. This product may comprise a motor fuel fraction of the desired boiling range and volatility or it may comprise a heavy naphtha fraction boiling above the end point of aviation motor fuel. The heat required for the stabilizing treatment may be provided by passing a portion of the liquid distillate withdrawn through line 107 through line 108, pump 109 into a reboiler 110 in which the oil is heated to the required temperature. The distillate after passing through the reboiler 110 may then return to the stabilizing tower 105 through line 111 at a point above the discharge of the unstabilized distillate discharging through line 104. The vapors liberated in the stabilizing tower 105 and consisting principally of the butane-butene fraction and lower boiling constituents are removed from the top of the stabilizer 105 through line 112. This product may be combined with the overhead product from the debutanizing tower 88 and the combined mixture subjected to further fractionation and absorption treatment for separation of desirable components therefrom. Under present conditions, the butane-butene fraction formed in the process forms a valuable product for the production of alkylate for aviation gasoline, as a source material for the production of synthetic rubber, and for other types of chemical products.

While I have shown for illustrative purposes the use of the same type of catalytic material for both the cracking and catalytic treatments, it may be of advantage in some cases to utilize a different type of catalyst in the second-stage catalytic treatment carried out in regenerator 47 than is utilized in the main cracking process carried out in the converter 17. For example, the catalytic material employed for the retreating process may comprise or contain catalytic material for promoting other types of hydrocarbon reactions, such as hydrogenation, polymerization, isomerization, and alkylation. The types of catalytic material employed for these operations are generally known and need not be referred to here in detail. It is preferred, however, to employ the same type of catalyst for carrying out

both the cracking operation and the treatment of the gasoline distillate resulting therefrom, since the catalytic material entrained in the vapors passing overhead from the retreating converter 47 will be intermixed with the fresh charging oil passing to the cracking operation. Consequently, in continuous operations the catalyst from the retreating reactor will tend to become intermixed with the catalyst from the cracking reactor.

In operations of the character above described wherein the finely divided catalytic material is circulated continuously through the system, it is necessary to provide means for restoring pressure on the catalyst during circulation. For example, in such a circulating system, there is inherently a certain drop in pressure due to the flow of the material through the equipment. This pressure must be restored in order to return the catalytic material and maintain the desired circulation. As illustrated, this pressure is restored by passing the catalytic material through suitable standpipes of a height which will develop a hydrostatic pressure sufficient to restore the pressure on the catalytic material being circulated.

For example, the conduits 15 and 46 employed for returning the hot regenerated catalytic material from the regenerator to the converters 17 and 47, respectively, may be utilized as a standpipe for developing the necessary pressure to overcome the pressure difference between the regenerator and the cracking zones and also to provide a substantial pressure drop across the feed valves 16 and 46' located in the conduits 15 and 46.

In order that the conduits 15 and 46 may serve as a standpipe for developing hydrostatic pressure, it is important to maintain the catalytic material flowing therethrough in a fluidized, freely flowing state so that the pressure may be transmitted throughout the full length of the conduits. The finely divided powdered catalytic material may be maintained in a freely flowing fluidized state necessary for developing hydrostatic pressure by keeping a small amount of an aerating or fluidizing gas in intimate mixture with the catalytic material passing through the conduits. To this end, it may be necessary to introduce a small amount of aerating or fluidizing gas at one or more points along the conduits 15 and 46 to maintain it in fluidized condition. This aerating gas may, for example, be introduced along the conduit 15 through lines 115, 116 and 117. Likewise, a fluidizing gas may be introduced into column 46 through lines 118, 119 and 120. In some cases, where the circulation of the catalytic material is relatively rapid the amount of gas occluded in the catalytic material being withdrawn from the reactor and regenerator may be sufficient to maintain the material in a highly fluid, mobile condition without the necessity of adding an additional fluidizing gas.

The pressure necessary for passing the catalytic material from the converters 17 and 47 into the air stream passing through line 64 may also be obtained by hydrostatic pressure developed on the catalyst during its passage through the conduits 22 and 49, respectively. A fluidizing gas may also be introduced into these conduits at spaced points to maintain the catalytic material in fluidized state during its passage therethrough.

Referring to the second catalytic converter 47, the catalytic material after being retained therein for the desired time, which may be of the order of from 15 seconds to 10 minutes or more, is passed continuously through the annular

space formed between the inlet nozzle 48 and the outer wall of the converter 47 into the bottom section of the converter. This bottom section forms a stripping zone into which a stripping gas, such as carbon dioxide, steam or other inert gas, may be introduced through line 122. The spent catalytic material then discharges from the bottom section of the converter 47 through line 49 into the air stream 64 which serves as a carrier for transferring it to the regenerating zone.

While a common regenerator has been shown for regenerating the catalytic material withdrawn from both the second converter 47 and the initial converter 17, it will be understood that, if desired, each converter may be provided with its own regenerator. This is, of course, necessary whenever the catalytic material in the converter 47 is of a different composition than the catalytic material used in the converter 17.

While a specific type of cracking equipment has been described in detail for carrying out the process, it will be understood that the invention in some of its broader phases may be carried out in equipment materially different from that described. For example, some phases of the invention might be employed in operations in which a fixed static bed of catalytic material is maintained in the individual reactors and the catalytic material subjected to alternate cracking and regenerating treatments. However, the invention in its narrower phases has particular application to operations in which the catalytic material is continuously passed through alternate cracking and regenerating zones.

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 the conversion of hydrocarbon oils which comprises passing a relatively heavy oil boiling above the end point of naphtha through a cracking zone maintained at active cracking temperature above about 700° F., contacting said oil within said cracking zone with a finely divided catalytic material, keeping said oil in contact with said catalytic material for a period sufficient to obtain the desired cracking thereof, thereafter separating the cracked products from the catalytic material, fractionating the cracked products to segregate a naphtha fraction therefrom, passing said naphtha fraction through a refining zone maintained at a temperature above about 500° F., contacting said naphtha fraction while in vapor form within said last-named refining zone with an active refining catalyst, keeping said naphtha vapors in contact with said refining catalyst for a period sufficient to obtain the desired refining treatment thereof, thereafter separating the bulk of said finely divided refining catalyst from the refined vapors, and thereafter passing the refined vapors containing entrained refining catalyst while at substantially said refining temperature in contact with fresh oil which is subjected to said first-named cracking treatment.

2. The invention defined by claim 1, wherein the catalytic material employed in said refining zone is of the same composition as that employed in the cracking zone.

3. A process for the conversion of hydrocarbon oils which comprises passing a relatively high-boiling hydrocarbon oil boiling above the boiling range of naphtha upwardly through a cracking

15

zone containing a body of finely divided catalytic material, regulating the velocity of the oil vapors passing upwardly through said body of catalytic material to maintain a dense turbulent mass of catalytic material within said cracking zone, keeping said cracking zone at a temperature above about 700° F., maintaining said oil vapors in contact with said finely divided catalytic material within said cracking zone for a period sufficient to obtain the desired cracking thereof, thereafter removing cracked vapors from said cracking zone, fractionating the cracked products to segregate a naphtha fraction therefrom, passing said naphtha fraction upwardly through a refining zone containing a body of finely divided catalytic material, regulating the velocity of the vapors passing upwardly through said last-named refining zone to maintain a dense turbulent mass of finely divided catalytic material therein, keeping said refining zone at a temperature above about 500° F., maintaining the naphtha vapors in contact with said catalytic material within said refining zone for a period sufficient to obtain the desired refining thereof, thereafter removing the refined naphtha vapors containing entrained catalytic material from said refining zone, and passing said naphtha vapors removed from said refining zone upwardly through a body of said higher boiling oil to be subjected to said first-named cracking treatment to thereby remove entrained catalytic material from said naphtha vapors and to preheat said higher boiling oil.

4. The process defined in claim 3, wherein the catalytic material employed in said refining zone is of substantially the same composition as that employed in said cracking zone.

5. A process for the conversion of hydrocarbon oils which comprises passing a relatively heavy oil boiling above the naphtha boiling range while in vapor form upwardly through a cracking zone containing a body of finely divided catalytic material, controlling the velocity of the oil vapors passing upwardly through said body of catalytic material to maintain a relatively dense turbulent mass of catalytic material therein, keeping said cracking zone at active cracking temperature above about 700° F., continuously removing catalytic material from said cracking zone containing carbonaceous deposits resulting from said cracking treatment, passing the catalytic material so withdrawn to a regenerating zone, subjecting the finely divided catalytic material within said regenerating zone to oxidizing atmosphere to burn off carbonaceous deposits contained thereon and

16

thereby heating said catalyst above the cracking temperature, returning the regenerated catalytic material while at substantially its regeneration temperature to the cracking zone, fractionating the cracked products to segregate a naphtha fraction therefrom, passing said naphtha fraction upwardly through a refining zone containing a mass of finely divided catalytic material of the same composition as that contained in said cracking zone, regulating the velocity of the naphtha vapors passing upwardly through said refining zone to maintain a dense turbulent mass of said catalytic material therein, keeping said refining zone at a temperature above about 500° F., maintaining said naphtha vapors in contact with said catalytic material for a period sufficient to obtain the desired refining thereof, thereafter removing the treated vapors containing entrained finely divided catalytic material from said refining zone, passing said treated naphtha vapors through a body of said first-named heavier oil to be subjected to said cracking treatment to thereby preheat said oil and remove entrained catalytic material from said naphtha vapors, and fractionating said naphtha vapors to segregate the desired distillate therefrom.

6. The process defined in claim 5, wherein the catalytic material is continuously removed from said refining zone and passed to said regenerating zone for removal of carbonaceous deposits formed during the refining treatment and wherein a portion of the regenerated catalyst from said regeneration zone is returned to said refining zone.

7. The process defined by claim 5, wherein the catalytic material is circulated through said cracking zone by hydrostatic pressure.

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