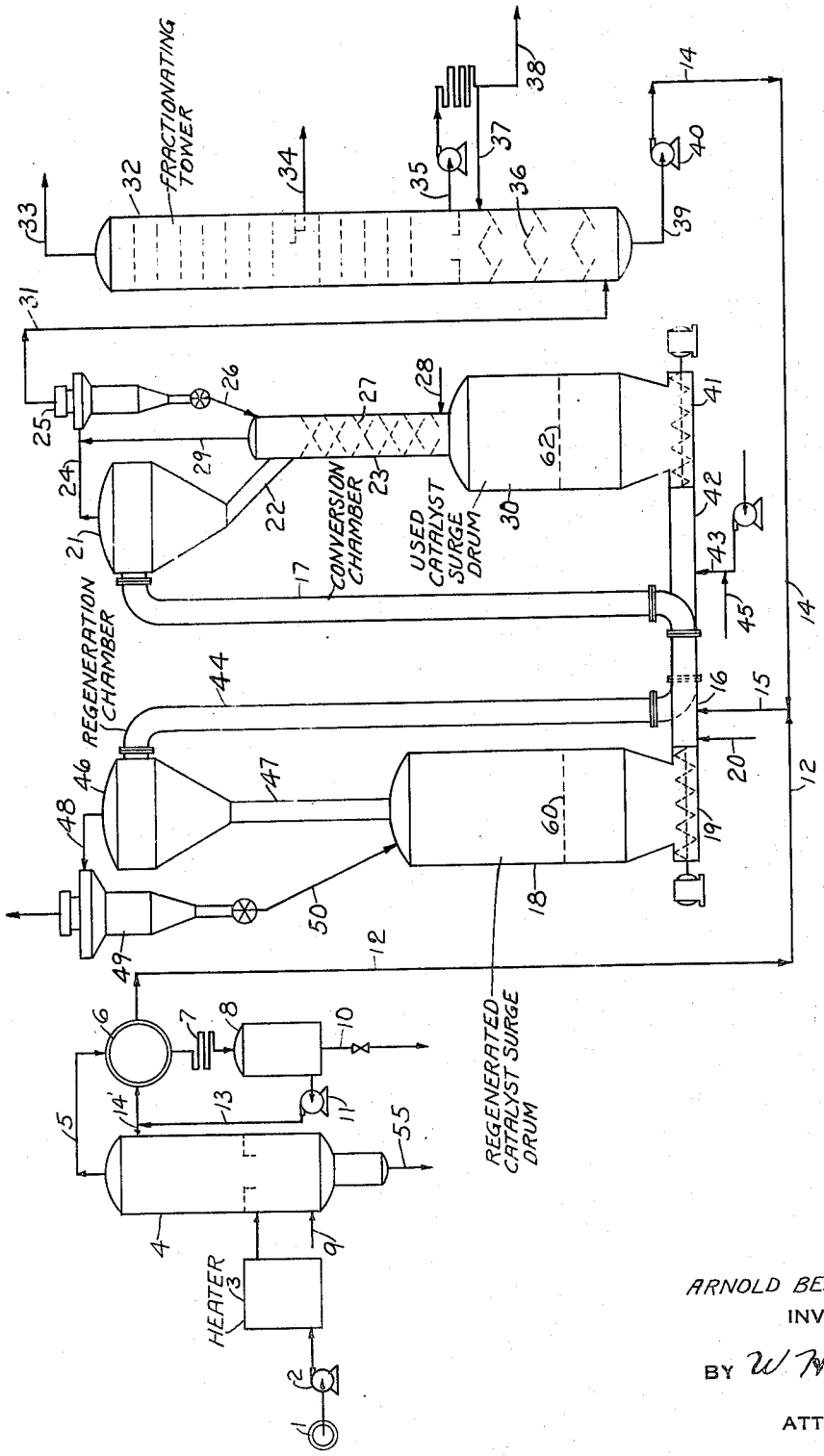
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CATALYTIC CONVERSION OF HYDROCARBONS

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CATALYTIC CONVERSION OF HYDROCARBONS

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2 Claims. (Cl. 196—52)

The present application is a divisional application of my co-pending application, Serial No. 343,222, filed June 29, 1940, the latter application being a continuation-in-part application of my co-pending application, Serial No. 274,670, filed May 20, 1939, now U. S. Patent 2,253,486.

The present invention relates to the catalytic conversion of hydrocarbons into lighter hydrocarbons of lower-boiling point or hydrocarbons otherwise altered in structure. More particularly, my invention relates to the catalytic conversion or cracking of high-boiling petroleum oils to low-boiling products, and the catalytic reforming of petroleum oil fractions such as naphtha and gasoline.

The catalytic conversion of hydrocarbons involves, in general, two stages, a conversion stage wherein the hydrocarbons undergoing treatment are contacted with the catalyst under conditions adapted to effect the desired conversion, and a regeneration stage wherein the carbonaceous deposit formed on the catalyst during the conversion stage is eliminated. In its preferred aspect, my invention contemplates particularly an improved process involving a conversion stage wherein the hydrocarbons undergoing treatment are passed through the conversion zone in the form of vapor having the catalyst in finely divided condition suspended therein; and a regeneration step wherein used catalyst, after separation from the gaseous conversion products, is suspended in oxygen-containing gas and carried thereby through the regeneration zone to regenerate it by burning off deposited carbonaceous material.

This method of catalytically converting hydrocarbons has certain advantages arising particularly out of the relative intimacy of contact which it affords between the suspended catalyst and the carrier gas both in the conversion and regeneration operations. It exhibits, however, various disadvantages the elimination of which is one of the primary objects of my invention.

One of the objects of this invention is the provision of a procedure for heating and vaporizing the hydrocarbon preparatory to its passage to the conversion zone under such conditions as to avoid undesired thermal decomposition effects and the accomplishment of this result by the direct utilization of the heat of regeneration.

Another object of the invention is the provision of a process whereby the removal of deposited carbonaceous material may be effectively controlled in the regeneration stage in such manner as to leave a predetermined quantity thereof on the catalyst. Various other objects and advantages of my invention will be evident to those skilled in the art as the description thereof proceeds.

One of the features described and claimed in said co-pending application, Serial No. 274,670 now U. S. Patent 2,253,486, resides in the charging of the catalyst and hydrocarbon feed to the conversion zone in proportions which are markedly different and advantageous compared with those indicated by conventional practice. In such practice, this ratio is determined primarily on the basis of the activity of the catalyst and the extent to which deactivation thereof occurs during the conversion stage, the objective being, in general, to limit the quantity of catalyst employed to the smallest feasible amount consistent with the production of the desired extent of conversion, both because of the cost of the catalyst and processing costs incident to its circulation. Limiting factors with respect to the proportion of the catalyst thus employed relative to the hydrocarbon charged, are the total carbonaceous material deposited during the conversion of a given amount of feed to the desired extent, and the quantity of carbonaceous deposit which the catalyst is capable of carrying before its activity drops to a point where its continued use is not feasible or desirable.

One feature of this invention involves the mixture of the liquid hydrocarbon feed with preheated catalyst, preferably at a temperature sufficient to vaporize the feed, the necessary preheating of the catalyst preferably being effected in the regeneration reaction.

Another feature of this invention involves the controlled combustion of the used catalyst in such manner that a predetermined quantity of carbonaceous material is left thereon.

The various features of this invention are interrelated in such manner that their conjoint use is desirable. However, various features thereof are susceptible of application independently of the others, as will be apparent to those skilled in the art.

The foregoing and various other features of the invention will be apparent from the following description thereof, given with reference to the appended drawing which illustrates diagrammatically suitable apparatus for its practice.

The drawing is a diagrammatic illustration of suitable form of apparatus for the practice of the embodiment of the invention involving the feature of the use of preheated catalyst to vaporize the feed stock.

Referring to the drawing, the feed to the system, for example, a reduced petroleum crude, enters from any convenient source indicated by the numeral 1 and is pumped by pump 2 to a heater or furnace 3 wherein it is preheated to a suitable temperature and then flash evaporated in evaporator 4. The volatile portion of the crude is taken overhead from evaporator 4 as a gas oil fraction through line 5 and a heavy residual fraction withdrawn from the process at the bottom through line 55. From line 5 the gas oil vapors pass through a heat exchanger 6, then through a condenser coil 7 into accumulator 8. Steam introduced through line 9, is condensed together with the gas oil and separated therefrom in accumulator 8 through line 10. The gas oil condensate is pumped by pump 11 through line 13 to heat exchanger 6 and into line 12. Part of the gas oil is returned as reflux to the evaporator through line 14'.

The apparatus described above is merely illustrative of conventional apparatus for supplying the gas oil or other treated hydrocarbon at a suitable temperature for the following conversion operation.

The preheated fresh feed in transfer line 12 may be advantageously combined with a hot recycle oil introduced through line 14, the combined streams passing to the conversion stage through line 15. The oil passes through line 15 into pipe 16 constituting an extension of the conversion reactor 17. Hot preheated catalyst is supplied from drum 18 by helical feeder 19 and mixed with the oil in pipe 16. Line 60 indicates the upper level of the catalyst collected in drum 18. The temperature of the catalyst and quantity of catalyst used are such as to cause vaporization of the oil thereby forming a suspension of the catalyst in the vapors. Sufficient steam or other suitable gas to initially disperse the catalyst as discharged from feeder 19 is preferably introduced through line 20. Steam or other suitable gas may be supplied in greater quantities through line 20 when required to supplement the vapors resulting from the vaporization of the feed stock to produce the required volume of gas to carry the catalyst through the conversion reactor 17. The ratio by weight of the catalyst to fresh feed stock is preferably maintained and regulated as set forth in detail hereinafter. The gaseous mixture of feed stock, catalyst and steam flows upwardly through reactor 17 during which flow conversion or cracking of the oil to the desired extent occurs.

Reaction products pass from the top of reactor 17 to a suitable separator system to separate the catalyst from the vaporous reaction products. That shown comprises a settling tank 21 in which the major proportion of the suspended catalyst is separated, the separated catalyst flowing by gravity from the bottom of tank 21 through conduit 22 to the top of a steam stripper tower 23 and the vapors containing a relatively small fraction of fine catalytic material are withdrawn at the top through line 24. These vapors pass through line 24 to a suitable separator such as a cyclone type of dust collector 25 wherein most of the remaining suspended catalyst is separated and then passed to tower 23 by gravity flow from the bottom of the separator through line 26.

Tower 23 serves to displace hydrocarbon vapors contained in the voids between the particles of catalyst and is suitably provided with baffles 27 to effectively expose the catalyst passing downwardly therethrough to the displacing action of a countercurrently flowing current of steam introduced at the base of the tower through line 28. Steam containing the oil vapors displaced from the catalyst is withdrawn from the top of the tower through line 29 and combined with the vapor stream from tank 21. Used catalyst falls from the bottom of tower 23 into a surge drum 30. The gaseous suspension withdrawn from separator 25 containing the gaseous conversion products, steam and a small residual amount of used catalyst, is passed through line 31 to a suitable type of fractionator 32 wherein a low-boiling fraction such as gasoline and fixed gases may be separated from the high-boiling products such as light and heavy cycle gas oils. In fractionator 32 the conversion products may, for example, be fractionated into a low-boiling fraction including gasoline and fixed gases withdrawn as the overhead product from the fractionator through line 33, an intermediate product such as light gas oil withdrawn as a side cut through line 34, and a residual high-boiling fraction such as heavy recycle gas oil withdrawn through line 35, cooled in cooling coil 61, and pumped to storage through line 38.

In the bottom of fractionator 32 suitable means may be provided for separating residual catalyst present in the vapors introduced through line 31. As shown, these means comprise a line 37 through which a portion of the high-boiling fraction withdrawn through line 35 is returned to the fractionator over baffles 36 which deflect the vapors from line 31 into intimate contact with the returned fraction which consequently adsorbs or scrubs out residual catalyst present in the vapor. After passing over baffles 36 the scrubbing liquid collects in the bottom of fractionator 32 from which it is withdrawn through line 39 and pumped by pump 40 into line 14 for utilization as a recycle oil, as previously described.

Used catalyst is fed from drum 30 by screw feeder 41 to pipe 42 and carried therein by a current of oxygen-containing gas such as air injected through line 43 to regeneration or combustion chamber 44, wherein combustion of the carbonaceous deposit on the spent catalyst occurs during the passage of the catalyst therethrough. Steam may be introduced when desired through line 45. Line 62 indicates the upper level of the catalyst in drum 30. The proportion of oxygen-containing gas injected relative to the quantity of used catalyst is preferably maintained and regulated, as described hereinafter in detail.

Combustion gases bearing the regenerated catalyst pass from chamber 44 into a suitable recovery system for separating the catalyst. As shown, this system comprises a settling tank 46 wherein most of the catalyst is separated and flows downwardly therefrom through conduit 47 to surge drum 18. The separated gases containing a small residual amount of catalyst fines leave separator 46 at the top through line 48 and pass to a cyclone type of dust collector 49, wherein substantially complete separation of the catalyst is effected. The separated catalyst from collector 49 then flows downwardly through line 50 and is combined with the initially separated catalyst in drum 18 from which it is fed to the conversion stage by feeder 19, as previously described. Drum 18 and feeder 19 may be suitably provided with heat insulation material to obviate loss of heat by the regenerated catalyst in its passage therethrough.

The range of catalyst-to-oil-feed ratio suitably and preferably employed and other preferred

processing conditions, is illustrated by the following examples.

In one example, a petroleum gas oil having a gravity of 31.4 A. P. I. was used as the feed stock to be catalytically converted or cracked by the process to a low-boiling stock having a required amount of hydrocarbon within the gasoline boiling range. This particular gas oil was produced by the flash evaporation of a reduced crude and constituted the volatile portion thereof amounting to about 90% of the crude charged to the evaporator. In the process of converting this particular oil to the desired extent, it was determined that coke or carbonaceous material appearing as a deposit on the catalyst would be produced to the extent of 3.5% by weight of the charged gas oil. A temperature of 865° F. was chosen as representing a suitable mean temperature for the reaction which, since the conversion reaction is endothermic, corresponded to an inlet temperature to the reactor of about 880° F., and an outlet temperature of 850° F. The "deactivation temperature" of the particular catalyst employed was ascertained to be approximately 1000° F., this temperature being the maximum temperature to which the catalyst could be safely subjected under the regeneration conditions without undue impairment of its catalytic activity.

The ratio of catalyst to oil charged may be and is preferably regulated as set forth in my original application, Serial No. 274,670 now U. S. Patent 2,253,486. Pursuant to the procedure set forth in said application, in fixing the ratio by weight of the catalyst charged to the fresh gas oil charged, for the particular oil and extent of conversion required, this ratio is determined in a manner adapted to assure the presence of the catalyst in sufficient amount to absorb a definite minimum amount of the heat of regeneration, this ratio R being determinable by the application of a generalized formula derived by the application of the principles of my invention, as follows:

$$R=\frac{CH}{S(T_1-T_2)}\cdot K$$

In this formula, R represents the catalyst-to-oil weight ratio; the symbol C, the fraction of the gas oil or other hydrocarbon charged, converted to coke or carbonaceous material and deposited on the catalyst during the conversion; H, the heat of combustion of the coke or carbonaceous material expressed in B. t. u.'s per lb.; S, the specific heat of the catalyst; T_1, the deactivation temperature in degrees Fahrenheit of the catalyst; T_2, the temperature in degrees Fahrenheit of the catalyst on entering the regeneration zone; and K, a fractional coefficient having a lower limit determined by the extent to which expedients other than the heat absorption capacity of the catalyst may be employed to dissipate the heat of regeneration.

In this particular example, the regeneration was effected in accordance with the preferred mode of practising my invention wherein the carbonaceous material is burnt off to the required extent without the provision of any means to absorb the heat developed during the regeneration other than the heat absorptive capacity of the catalyst and combustion gases. For these conditions, it was determined that K should have a value of approximately .83. The values of C, H, S, and T_1, for this particular example, were fixed by the specific characteristics of the conversion and substances concerned, and were respectively, 0.035; 16,400; 0.22; and 1000. Since the used catalyst may be advantageously transferred directly from the conversion zone to the regeneration zone without substantial intermediate cooling in accordance with my invention, which procedure was followed in this instance, the value of T_2 corresponded approximately to the outlet temperature of the conversion zone, namely, 850. Accordingly, substituting these values for the corresponding symbols in the above formula it is evident that the maintained catalyst-to-oil weight ratio, R, is equivalent to the ratio,

$$\frac{.035\times16,400}{.22\times(1000-850)}\times.83=14.5$$

By the maintenance of the catalyst-to-oil ratio at the relatively high value of 14.5, as determined above, the absorption of the heat of regeneration at a temperature below the deactivation temperature of the catalyst, was readily and effectively accomplished solely through the medium of the heat absorption capacity of the catalyst and the combustion gases without the use of extraneous cooling means.

It is to be noted that the ratio as above determined, is not sharply critical and may be increased or decreased, these variations in general corresponding to permissible variations in the numerical limits of the coefficient K. In the above specific example, for instance, the catalyst-to-oil ratio may be maintained at a larger figure than 14.5, thereby assuring the circulation of a quantity of catalyst not only sufficient but in excess of that needed for the desired minimum absorption of heat by the catalyst during the regeneration reaction. The amount of such surplus catalyst will normally be controlled by economic considerations dependent upon the cost of the surplus catalyst and the processing expense incident to its circulation. Since these factors will normally outweigh any advantage to be gained by the circulation of surplus catalyst, it is contemplated that the practice of my invention will usually and preferably be practised with an oil-to-catalyst ratio wherein K has a value not very greatly in excess of that employed in the above example.

The oil-to-catalyst ratio, as above determined, may also be decreased to some extent, such changes corresponding to the lower limiting value of the coefficient K. For example, the use of a lower ratio and corresponding lower K value may be feasible through the use to a limited extent of cooling coils or similar extraneous cooling means in the regeneration zone. It is contemplated, however, that in the practice of my invention in its preferred aspect wherein the heat of regeneration is largely absorbed by the catalyst that the value of K, will be greater than 0.2 and preferably greater than 0.5.

In the conversion of the gas oil used in the above example, the procedure followed was that previously described in connection with the appended drawing, the catalyst-to-oil ratio being maintained at a minimum of 14.5 to 1, as above determined, and air being introduced through line 43 in quantity sufficient to supply only the theoretically required amount of oxygen to burn off or reduce the concentration of the carbonaceous deposit to the desired extent; also the hot regenerated catalyst was withdrawn from drum 18 and thereafter mixed with the feed stock without any substantial intervening cooling, and contained sufficient heat to vaporize the feed stock introduced at a temperature of about 550°

to 600° F. at the pressure maintained in the reactor of 25 lb. gauge. In this particular example the feed stock consisted of about 85% gas oil feed introduced through line 12 at a temperature of 550° and about 15% of the heavy recycle fraction introduced through line 14 at a temperature of 600° F.

Also, in this example, air was admitted to the regeneration zone in amount sufficient only to reduce the concentration of carbonaceous deposit to 1.5% by weight of the catalyst, and consequently the catalyst was circulated at all times with a minimum amount of carbonaceous material thereon amounting to 1.5% by weight of the catalyst. In passing through the conversion zone the carbonaceous material concentration on the catalyst under the conditions of this particular example increased to 1.74% and accordingly, in the regeneration stage, the carbon concentration of the catalyst was reduced from 1.74% to 1.5%.

The average velocity of the vapors through the reactor may be of the order of about 10 feet per second and the vapor contact time of the order of about 6 seconds; such conditions correspond to an average catalyst concentration in the reactor of about 6 pounds per cubic foot.

The maintenance of a definite minimum concentration of carbonaceous material on the catalyst as exemplified by the above example, has important and distinctive advantages. It assists in the regeneration reaction since the rate of combustion is accelerated and more readily controlled by the presence of an amount of carbonaceous material in excess of that which is to be removed by combustion. The retention of residual carbonaceous material also makes it possible to discharge the regeneration combustion gas with a relatively low percentage or in some cases, entirely free of oxygen, and the gas is thus better adapted for use for various purposes. Also, in certain instances, particularly in catalytic cracking in the presence of alumina-silica type of cracking catalyst such as "Super-Filtrol," the conversion reaction is facilitated by the presence of a small amount of residual carbon and in most instances the advantages obtained in regeneration by the maintenance of a residual carbon concentration will outweigh the disadvantages, if any, resulting in the conversion stage. The residual carbon concentration maintained may depart somewhat from the value of 1.5% regarded as the approximate optimum in the foregoing example wherein a "Super-Filtrol" type of alumina-silica cracking catalyst was employed. Preferably, this permissible range is confined to about 0.5% to 2.0%, by weight of the catalyst, or the narrower range of about 0.8% to 1.5%.

A number of highly advantageous results are secured by mixing the liquid feed stock with the regenerated catalyst while the latter retains the heat imparted to it in the regeneration reaction. Conventional methods for vaporizing and preheating the oil to the required conversion temperature would frequently result in substantial thermal decomposition or "cracking," which is undesirable because of the low quality of products thus obtained, particularly with respect to octane number and ultimate amount of coke formed, compared with those produced by complete catalytic conversion. Due to the intimate contact between the hot catalyst and feed stock and resultant rapid and efficient vaporization, undesired thermal "cracking" is largely obviated. Substantial savings are further secured by the resulting direct use of the major proportion of heat evolved during the regeneration stage.

Any type of catalyst suitable for effecting the desired conversion may be employed in the practice of my invention. For the conversion or cracking of high-boiling fractions such as gas oil to low-boiling fractions such as gasoline, I regard cracking catalysts of the "alumina-silica" type as especially suitable, this term being inclusive of cracking catalysts such as certain types of activated clays or synthetically produced mixtures or compounds of alumina and silica. The circulated catalyst may be composed entirely of the active catalytic material and is preferably predominantly composed thereof. However, the active catalyst material may be associated with supports, extenders or solid diluents which for the purpose of my invention are to be considered as part of the catalyst, since such solid diluents, etc., will function in a manner similar to the active part of the catalyst relative to the absorption of heat in the regeneration zone and the transfer of this heat to the hydrocarbons undergoing treatment. When alumina-silica type of cracking catalysts are employed, the practice of my invention will usually involve catalyst-to-oil weight ratios greater than 2.5 to 1, and preferably greater than 5.0 to 1.

From the foregoing it will be apparent that the process therein described accomplishes the objects of my invention, and that various features thereof may be utilized to advantage either conjointly or separately. It will further be readily apparent to those skilled in the art that while the invention has been illustrated and described with respect to a preferred operation and examples, and with references to suitable apparatus for its practice, the invention is not limited to such exemplifications but may variously be practised and embodied within the scope of the claims hereafter made.

I claim:

1. In a process for the catalytic conversion of high-boiling hydrocarbons into low-boiling hydrocarbons within the gasoline boiling range involving passing a stream of the high-boiling hydrocarbons having a solid, incombustible cracking catalyst suspended therein through a conversion zone for a time and at a temperature adapted to effect the required degree of conversion to low-boiling hydrocarbons and also resulting in a carbonaceous deposit on the catalyst, separating the used catalyst from the vaporous conversion products, suspending the used catalyst in an oxygen-containing gas and passing the suspension through a regeneration zone to burn off carbonaceous material deposited on the catalyst, and returning the catalyst for reuse in the conversion reaction, the improvement which consists in introducing the used catalyst into the regeneration zone and burning off the carbonaceous material in said zone under such conditions as to leave a residual quantity of carbonaceous material on the catalyst amounting to about 0.5% to 2.0% of the weight of the regenerated catalyst as discharged from said regeneration zone and reused in the conversion zone, withdrawing the regenerated catalyst from said regeneration zone and admixing it with liquid hydrocarbon feed stock while retaining sufficient heat to vaporize the feed stock, and returning said catalyst in suspension in the vapors thus produced to said conversion zone.

2. A process for the catalytic conversion of

high-boiling hydrocarbons into low-boiling hydrocarbons within the gasoline boiling range which comprises passing a vapor stream of hydrocarbons having the catalyst suspended therein through a conversion zone to effect the required degree of conversion, whereby reaction products are produced including converted hydrocarbons and a carbonaceous deposit on the catalyst, separating the used catalyst from the gaseous reaction products and regenerating it by passage through a regeneration zone, while suspended in an oxygen-containing gas, withdrawing the regenerated catalyst from said regeneration zone and admixing it with liquid hydrocarbon feed stock while retaining sufficient heat to vaporize the feed stock, and returning said catalyst in suspension in the vapors thus produced to said conversion zone.

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