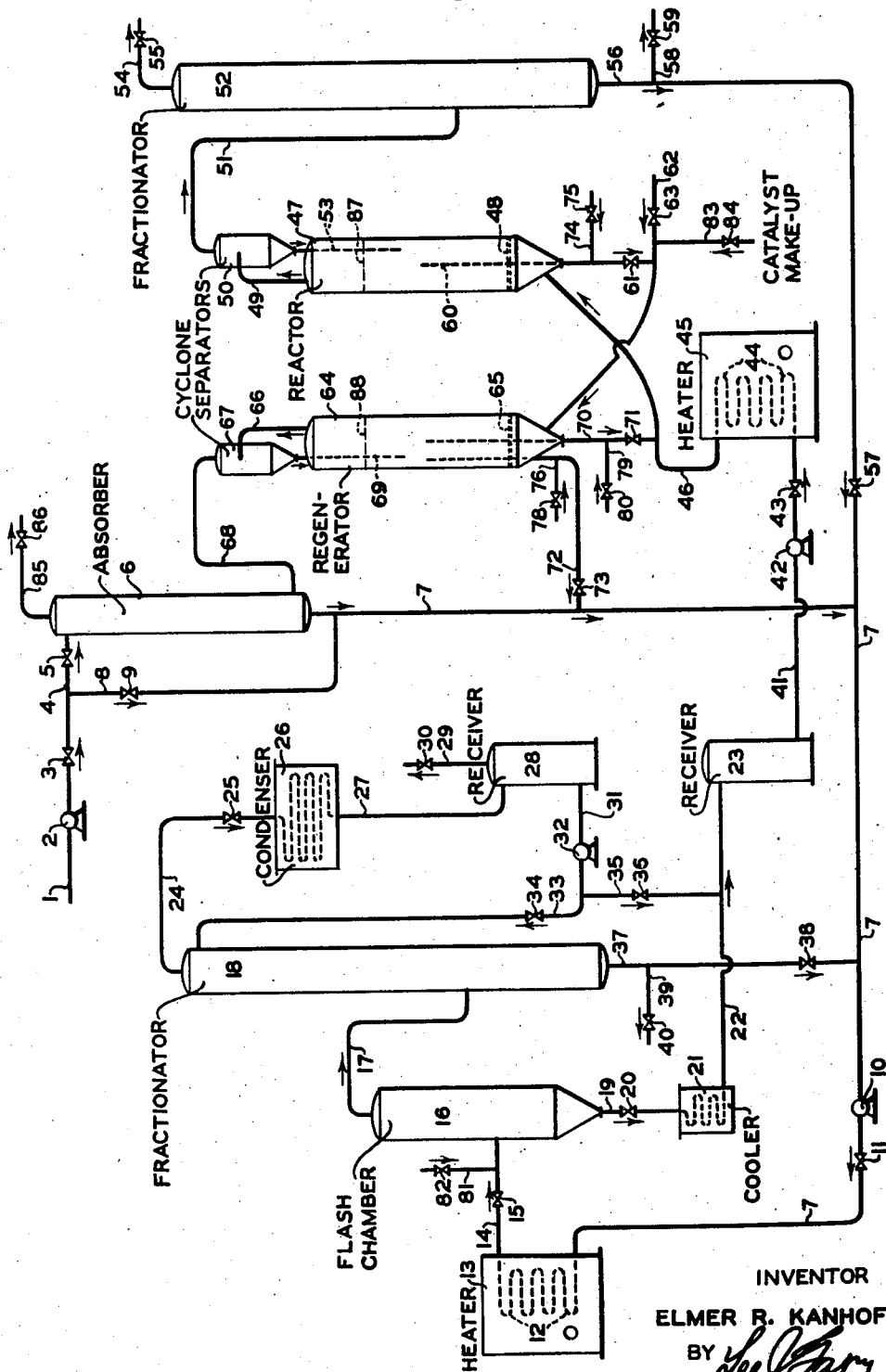


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HYDROCARBON CONVERSION

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This invention relates to a process for the conversion of hydrocarbon oil into lower boiling hydrocarbons including gasoline, and more particularly to a cracking process wherein the hydrocarbon oil may be converted in two closely inter-related steps into a motor fuel of very good antiknock quality and high lead susceptibility.

More specifically, this invention comprises a combination process in which hydrocarbon oil is first treated in a slurry catalyst cracking step and the light and heavy products therefrom re-treated in a fluidized catalyst cracking and re-treating step.

It is old in the art to employ powdered catalysts both in the form of a slurry and in the form of a fluidized mass in oil conversion processes. Another recent development has been the process for re-treating cracked gasoline in a second catalytic step to improve the antiknock quality and lead susceptibility of the motor fuel.

In a one stage catalytic cracking process the conditions of operation are usually maintained to produce a high yield of gasoline boiling range material. When this is the case, however, a highly olefinic gasoline is produced. It is possible to produce a relatively saturated product in a single stage when operating at low temperatures, but the available charging stocks suitable for this operation are limited.

In a two step unit a more flexible operation is obtainable which may be employed to process a wide range of charging stocks to produce a very high yield of highly saturated product. The improvement which is realized in the second or re-treating stage of a two step unit is not entirely due to the saturation of the product but is partially due to the rearrangement of the molecules, that is, the formation of branched chain compounds which have a high antiknock quality.

The features of my invention make it possible to employ existing thermal cracking equipment to produce aviation grade gasoline with only a relatively small amount of additional new equipment. Another feature of my invention provides for reactivating slurry catalysts employed in the first step of my process. This is accomplished in the regenerator of the second step or fluidized conversion step.

In one specific embodiment, my invention comprises heating and supplying a hydrocarbon oil containing powdered catalyst together with heated insufficiently converted hydrocarbons formed as hereinafter set forth to a primary conversion zone, separating the non-vaporous conversion products containing spent catalysts from

the vaporous conversion products, fractionating the vaporous conversion products into a fraction containing relatively olefinic gasoline boiling range hydrocarbons and a heavier fraction containing insufficiently converted hydrocarbons, heating and supplying said fraction containing relatively olefinic gasoline boiling range hydrocarbons and heated non-vaporous conversion products containing spent catalyst to a secondary conversion zone containing a relatively dense turbulent mass of powdered catalyst wherein they are converted into substantial quantities of relatively saturated motor fuel having good antiknock quality and high lead susceptibility, separating and recovering said motor fuel from insufficiently converted hydrocarbons and returning said insufficiently converted hydrocarbons to the primary conversion zone as hereinbefore set forth.

In order that my invention may be more clearly understood, reference is made to the accompanying diagrammatic drawing and the following description thereof. The drawing illustrates schematically in a conventional side elevation equipment suitable for accomplishing the process of my invention.

Referring to the drawing, the raw oil to be converted is introduced to the system through line 1, suitable charge pump 2 and valve 3. This oil may be diverted all or in part by means of line 4 and valve 5 to absorber 6 wherein the oil may be employed to scrub catalyst fines from combustion gases produced as hereinafter set forth. Part or all of the charging oil may be diverted around absorber 6 by means of by-pass line 8 and valve 9 to line 7.

In cases wherein an insufficient quantity of catalyst is picked up in absorber 6, additional catalyst may be introduced into the oil in line 7 by means which will hereinafter be described. The quantity of catalyst to be entrained in the charging oil will be dependent upon the particular charging stock to be converted and will range from about .1 of 1% catalyst by weight of oil up to about 10% by weight of oil or more depending upon the capacity of the oil to form a slurry with the catalyst.

The charging stock including the entrained catalyst is directed by means of line 7 through pump 10 interposed in line 7 and valve 11 to heating coil 12 disposed within heater 13. Within this coil the oil will be heated to a cracking temperature of from about 800 to about 1150° F., or more, but preferably within the range of from about 900° to about 1050° F. and will normally

be maintained at a pressure of from about atmospheric to about 400 pounds per square inch or more. At these conditions relatively olefinic gasoline is produced. Coil 12 will normally be of a length to give the oil sufficient time for conversion, but in some cases it may be desirable to include a reaction chamber for additional cracking time. This reaction chamber, however, is not essential to the process so in order to simplify the drawing, it has not been included therein.

The oil after being maintained for a sufficient time at the desired temperature is directed by means of line 14 through pressure reducing valve 15 to flash chamber 16. To arrest any further undesired cracking a suitable quenching oil may be introduced into line 14 by means of line 81 controlled by valve 82. In this flash chamber, the lighter converted materials will be vaporized and passed overhead through line 17 to fractionator 18 and the heavier unvaporized materials containing catalyst will settle and be diverted by means of line 19 and valve 20 to cooler 21 wherefrom by means of line 22 they will be directed to receiver 23.

In fractionator 18 the vaporous conversion products from flash chamber 16 will be separated into an overhead cut containing gasoline which will be diverted by means of line 24 and valve 25 through condenser 26 and line 27 to receiver 28. The unliquefied material may be vented from the system at this point by means of line 29 and valve 30. The liquefied portion of the oil charged to receiver 28 is withdrawn through line 31 and pump 32 interposed in line 31. A portion of this material will be returned by means of line 33 and valve 34 to the top of fractionator 18 to serve as a reflux, and the balance of the material will be directed by means of line 35 and valve 36 to line 22 wherein it will be mixed with the unvaporized material containing catalyst which was separated from the lighter materials in flash chamber 16. This stream of admixed heavy materials, catalyst and lighter overhead materials from fractionator 18 is then directed to receiver 23.

The bottom cut from fractionator 18 may be recycled to heating coil 12 by means of line 37, valve 38, line 7 and pump 10, or in some cases it may be withdrawn from the system by means of line 39 and valve 40.

From receiver 23 the commingled heavy and lighter materials containing catalyst will be directed by means of line 41, pump 42 interposed in line 41 and valve 43 to the heating coil 44 located in heater 45. From heating coil 44 the oil will be directed by means of line 46 to reactor 47. The temperature of the oil leaving heater 45 will be such that a temperature within the range of about 750° F. to about 1000° F. or preferably in the range of about 800° to 950° F. is maintained in reactor 47. Regenerated catalyst is introduced into line 46 as hereinafter described.

Within reactor 47, the mass of catalyst is maintained in a turbulent state by the action of the fluid reactants introduced through line 46. A perforated distribution plate 48 may be disposed in the lower part of reactor 47 to aid in the uniform distribution of reactant materials introduced thereinto. The catalyst particles in reactor 47 are maintained in a turbulent state by the upward flow of reactant materials which have a velocity not quite sufficient to overcome all the gravitational forces on the catalyst par-

ticles with the result that a relatively dense turbulent mass of catalyst particles and reactants is maintained in the lower portion of reactor 47.

The upper limit of this relatively dense mass or interface between it and the relatively light phase in the upper portion of the reactor is indicated by dotted line 87. The zone above the interface will act as a settling space to effect the separation of a large portion of the entrained catalyst particles from the effluent stream leaving reactor 47. This stream after leaving reactor 47 is directed by means of line 49 through a suitable cyclone separator (or a plurality of separators) 50 and line 51 to fractionator 52. In cyclone separator 50, additional entrained catalyst will be separated from the effluent stream and be directed by means of line 53 back into the relatively dense zone within reactor 47.

In fractionator 52 the converted materials of the desired boiling range will pass overhead through line 54 and valve 55 to additional separation equipment depending upon the final boiling range desired. The heavier and insufficiently converted materials will be withdrawn from the bottom of fractionator 52 by means of line 56 and valve 57 to be recycled to the slurry cracking zone, or this material may be withdrawn from the system by means of line 58 and valve 59.

In reactor 47 the pressure maintained will preferably be within the range of atmospheric to approximately 100 pounds per square inch and the rate of oil charged per hour per unit weight of catalyst in the reactor, that is weight space velocity, will be on the order of approximately .25 to 6, but preferably within the range of .5 to 2. The conditions at which reactor 47 is maintained are such that the olefinic gasoline from the first step is converted into a relatively saturated product.

The catalyst in reactor 47 will become contaminated by carbon and hydrocarbonaceous materials and in my process the contaminated catalyst may be continuously withdrawn from reactor 47 by means of line 60 and valve 61. Flue gases or other inert gases containing a regulated proportion of oxygen or air is directed through line 62 and valve 63 and will pick up the contaminated catalyst from line 60 and carry it into regenerator 64 wherein the carbonaceous materials will be burned from the catalyst. The air introduced through line 62 may be regulated so that the combustion within regenerator 64 will be maintained within a temperature range of approximately 1000° to 1300° F., but preferably within the range of 1050 to 1200° F.

Regenerator 64 will contain a relatively dense phase separated by an interface indicated by dotted line 88 from a lighter phase in the upper portion of the regenerator. This upper portion will act as a settling space for entrained catalyst particles and the effluent combustion gases will leave the regenerator by means of line 66 and pass through cyclone separator 67 and line 68 to the aforementioned absorber 6. Catalyst particles entrained in the stream passing through line 66 will be separated in separator 67 and will be returned by means of line 69 to the dense phase in regenerator 64. Finely divided catalyst particles remaining in the effluent gas stream will be scrubbed therefrom by the raw oil charge in absorber 6 and the substantially catalyst free gases will leave the system by means of line 85 and valve 86.

The regenerated catalyst particles will be withdrawn from regenerator 64 by means of line

70 and valve 71 and introduced into the heated reactant stream in line 46. The ratio by weight of catalyst: oil in line 46 may be regulated by means of valve 71 and normally will be within the range of .25 to 25, but preferably will be within the range of 2 to 10. When it is desired to include more catalyst in the raw oil than is picked up in absorber 6, additional catalyst may be withdrawn from regenerator 64 by means of line 72 controlled by valve 73. As is the case in reactor 47, a perforated plate 65 may be disposed in the lower portion of regenerator 64 to aid in the uniform distribution of incoming materials.

Catalyst make-up may be introduced into the system through line 83 and valve 84 to line 62.

The contaminated catalyst passing through line 60 may be stripped of vaporizable hydrocarbon materials by means of steam or other inert fluids introduced through line 74 and valve 75, and the regenerated catalyst leaving regenerator 64 by means of line 70 and 72 may be stripped of air by means of suitable inert fluids introduced respectively through lines 79 and 76 controlled by valves 80 and 78.

The catalyst which may be employed in my process may include suitable finely divided refractory oxide cracking catalysts such as those of the silica alumina type obtained either by precipitation of hydrous silica and hydrous alumina from solutions of suitable compounds of silicon and aluminum or by the treatment of certain types of clay materials.

I claim as my invention:

1. A conversion process which comprises subjecting a hydrocarbon oil containing suspended powdered cracking catalyst to a cracking temperature for a time period sufficient to form olefinic gasoline, separating the resultant conversion products into a vapor fraction containing the olefinic gasoline and a liquid fraction containing the powdered catalyst, fractionating said vapor fraction to separate the olefinic gasoline, introducing the olefinic gasoline and said fraction containing the powdered catalyst into a zone containing a bed of powdered cracking catalyst at a rate such that the bed of catalyst is maintained in a state of motion and therein treating the gasoline fraction under conditions regulated to produce a substantially olefin-free gasoline while simultaneously separating catalyst from said fraction as the latter passes in contact with said bed of catalyst.

2. A conversion process which comprises subjecting a hydrocarbon oil containing suspended powdered cracking catalyst to a cracking temperature for a time period sufficient to form olefinic gasoline, separating the resultant conversion products into a vapor fraction containing the olefinic gasoline and a liquid fraction containing the powdered catalyst, fractionating said vapor fraction to separate the olefinic gasoline, combining the olefinic gasoline with said

fraction containing the powdered catalyst, adding additional catalyst to the mixture, introducing the resultant mixture into a zone containing a bed of powdered cracking catalyst at a rate such that the bed of catalyst is maintained in a state of motion and therein treating the gasoline fraction under conditions regulated to produce a substantially olefin-free gasoline while simultaneously separating catalyst from said fraction as the latter passes in contact with said bed of catalyst.

3. A conversion process which comprises subjecting a hydrocarbon oil containing suspended powdered cracking catalyst to a cracking temperature for a time period sufficient to form olefinic gasoline, separating the resultant conversion products into a vapor fraction containing the olefinic gasoline and a liquid fraction containing the powdered catalyst, fractionating said vapor fraction to separate the olefinic gasoline, combining the olefinic gasoline with said fraction containing the powdered catalyst, heating the mixture to a temperature of from about 750 to about 1000° F., adding additional catalyst to the thus heated mixture, introducing the resultant mixture into a zone containing a bed of powdered cracking catalyst at a rate such that the bed of catalyst is maintained in a state of motion and therein treating the gasoline fraction under conditions regulated to produce a substantially olefin-free gasoline while simultaneously separating catalyst from said fraction as the latter passes in contact with said bed of catalyst.

4. A conversion process which comprises subjecting a hydrocarbon oil containing suspended powdered cracking catalyst to a cracking temperature for a time period sufficient to form olefinic gasoline, separating the resultant conversion products into a vapor fraction containing the olefinic gasoline and a liquid fraction containing the powdered catalyst, fractionating said vapor fraction to separate the olefinic gasoline, combining the olefinic gasoline with said fraction containing the powdered catalyst, heating the mixture to a temperature of from about 750 to about 1000° F., adding additional catalyst to the thus heated mixture, introducing the resultant mixture into a zone containing a bed of powdered cracking catalyst at a rate such that the bed of catalyst is maintained in a state of motion and therein treating the gasoline fraction under conditions regulated to produce a substantially olefin-free gasoline while simultaneously separating catalyst from said fraction as the latter passes in contact with said bed of catalyst, withdrawing resultant vaporous conversion products from said zone, and separating entrained catalyst therefrom, fractionating said vaporous conversion products to separate the substantially olefin-free gasoline and to form reflux condensate and supplying the latter to the first-mentioned cracking step.

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