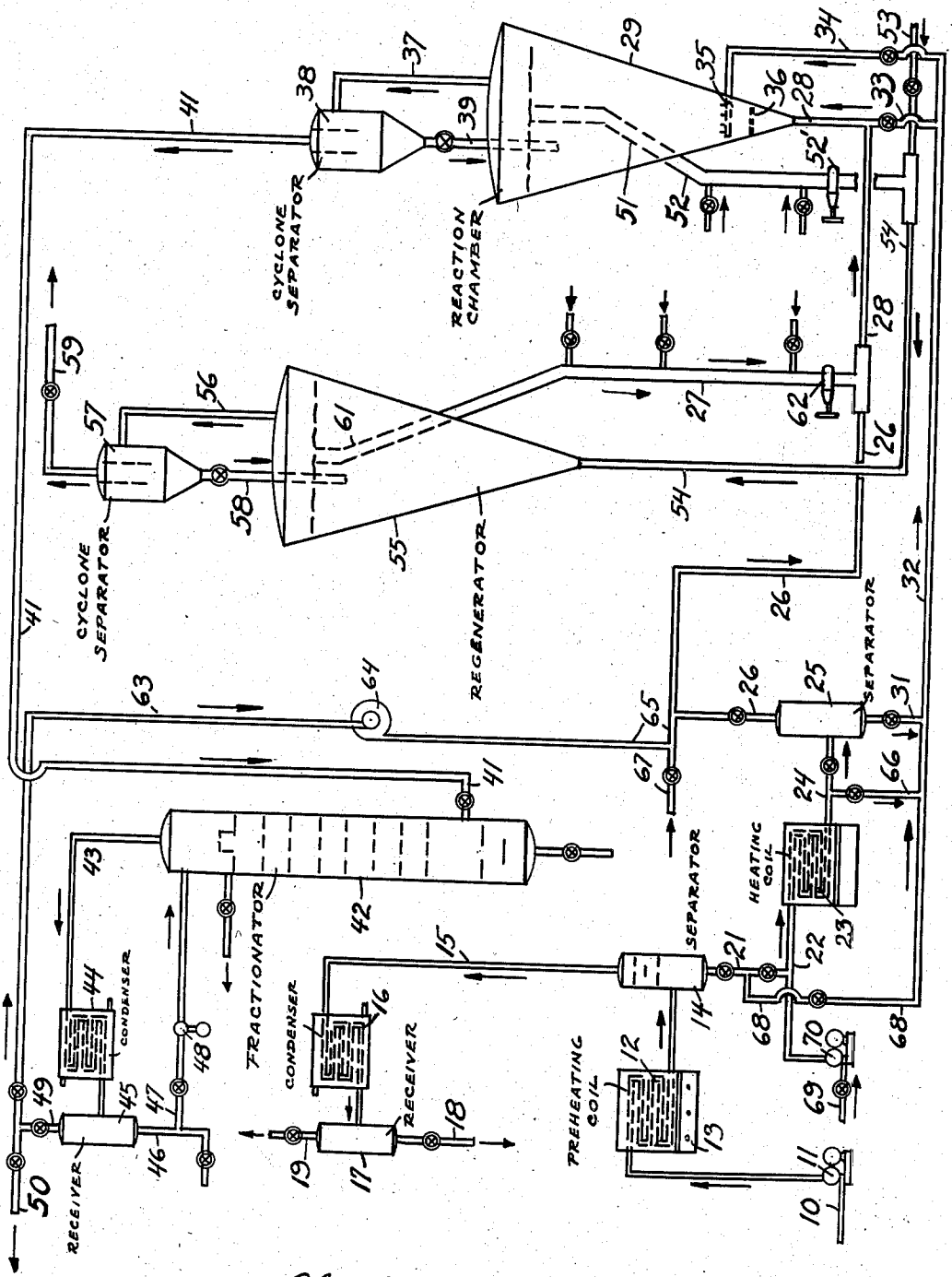
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CATALYTIC CONVERSION OF HYDROCARBON OILS

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CATALYTIC CONVERSION OF HYDROCARBON OILS

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This invention relates to the catalytic cracking of hydrocarbon oils and pertains more particularly to a process of cracking heavy oils, such as heavy gas oils, reduced crudes or other heavy oils, into motor fuels in the presence of a catalyst in finely-divided form.

Heretofore it has been proposed to crack oils in the presence of a cracking catalyst to form gasoline of relatively high octane rating. According to one general mode of operation, the oil in dry vapor form is passed through a cracking zone containing a fixed mass of catalyst in the form of a single bed or a plurality of beds suspended upon trays located within the cracking chamber.

During the cracking process the activity of the catalyst rapidly depreciates due to the formation of carbonaceous deposits which accumulate on the catalyst. In view of this, it is necessary to interrupt the cracking process frequently and regenerate the catalyst by burning the carbonaceous deposits therefrom.

In order to reduce the amount of carbonaceous deposits formed on the catalyst during the cracking period, it has been the practice in such cases to pass a relatively dry vapor in contact with the catalyst. For example, the general procedure in such processes is to first pass the oil to be cracked through a vaporizing coil to vaporize the bulk of the oil and then to pass the products from the vaporizing coil to a separator so as to segregate the vapors formed from any unvaporized residue. Following this, the vapors are passed through a superheating furnace wherein the oil is heated to a temperature materially above its dew point and the superheated vapors then pass to the cracking zone where they are contacted with the catalyst contained therein. Expressed in other words, it has been the practice heretofore to avoid contacting the catalyst with any liquid oil so as to avoid the accumulation of excessive deposits during the cracking operation.

This method of operating not only requires considerable investment in preheating, vaporizing and separating equipment for the preparation of the feed for the catalytic process but, in cases of residual stocks such as topped or reduced crudes, it also requires the rejection of a residual fraction which is not suitable for catalytic cracking without further processing. This fraction may comprise from 5% to 25% or more of the original crude, depending upon the source and nature thereof. While it has been suggested heretofore to subject this residual fraction to further processing, such as a viscosity breaking or coking treatment to recover additional vaporizable oil for the catalyst cracking process, such treatment results in the production of substantial quantities of low-grade gasoline. In view of this, it is a practice in many cases to market the residual fraction as a fuel rather than attempt to recover any additional motor fuel therefrom.

One of the principal objects of the present invention is to provide an improved process for the production of motor fuel which will reduce the amount of equipment necessary for a catalytic cracking unit of given capacity.

A further object of the invention is to provide a process for cracking heavy oils which will produce a higher yield of gasoline of improved quality from a given amount of said oil.

An additional object of the present invention is to provide a process for catalytic cracking of oils which is capable of converting a greater proportion of the heavy oils into high octane gasoline.

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

In the past it has frequently been desirable to crack catalytically relatively heavy distillates, such as heavy oils obtained from distillation of pitches, tars and the like, or from coking processes in which said heavy residues are converted into a solid coke residue. To utilize these heavy oils as a stock for catalytic cracking processes, it has been necessary in the past to either distill them under a high vacuum, which is uneconomical, or to employ relatively large volumes of steam to effect the vaporization. The presence of steam in the products to be cracked reduces the capacity of the equipment, or, expressed in another way, increases the size of the cracking and fractionating equipment for a cracking plant of given capacity.

I have discovered that the catalytic cracking process can be carried out without excessive formation of low-grade products, such as coke and gas, without completely vaporizing the oil. This discovery makes it possible to employ as feed stock for the catalytic cracking process not only heavy condensates but permits the use of residual stocks which cannot be readily vaporized without substantial decomposition and which could not heretofore be used for catalytic cracking.

In accordance with the present invention, an adsorptive cracking catalyst in finely-divided form is first suspended in a gas or vapor stream. Following this, a hydrocarbon oil to be cracked, either in liquid phase or in a mixed phase con-

taining a substantial amount of liquid, is combined with the suspension and the resulting mixture subjected to cracking conditions of time and temperature to obtain the desired conversion. The gas stream into which the catalyst is suspended may comprise oil vapors to be cracked, natural gas, refinery gas obtained from the same or different cracking unit, or it may be a relatively inert gas from an extraneous source, such as steam, nitrogen, hydrogen, carbon dioxide, spent combustion gases, or the like.

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

Referring to the drawing, the reference character 10 designates a charge line into which the oil to be processed is introduced into the system. For illustrative purposes, equipment has been shown for treating a total crude which may contain straight-run gasoline or other low-boiling distillates which are not to be utilized as cracking stock for the catalytic cracking process. The crude introduced through line 10 is pumped by means of pump 11 through a preheating coil 12 located in furnace 13 in which the oil is heated to a temperature sufficient to vaporize the low-boiling distillate fractions of the crude which are to be removed from the oil before passing the same to the cracking process. For example, the oil during its passage through the preheating coil 12 may be heated to a temperature of the order of from 400° F. to 600° F. The heated oil after passing through the coil 12 discharges into a separator 14 in which the vapors formed during the heating treatment separate from unvaporized residue. Vapors liberated in the separator 14 pass overhead through line 15 to a condenser 16 in which the normally liquid products are condensed. Products from the condenser 16 then discharge into a product receiver 17 from which the liquid distillate is removed through line 18. Any normally gaseous constituents liberated during the distilling operation may be removed from the receiver 17 through line 19.

As previously mentioned, the distillate removed overhead from the separator 14 may comprise a straight-run gasoline from the original crude, or it may consists of such straight-run gasoline together with heating oil or any other low-boiling distillate fraction which is not intended to be utilized for further processing, as later described.

Unvaporized liquid separated in separator 14 is removed from the bottom thereof through line 21 and may be discharged through line 22 to a further heating coil or other equivalent heating device wherein it is raised to a higher temperature for effecting further vaporization. For example, according to one phase of the present invention, the oil during passage through the heating coil 23 may be raised to a temperature of from 700° F. to 850° F. In cases where the temperature of the oil is raised above active cracking temperature, the heating within the furnace 23 should be sufficiently rapid to avoid any substantial amount of thermal cracking therein. The products from the heating coil 23 are then discharged through transfer line 24 into a separator 25 in which additional vapors formed during the heating may separate from unvaporized residue.

In some cases, the oil from the bottom of the primary separator 14 hereinbefore described may be passed directly to the catalytic cracking zone without being subjected to further heating, and, according to another alternative, preheated products from the coil 23 may be passed directly to the cracking zone without intermediate separation of vapors and liquid, as later described.

Returning again to the separator 25, when operating in this manner vapors liberated therein are removed overhead through line 26 into which is introduced a finely-divided adsorptive cracking catalyst through conduit 27. This cracking catalyst may be any suitable adsorptive material capable of effecting or modifying the cracking reaction, such as, for example, acid-treated or other activated clays, synthetic gels of silica and alumina, silica and magnesia, alumina and boron oxide, and the like. The size of the catalyst particles introduced into the gas stream passing through line 26 should be such as to permit the gas stream carrying the particles into the cracking zone and may vary over an extended range, such as from 30 mesh to 400 mesh or finer. The suspension of oil vapors and catalyst formed by the introduction of the catalyst into the oil vapor stream then passes through line 28 into the bottom section of a reaction chamber 29 which, for illustrative purposes, has been shown in the form of an inverted cone through which the oil vapors are passed in an upward direction against the force of gravity.

Returning to the secondary separator 25, unvaporized liquid is removed from the bottom thereof through line 31 and may be passed through lines 32 and 33 and combined with the suspension of oil vapors and catalyst passing to the inlet of the reactor 29. Instead of combining the liquid residue from the separator 25 with the stream of gases introduced into the reactor, it may be desirable in some instances to separately introduce the liquid stream into the reactor. To this end, a part or all of the liquid flowing through line 32 may be passed through line 34 which preferably terminates in a spray ring or nozzle 35 where it mixes with a suspension of catalyst and oil vapors introduced through line 28.

In some cases it may be desirable to provide a perforated plate or grid 36 in the bottom section of the reactor 29 to improve the distribution of the suspension into the reaction section of the chamber.

The velocity of the vapor stream passing upwardly through reaction chamber 29 is controlled so as to form a relatively dense phase of catalyst and gases within the major portion of the reaction chamber. By properly proportioning the diameter of the cone forming the wall of the reactor 29, the velocity of the vapors passing therethrough may be reduced to such a point that the bulk of the catalyst particles settles out of the oil vapors before the latter are removed from the cracking chamber. When operating in this manner, a bed of finely-divided catalyst is built up within the reaction chamber 29 which is continuously subjected to violent agitation by the current of rising vapors passing therethrough. As a result, a substantially uniform temperature may be maintained throughout the entire length and breadth of the reaction zone.

The amount of catalyst present in the reaction zone should be sufficient to completely absorb all liquid constituents introduced therein through lines 33 or 34 so as to avoid the formation of a sticky, tacky mass which might cause agglomeration of the catalyst particles and give rise to oper-

ating difficulties. The density of the catalyst bed within the reaction chamber 29 may, for example, be between 10 and 30 pounds per cubic foot when employing activated clays as a catalyst and the velocity of the oil vapors passing through the reaction zone may range from 1 to 10 feet per second in the lower section of the cone to from ½ to 2 feet per second in the top section of the cone. The time of passage of the oil vapors through the catalyst bed within the reaction chamber 29 is controlled to obtain the desired conversion and will vary with the type of catalyst, temperature maintained, and other factors. In general, the time of contact of the oil within the reaction zone may be of the order of from 5 to 20 seconds or more. In this connection, it might be mentioned that the liquid oil introduced into the reaction chamber 29 and absorbed on the catalyst may be retained within the zone for a period materially greater than the time of residence of the oil vapors introduced through line 28. The cracking zone should be maintained at active cracking temperature, such as from 800° F. to 1100° F.

All of the heat may be supplied to the reaction chamber by the hot regenerated catalyst introduced through line 27, as later described. In some cases, it may be desirable to subject either the vapors or the liquid stream passing to the reaction chamber to further heating. For example, either the overhead vapors from separator 25 or the liquid bottoms, or both, may be passed through further heating furnaces (not shown) located in lines 26 and 32, respectively.

The cracked vapors and gases after passing through the reaction chamber 29 pass overhead through line 37 and may be discharged into a suitable separating device such as a cyclone separator 38 for the removal of any entrained catalyst particles. The entrained catalyst separated by the separator 38 may be discharged through conduit 39 back into the reaction chamber 29, preferably below the level of catalyst maintained therein.

The cracked products are removed from the separator 38 through line 41 which leads to a product fractionator 42 in which the products are subjected to fractional condensation to condense constituents boiling below the desired motor fuel range.

While only one separator has been shown for the removal of the entrained powder from the cracked vapors, it may be desirable in some cases to subject the cracked products to further purification before passing to the product fractionator. For example, the cracked products may be passed to additional cyclone separators, electrical precipitators, bag filters, and the like to effect further purification.

The cracked vapors passing through the product fractionator 42 are subjected to fractional condensation to condense the higher boiling constituents and to segregate the same from the desired motor fuel fraction. Vapors remaining uncondensed and comprising the desired motor fuel fraction together with the lower boiling normally gaseous constituents formed in the cracking process are removed from the product fractionator 42 through line 43 which leads to a condenser 44 in which the desired motor fuel distillate is liquefied. Products from the condenser 44 may then pass to a product receiver 45 in which the liquid distillate segregates from normally gaseous constituents. The liquid distillate collected in the receiver 45 is removed therefrom through line 46 as a final product of the process. This product may be subjected to further stabilizing, refining and finishing treatment for the production of the final market product. If desired, a portion of the distillate removed from the receiver 45 may be pumped back through line 47 and pump 48 to the top section of the fractionating tower 42 as a reflux medium therefor.

The normally gaseous constitutents separated from the liquid distillate in the receiver 45 are removed overhead through line 49 and may be rejected from the system through line 50 which may lead to suitable absorption or other equipment for further drying and purification. However, according to one of the phases of the present invention, a portion of this gas formed may be returned to the cracking zone and employed as a carrier for the catalyst, as later set forth.

During the cracking process the catalyst contained in the reaction chamber 29 rapidly becomes contaminated with carbonaceous deposits which reduce the activity thereof and as a result it is necessary to continuously regenerate the catalyst in order to maintain the desired activity.

Returning to the reaction chamber 29, a conduit 51 may be provided within the reaction chamber 29 for the continuous removal of catalyst from the reaction zone. As illustrated, the conduit 51 terminates in the upper section of the reaction chamber 29 at the catalyst level or at a point below the catalyst level so that the catalyst continuously discharges into the conduit and is withdrawn therefrom through line 52. The catalyst to be regenerated, which is removed from the reaction chamber through conduits 51 and 52, may discharge through a control valve 52' into a stream of oxidizing gas introduced through line 53 which carries the catalyst through line 54 into a regenerating chamber 55. The regenerating chamber 55 may be of conical shape and of the same general construction as the reaction chamber 29. The velocity of the oxidizing gas passing through the regenerator 55 is preferably controlled to build up a relatively dense phase of catalyst therein which is subjected to constant agitation by the rising stream of oxidizing gas in a manner similar to that described with respect to the reaction chamber 29.

The passage of the oxidizing gas through the mass of catalyst in the regenerator 55 causes the burning of the combustible or carbonaceous deposits formed on the catalyst as a result of the cracking treatment. This burning of the carbonaceous deposits results in the liberation of considerable heat which causes a rise in the temperature of the catalyst. In most cases it is necessary to control the regenerating temperature below a predetermined value in order to avoid permanently impairing or deactivating the catalyst particles. For example, in the case of activated clays it is desirable in most cases to maintain the regenerating temperature below a maximum of 1200° F.

The temperature within the regenerating chamber may be controlled in any conventional manner. For example, suitable cooling elements may be positioned within or around the regenerating chamber to remove excess heat. As another example, a part of the spent regenerating gas may be cooled and recirculated, or a part of the regenerated catalyst may be cooled and returned to the regenerating zone. Another method of maintaining the regenerating chamber at the required temperature is to provide sufficient solid material therein to absorb all the heat liberated by burn-

ing the combustible deposits without raising the temperature above the deactivating temperature.

As previously described in connection with the reaction chamber 29, the provision of an inverted conical regenerator permits a reduction in the velocity of the oxidizing gas passing therethrough and permits the settling of the bulk of the catalyst from the oxidizing gas within the regenerator 55. The density of the catalyst mass within the regenerator and the velocity of the oxidizing gas passing therethrough may be controlled in the same manner as described with respect to the reaction chamber 29.

Spent regenerating gas after passing through the regenerator 55 is removed therefrom through line 56 from whence it may be introduced into a suitable separating device such as a cyclone separator 57 for the removal of any entrained catalyst present therein. The entrained catalyst separated in the separator 57 may discharge through conduit 58 back into the regenerator 55. After passing through the separator 57, the spent regenerating gases may be rejected from the system through line 59, or it may be passed to other suitable purification and heat recovery equipment which, for simplicity, has not been shown in the drawing.

The catalyst after being subjected to the desired degree of regeneration within the chamber 55 is removed therefrom through a central conduit 61 which has an open end terminating at or below the level of the catalyst bed within the regenerating chamber. The regenerated catalyst collected in the conduit 61 discharges into the vertical conduit 27 from whence it is discharged at the desired rate through control valve 62 into the stream of gases in line 26.

Since the regenrating temperature is usually considerably above the desired cracking temperature, a substantial amount of heat for carrying out the cracking treatment may be supplied by hot catalyst from the regenerating zone and the amount of heat supplied from this source may be regulated within limits by the amount of hot regenerated catalyst mixed with oil vapors and the relative temperatures employed for cracking and regeneration.

In order to circulate the catalytic material through the reaction and regenerating chambers, it is necessary to build up a sufficient pressure on the catalyst to feed the same into the gaseous streams passing to the reaction and regenerating chambers. These gaseous streams must in turn be under sufficient pressure to overcome the pressure drop through the equipment. For example, the gas stream passing into the reaction chamber 29 should be under sufficient pressure to force the oil vapors through the reaction chamber and the subsequent separating, fractionating and refining equipment. The pressure drop through the cracking and fractionating sections of the equipment may be, for example, of the order of from 5 to 25 pounds per square inch. On the other hand, pressure of the air or oxidizing gas passing through lines 53 and 54 to the regenerator 55 must be under sufficient pressure to overcome the pressure drop through the regenerating chamber and the subsequent recovery equipment. This pressure drop may be of the order of from 2 to 20 pounds per square inch. As a result, sufficient pressure must be built up on the catalyst to return the same from the outlet of the regenrator to the inlet of the cracking chamber and from the outlet of the cracking chamber to the inlet of the regenerating chamber. Any suitable means may be provided for building up the required pressure, such as by means of double bell hoppers, compression screws, feed pumps, and the like. As illustrated, the conduits 52 and 27 employed for feeding the catalyst from the reaction chamber to the regenerating gas stream and from the regenerating chamber to the oil vapor stream, respectively, are of such height as to develop sufficient static head to overcome the pressure drop through the system. In order to develop the necessary static head of pressure in the conduits 27 and 52, the catalyst therein should be maintained in a freely flowing state. To this end, a fluidizing gas may be introduced at one or more spaced points along the conduits. Such fluidizing gas may also serve to purge or strip spent catalyst of volatile hydrocarbons retained on the catalyst.

According to the process previously described, which constitutes the preferred embodiment of the invention, the oil vapors liberated in the separator 25 are utilized as a carrier for transferring the catalyst from the regenerator into the reaction zone. As previously mentioned, however, the present invention contemplates the use of other types of gases for this purpose. For example, a part of the gases formed in the process and removed from the system through line 49 may be passed through line 63 to compressor 64 which builds up sufficient pressure on the gases to force the same through line 65 to line 26 into which the regenerated catalyst is injected through line 27. When operating in this manner, the second separator 25 may be omitted and the total products from the heating coil 23 may be passed through line 66 which merges with line 32 leading to the inlet line 28 through line 33 or the reactor 29 through line 34.

Instead of employing the residual gas from the process for carrying the catalyst from the regenerating chamber back to the reaction chamber, an extraneous gas, such as nitrogen, hydrogen, carbon dioxide, and the like, may be introduced through line 67 which merges with line 65 which in turn merges with line 26.

When employing off gases from the cracking process or an extraneous gas as a carrier for the catalyst, both the preheating coil and separator 25 may sometimes be omitted and the bottoms from the primary separator 14 may be pumped directly to the reaction chamber through lines 21, 68, 32, 33 or 34, or both 33 and 34.

The process hereinbefore described contemplates the employment of a total crude containing a substantial quantity of straight-run gasoline as a feed stock for the process. In cases where reduced crudes or topped crudes are available, or in cases where the total crude contains only a small quantity of straight-run gasoline, preheating coil 12 and separator 14 may be eliminated. For example, a topped crude, reduced crude or a total crude containing a small fraction of gasoline may be introduced into the system through line 69 rather than line 10. This feed introduced through line 69 may be forced by means of pump 70 to the heating coil 23 in which it may be preheated before passing the same to the cracking zone.

From the above description it will be understood that the present invention comprehends the processing of heavy oils such as heavy distillates or residual stocks without intermediate vaporization before contacting the same with the catalyst material and in which the catalyst material is first suspended in a gaseous stream and introduced into the reaction chamber.

The use of inverted cone-shaped reaction chambers finds particular application in the present process, since the use of steam or other gases to effect complete vaporization of the oil is unnecessary. As a result, the increase in volume of vapors due to the cracking reaction is substantially greater than in cases where substantial amounts of steam or other vapors or gases employed to vaporize the feed are present in the oil vapors.

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 higher boiling hydrocarbons into lower boiling hydrocarbons suitable for motor fuel which comprises introducing hot finely-divided absorptive cracking catalyst into a stream of oil vapors to be cracked to form an oil vapor-catalyst suspension, thereafter combining with said suspension a stream of oil having a substantial portion thereof in liquid form in an unheated reaction zone whereby heat is supplied directly from the catalyst to effect the decomposition of the oil and subjecting the resulting mixture of oil and catalyst to cracking conditions to convert a substantial portion of said oil into lower boiling motor fuel constituents, thereafter separating the cracked products from the catalyst and segregating a motor fuel fraction therefrom.

2. A process for the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons suitable for motor fuel which comprises preheating the hydrocarbon oil to be converted to vaporize a substantial portion thereof and to retain another portion in unvaporized condition, separating the vapors from the unvaporized liquid, mixing with said vapors a hot finely-divided absorptive cracking catalyst to form a catalyst-vapor suspension, thereafter mixing with said hot suspension a stream of the unvaporized oil, subjecting the resulting mixture to cracking conditions of time and temperature in an unheated reaction zone to form a substantial portion of lower boiling hydrocarbons suitable for motor fuel, providing sufficient catalyst within said cracking zone to supply heat to effect the reaction and completely absorb unvaporized liquid hydrocarbons to thereby form a relatively dry mixture of cracked vapors and catalyst, thereafter separating the cracked vapors from the catalyst, segregating a motor fuel product from the cracked products, regenerating the catalyst by removing combustible deposits formed on said catalyst during the cracking treatment and combining hot regenerated catalyst directly with said first-named hydrocarbon vapors.

3. In the process defined by claim 2, the further improvement which comprises gradually reducing the velocity of the oil vapors passing through the cracking zone to maintain said cracking catalyst within said zone for a period materially greater than the time of residence of the oil vapors therein.

4. An improved process for converting difficultly vaporizable oils into lower boiling products which comprises preparing a dense suspension of a hot, finely divided catalyst in a completely vaporized hydrocarbon distillate, admixing a stream of said suspension with the heavier oil, which is incompletely vaporizable without decomposition, in a vertical reaction zone wherein the catalyst is maintained in a fluidized condition, maintaining the reaction zone at the decomposition temperature by heat supplied from the catalyst and providing time therein to effect the decomposition of the heavier oil with deposition of coke on the catalyst and withdrawing streams of fluidized catalyst fouled with coke and vaporized cracked hydrocarbons.

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