

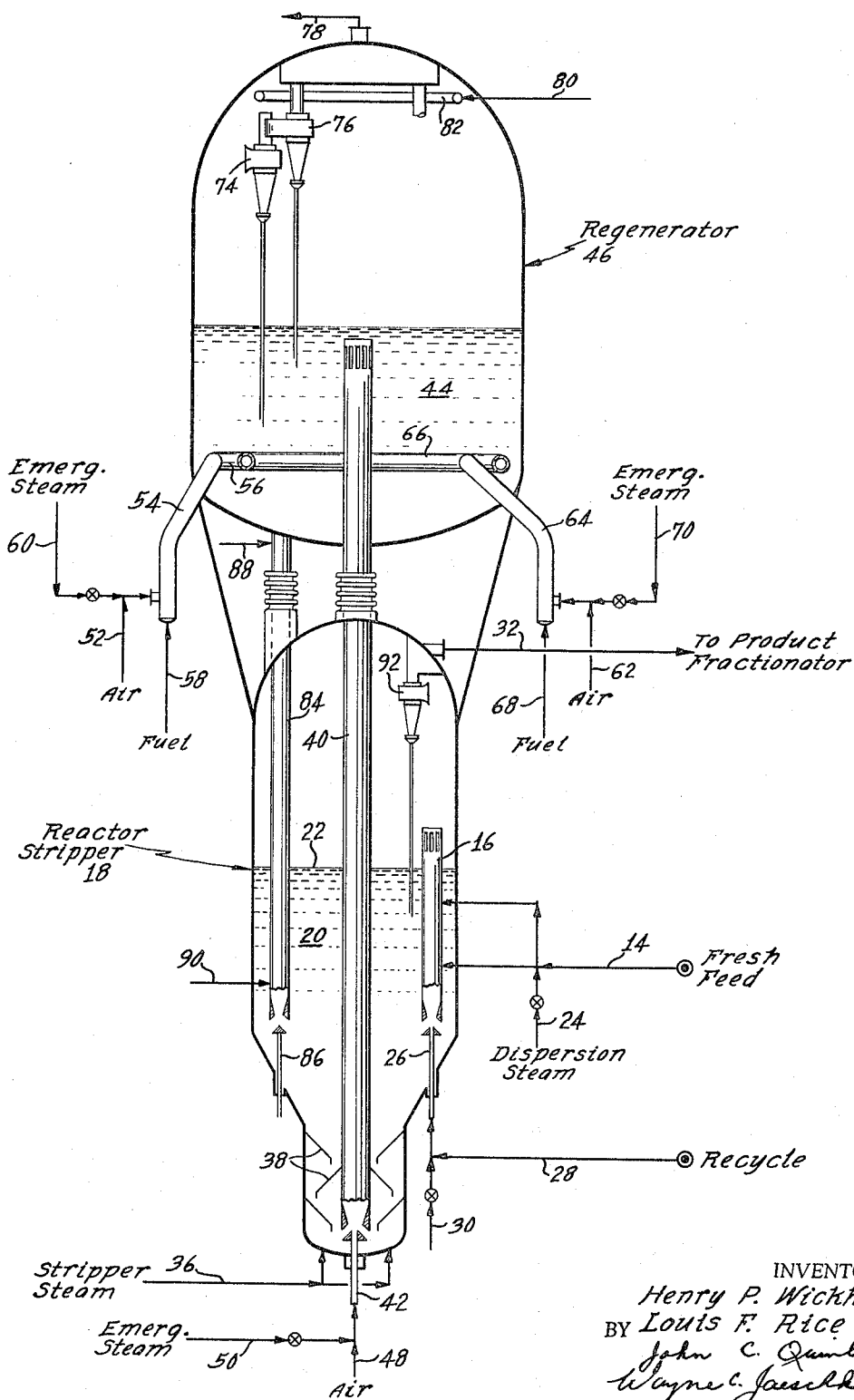
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CATALYTIC HYDROCARBON CONVERSION AND STRIPPING PROCESS

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3,290,241 CATALYTIC HYDROCARBON CONVERSION AND STRIPPING PROCESS

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This application is a continuation-in-part of applica-
tion Serial No. 115,803, filed June 8, 1961 now aban-
doned.

The present invention relates to the conversion of
hydrocarbons. More specifically, the invention pertains
to a method of converting relatively heavy or high-boiling
hydrocarbons including topped or reduced crudes or
similar heavy residue fractions to lower boiling range
fractions. Still more specifically, this invention is directed
to a method for cracking heavy gas oils and hydrocar-
bons boiling above gas-oil boiling range in the presence
of fluidized solid catalytic material to produce lower
boiling range hydrocarbons and hydrocarbon feeds suit-
able for further cracking.

In petroleum refining, crude petroleum is first distilled
to produce desired distillate fractions and a residue frac-
tion. Motor fuels are produced from the distillate frac-
tions by a plurality of refining techniques known in the
art, while the residue fraction is processed to obtain lubri-
cating oils, waxes, asphalt, fuel oil, etc. However, dif-
ficulties have been experienced when attempting to crack
residue fractions in the prior art processes because of the
high ash content of the feed and the high rate of carbon
formation which have led those skilled in the art to con-
clude that a crude residue is a highly undesirable feed for
a fluidized catalytic cracking process.

It is an object of this invention to provide an improved
method and means for converting relatively high-boiling
hydrocarbon feed materials in the presence of fluidized
catalytic material.

Another object of this invention is to provide an im-
proved method for converting residual oils including
topped and reduced crudes in the presence of fluidized
particle material.

Other objects and advantages of the present invention
will become more apparent from the following descrip-
tion.

In catalytic cracking operations, the conversion level
described in terms of severity of operation may be at-
tained by regulating the temperature, time of contact,
catalyst to oil ratio and level of catalyst activity. It is
the relative effect of these variables and the method of
controlling these variables with which the method and
means of this invention is particularly concerned. Ac-
cordingly, the method of this invention is directed in one
aspect to maintaining relatively mild conversion con-
ditions for the fresh feed material and substantially more
severe conversion conditions for residual components
thereof.

The residual oil to be converted in accordance with
this invention may or may not contain gas oil components
which can be satisfactorily processed in separate crack-
ing operations to primarily gasoline boiling range prod-
ucts. If the feed does contain such gas oil components,
it is preferred and an object of this invention to minimize
conversion of such gas oil components while maximizing
conversion of any residual materials separated therefrom
to a principal gas oil product. The residual oil to be
processed in the method of this invention may be a re-
duced crude constituting from about 20 percent to about
50 percent of the total crude and having an API° gravity
in the range of from about 10° to about 25° API. Gen-

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erally, reduced crudes contain from about 30 percent to
about 90 percent of the components boiling above 700°
F., which, if properly handled, may be cracked to lower
boiling range products and coke.

In the method of this invention, any suitable siliceous
cracking catalyst may be employed for effecting the re-
latively mild and severe cracking operations and the cata-
lyst may be silica-alumina, silica-magnesia, silica-zirconia
or mixtures thereof.

These and other objects are accomplished in accord-
ance with the present invention for catalytically convert-
ing relatively high boiling products to relatively lower
boiling products in a heat balanced conversion system by
maintaining a first relatively dense fluidized bed of cata-
lyst undergoing regeneration by burning carbonaceous
and hydrocarbonaceous material contained on the sur-
face of the catalyst in an atmosphere containing oxygen.
The regeneration zone is superimposed vertically above a
relatively dense bed of catalyst participating in conver-
sion in a reaction zone. Regenerated catalyst is flowed
downwardly from the regeneration zone for discharge
exclusively into the second dense bed at the lower eleva-
tion. Freshly regenerated catalyst which is at a high
temperature relative to the catalyst undergoing conver-
sion in the second zone is mixed therewith in order to
provide a catalyst mixture having reduced activity and
a temperature which is substantially lower than that of
the freshly regenerated catalyst for initial contact with
relatively high boiling range hydrocarbon feed material
in order to avoid overcracking of low boiling range com-
ponents which may be present in the feed. A confined
upflowing suspension of such catalyst mixture and oil is
produced by contacting relatively high boiling range
liquid hydrocarbon oil and solid material consisting of
the aforementioned catalyst mixture. The upflowing
suspension is, preferably, contacted with a relatively low
boiling hydrocarbon liquid at a point above the bottom
of the suspension. In another embodiment such catalyst
mixture is contacted with inert gaseous material, e.g.,
steam, in order to produce a confined upflowing suspen-
sion which is contacted above the bottom thereof with
liquid hydrocarbon feed material for conversion. The
catalyst and oil suspension is discharged adjacent the up-
per level of the dense bed in the reaction zone and, pre-
ferably, above the level of the dense bed under conditions
to separate vaporous hydrocarbon material from catalyst
containing absorbed residual oil material which is re-
turned to the dense bed. The residual material is con-
verted to lower boiling range products in the dense bed
which affords extended contact time for the residual
material at an elevated temperature. The catalyst mix-
ture is stripped to remove volatile hydrocarbonaceous ma-
terial and passed upwardly into the regeneration zone.

The upflowing confined suspension of catalyst and hy-
drocarbon material produced by contacting hydrocarbon
liquid feed material and the catalyst mixture contained
in the second dense bed is maintained under hydrocarbon
conversion conditions while maintaining a catalyst to oil
ratio in the suspension, preferably, between about 25 and
about 50:1 and, most preferably, between about 35 and
about 45:1. A short contact time is employed in the
confined suspension, preferably, between about 0.5 to
about 2.5 seconds. Preferably, the catalyst mixture pro-
duced in the dense bed in the reaction zone is main-
tained at a temperature between about 925° F. and about
1075° F. The relatively high boiling range liquid hydro-
carbon oil, for example, which is introduced as feed, and
the catalyst mixture having a reduced activity, i.e., an
activity intermediate between that of the freshly regen-
erated catalyst and catalyst which has been in the reaction
bed for an extended period of time, are initially contacted

at the base of the upflowing confined suspension within the above-stated temperature range.

In accordance with the method of the present invention, the catalyst circulation between the lower and the upper portion of the dense bed of catalyst in the reaction zone can be adjusted independently of the catalyst circulation between the reaction zone and the regeneration zone in order to achieve the severity of conditions desired in both the confined upflowing suspension and the dense reaction bed. Preferably, the catalyst circulation in the upflowing confined suspension is maintained above about 3 times the catalyst circulation between the regeneration zone and the dense bed in the reaction zone.

The vaporous hydrocarbon material which is separated from catalytic material above the dense bed in the reaction zone is passed to a product fractionator for separation into desired boiling range fractions. Preferably, the relatively high boiling liquid fraction separated in a lower portion of the fractionation zone is recycled to the conversion zone and contacted with the catalyst mixture of reduced activity at the base of the confined upflowing suspension.

The removal and recovery of hydrocarbons from the catalyst is enhanced by positioning a stripping zone beneath and contiguous with the fluid bed of catalyst in the reaction zone so that hot freshly regenerated catalyst discharged into the dense fluid bed of catalyst is entrained with the catalyst entering the stripping section and stripping gas introduced to the bottom portion thereof passed upwardly through the total fluid bed of catalyst thereabove in the reaction zone. Accordingly, the continuous dense fluid bed of catalyst in the reaction and stripping zones function in part as an enlarged high temperature stripping zone wherein hydrocarbon constituents retained with the catalyst are converted to lower boiling range products and recovered from the catalyst. The stripped catalyst is thereafter removed from the bottom or lower portion of the stripping zone and passed to a regeneration zone for the removal of unstripped carbonaceous material from the catalyst by burning in the presence of an oxygen-containing gas. During regeneration the catalyst is heated to an elevated temperature in the range of from about 1050° F. to about 1250° F., or higher and sufficiently elevated for recycle to the fluid bed of catalyst in the reaction zone to maintain the desired temperature conversion conditions therein.

In the method of operation described with respect to this invention, the activity of the freshly regenerated catalyst is reduced or modified by admixture with the partially used catalyst of the process for treating the high boiling hydrocarbon feed material while simultaneously providing the necessary endothermic heat to the fluid bed of catalyst in the reaction and stripping zones wherein conversion and removal of adsorbed hydrocarbons retained in the catalyst is effected at a higher temperature than that encountered by the feed material upon initial contact with the catalyst. Accordingly, contact of hydrocarbon material with catalytic material under a relatively wide range of conversion conditions of time and temperature is permitted and the conditions of severity desired for conversion of different high boiling hydrocarbons is readily obtainable in the method of this invention. A hydrocarbon feed to be converted is introduced into the upflowing confined stream of catalyst or riser-reactor within the reaction zone through a plurality of separate and spaced apart nozzles or inlet points which are located at the bottom, intermediate and, preferably, in an upper portion of the riser, thereby permitting control of contact time with respect to the separate hydrocarbon feeds and the catalyst. Where it is desired to introduce hydrocarbon feed to the riser solely above the bottom thereof, relatively inert gasiform material, such as steam, is preferably employed as lift gas to form an upwardly flowing suspension of the catalyst mixture. When converting heavy or high boiling hydrocarbons, such as reduced

crudes, relatively inert gaseous material is preferably employed with the hydrocarbon feed to assist with atomization and partial vaporization of the hydrocarbon feed for more suitable distribution and intimate contact of the feed with the catalyst within the riser.

While the method of this invention is particularly directed to the conversion of high boiling hydrocarbons such as topped and reduced crudes or residual fractions, it is to be understood that lower boiling range hydrocarbons, such as gas oils may also be converted to desired products employing the method and means of this invention.

It is to be understood that a plurality of substantially vertically disposed hydrocarbon riser-reactors can be employed within the dense bed of catalyst in the reaction zone for contact with a plurality of hydrocarbon feed material. The riser-reactors are provided with variable orifice means at the bottom end thereof and a suitable discharge means at the upper end thereof which will change the direction of the vertically flowing suspension outwardly and in a generally horizontal direction. A preferred discharge means is a "bird cage" separator which is more fully described with reference to the figure of the drawing.

Having thus given a general description of the improved method and means of this invention, reference is now made to the drawings by way of example, which present a preferred embodiment of this invention.

Referring now to the figure of the drawing, by way of example, a fresh hydrocarbon liquid feed material of about 23.8° API gravity at a temperature of about 450° F. is introduced in conduit 14 which leads into branched conduits 15 for introduction into riser conduit 16 confined within a reactor-stripper zone 18. It is to be understood that one or more risers 16 can be employed and the risers can be discharged above or adjacent the dense fluid bed of catalyst interface depending upon the height of catalyst bed maintained in the reaction zone. Riser 16 extends, in a specific embodiment, substantially vertically upward from a lower portion of a dense fluid bed of catalyst 20 maintained in the lower portion of the reaction zone and discharges above the upper dense bed level 22 of the fluid bed of catalyst. Suitable dilute gasiform material, such as dispersion steam, may be introduced by conduit 24 for admixture with the fresh feed in conduit 14 passed to riser 16 via branched conduits 15. A vertically movable hollow stem plug valve 26 is aligned with the bottom open end of riser 16 through which a recycle feed material, more fully defined hereinafter, either with or without dispersion steam, is passed by conduit 28 to valve 26. Conduit 30 connected to conduit 28 is provided for introducing gasiform material such as steam thereto. It is contemplated, in another embodiment of this invention, to introduce fresh feed to the bottom of riser 16 by valve 26 and to introduce the recycle feed directly into the fluid bed of catalyst in the reaction zone.

In this specific example, the fluid bed of catalyst 20 comprises a mixture of freshly regenerated catalyst and catalyst of modified activity having been circulated through zone 16. The catalyst mixture is controlled by withdrawal of catalyst from the bed and the addition of hot freshly regenerated catalyst thereto to maintain a bed temperature of at least about 950° F., in this example. Accordingly, the catalyst withdrawn from bed 20 and passed upwardly as a suspension in riser 16 comprises a mixture of used and freshly regenerated catalyst for initial contact with the hydrocarbon feed material introduced thereto. The quantity of catalyst employed in riser 16 is sufficient to maintain a catalyst to oil ratio in the range of from about 25 to about 50, preferably from about 35 to about 45 to 1, with the contact time within the riser 16 being in the range of from about 0.5 to about 2 seconds. In this specific example, a catalyst to oil ratio of about 43.5 to 1 is employed in riser 16 and the riser discharge temperature is about 900° F. The suspension passed upwardly through riser 16 is discharged into the

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dilute catalyst phase above the dense fluid bed of catalyst 20 wherein vaporous hydrocarbon products are separated from the catalyst and withdrawn from the reactor-stripper zone 18 for passage by conduit 32 to the product fractionator (not shown).

The catalyst separated from the suspension discharged into the dilute phase of the reactor-stripper zone 18 together with any hydrocarbon material absorbed on or entrained with this catalyst is returned to the dense bed of catalyst so that these hydrocarbons or hydrocarbonaceous material are subjected to more severe conversion conditions with extended contact time and a higher temperature of about 950° F., substantially above the temperature employed in the riser.

As discussed hereinbefore, catalyst is continuously added to and removed from the dense bed of catalyst in the reaction zone with a portion of the withdrawn catalyst passing directly as a continuous downwardly moving fluid bed of catalyst into a stripping zone beneath the reaction zone. Stripping gas introduced to the bottom of the stripping zone through branched conduit 36 flows upwardly therethrough and through the fluid bed of catalyst in the reactor-stripper zone. Stripping gas and stripped products of reaction join with the hydrocarbon conversion products in the dilute phase and are passed to the product fractionator in conduit 32. The stripping section is provided with a plurality of downwardly sloping disc shaped baffle members 38. It is contemplated, however, to employ a plurality of vertically extending transverse baffle members within the annular stripping section to provide a plurality of elongated stripping sections in place of the sloping baffles shown.

The stripping section is an annular section in view of riser conduit 40 extending from the lower portion of the stripping section upwardly through the reactor and discharging in a regeneration zone positioned above the reaction zone. In the specific arrangement shown, the stripped catalyst enters the bottom open end of riser 40 wherein it is mixed with a gaseous material such as a portion of the oxygen-containing gas required to regenerate the catalyst introduced by hollow stem plug valve 42 for flow upwardly through the riser as a suspension. The thus formed suspension passes upwardly through riser 40 and is discharged at a temperature of about 960° F., adjacent the upper or top portion of a dense fluid bed of catalyst 44 maintained in the lower portion of regeneration zone 46. Air or a suitable oxygen-containing gas is passed to valve 42 by conduit 48 either with or without relatively inert gaseous material such as steam introduced by conduit 50. Generally, the quantity of oxygen employed in riser 40 is from about 5 to about 40 percent of that required to regenerate the catalyst by burning of carbonaceous material deposited on the catalyst during the hydrocarbon conversion steps. The remaining portion of air or oxygen containing gas required to regenerate the catalyst is supplied to the lower portion of the fluid bed of catalyst in the regeneration zone, as hereinafter described. That is, a portion of the required regeneration air is passed by conduit 52 to air heater 54 connected to distributor manifold 56 positioned in the lower portion of the regeneration zone. Conduit 58 is provided for introducing fuel to heater 54 and conduit 60 connected to conduit 52 is provided for introducing emergency steam in the event of loss of air to the system. The remaining portion of regeneration air is passed by conduit 62 to heater 64 connected to distributor manifold 66. Conduit 68 is provided for introducing fuel to heater 64 and conduit 70 connected to conduit 62 is provided for introducing emergency steam. In the regeneration zone, carbonaceous material remaining on the catalyst is removed by burning under conditions to maintain a regeneration dilute phase temperature above the dense fluid bed of catalyst of about 1100° F. When operating the apparatus so that riser 40 discharges into the dilute catalyst phase above the dense fluid bed of catalyst in the regen-

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eration zone, the temperature of the discharged suspension will be usually sufficiently low to have a cooling effect on the dilute catalyst phase sufficient to minimize secondary burning occurring in the cyclone separators positioned in the regenerator dilute phase.

Gaseous products of combustion pass from the regenerator dilute phase through a plurality of cyclone separators 74 and 76 for removal of entrained catalyst therefrom before removal from the regeneration zone by conduit 78. The gaseous products of combustion or hot flue gases may be passed to a CO boiler or other suitable arrangement (not shown) for the production of steam required in the process or they may be used to develop power to drive a regeneration gas compressor by expansion in fired turbines employed to generate process steam in a CO boiler or other suitable device. Conduit 80 connected to distributor manifold 82 is provided in the top portion of the regeneration zone for the introduction of steam thereto.

Regenerated catalyst at a desired elevated temperature is withdrawn from the bed of catalyst in the regeneration zone and passed to the lower portion of the fluid bed of catalyst in the reaction zone to maintain a desired temperature therein by standpipe 84 having a vertically movable catalyst flow control plug valve 86 aligned with the bottom end thereof. Conduits 88 and 90 connected to standpipe 84 are provided for introducing aeration gas to the upper and lower portions of the standpipe and maintain the catalyst therein in a flowable condition.

The hydrocarbon conversion products containing entrained catalyst not completely removed by cyclone separator 92 are removed from the upper portion of the reaction zone and passed by conduit 32 to the product fractionator (not shown) for separation into desired fractions.

Having thus given a general description of the improved method and means of this invention and set forth a specific example thereof, it is understood that no undue restrictions are to be imposed thereon by reason thereof, except as defined by the claims.

What is claimed is:

1. A method for catalytically converting relatively high boiling hydrocarbons to lower boiling products in a heat balanced conversion system which comprises: maintaining a first relatively dense fluidized bed of catalyst undergoing regeneration in a regeneration zone superimposed vertically above a second relatively dense bed of catalyst participating in conversion in a reaction zone, flowing regenerated catalyst downwardly from said regeneration zone exclusively into the second dense bed to provide a catalyst mixture having reduced activity and a temperature which is substantially lower than that of the freshly regenerated catalyst, contacting a relatively high boiling liquid hydrocarbon oil and solid material consisting of said catalyst mixture to vaporize at least a portion of such liquid and to produce an upflowing confined suspension of catalyst and hydrocarbon material, and maintaining hydrocarbon conversion conditions within the said suspension, discharging said suspension adjacent the upper level of said second dense bed under conditions to separate vaporous material which is withdrawn overhead and catalyst containing adsorbed residual oil material which is returned directly to said dense bed, stripping said catalyst mixture and passing such stripped catalyst upwardly into said regeneration zone.

2. A method for catalytically converting relatively high boiling hydrocarbons to lower boiling products in a heat balanced conversion system which comprises: maintaining a first relatively dense fluidized bed of catalyst undergoing regeneration in a regeneration zone superimposed vertically above a second relatively dense bed of catalyst participating in conversion in a reaction zone, flowing regenerated catalyst downwardly from said regeneration zone exclusively into the second dense bed to provide a catalyst mixture having reduced activity and a temperature which is substantially lower than that of the freshly

regenerated catalyst, contacting a relatively high boiling liquid hydrocarbon oil and solid material consisting of said catalyst mixture to vaporize at least a portion of such liquid and to produce an upflowing confined suspension of catalyst and hydrocarbon material, contacting such confined upflowing suspension above the bottom thereof with a relatively low boiling hydrocarbon liquid, and maintaining hydrocarbon conversion conditions within the said suspension, discharging said suspension adjacent the upper level of said second dense bed under conditions to separate vaporous material which is withdrawn overhead and catalyst containing adsorbed residual oil material which is returned directly to said dense bed, stripping said catalyst mixture and passing such stripped catalyst upwardly into said regeneration zone.

3. A method for catalytically converting relatively high boiling hydrocarbons to lower boiling products in a heat balanced conversion system which comprises: maintaining a first relatively dense fluidized bed of catalyst undergoing regeneration in a regeneration zone superimposed vertically above a second relatively dense bed of catalyst participating in conversion in a reaction zone, flowing regenerated catalyst downwardly from said regeneration zone exclusively into the second dense bed to provide a catalyst mixture having reduced activity and a temperature which is substantially lower than that of the freshly regenerated catalyst, contacting a relatively high boiling liquid hydrocarbon oil and solid material consisting of said catalyst mixture to vaporize at least a portion of such liquid and to produce an upflowing confined suspension of catalyst and hydrocarbon material, and maintaining hydrocarbon conversion conditions within said suspension while maintaining a catalyst to oil ratio between about 25 and about 50:1, discharging said suspension adjacent the upper level of said second dense bed under conditions to separate vaporous material which is withdrawn overhead and catalyst containing adsorbed residual oil material which is returned directly to said dense bed, stripping said catalyst mixture and passing such stripped catalyst upwardly into said regeneration zone.

4. The method of claim 3 in which said catalyst to oil ratio is between about 35 and about 45:1.

5. The method of claim 3 in which the contact time in said confined suspension is between about 0.5 and about 2 seconds.

6. The method of claim 1 in which said vaporous material withdrawn overhead is separated in a fractionating zone to obtain relatively low boiling product and said relatively high boiling liquid fraction which is employed in contacting said catalyst mixture.

7. A method for catalytically converting relatively high boiling hydrocarbons to lower boiling products in a heat balanced conversion system which comprises: maintaining a relatively dense fluidized bed of catalyst undergoing regeneration in the regeneration zone superimposed vertically above the second relatively dense bed of catalyst participating in conversion in a reaction zone, flowing regenerated catalyst downwardly from said regeneration zone in a confined zone discharging exclusively into the

second dense bed and mixing such regenerated catalyst and catalyst undergoing conversion to provide a catalyst mixture having desired temperature and activity for contact with hydrocarbon feed material as hereinafter defined, contacting a stream consisting of relatively high boiling hydrocarbon liquid and solid material consisting of said catalyst mixture to vaporize at least a portion of such liquid and to produce an upflowing confined suspension of catalyst and hydrocarbon oil, contacting such confined upflowing suspension and a relatively low boiling hydrocarbon liquid above the bottom thereof, and maintaining hydrocarbon conversion conditions within the said suspension including a catalyst to oil ratio between about 25 and about 50:1, discharging said suspension adjacent the upper level of said second dense bed under conditions to separate vaporous material which is withdrawn overhead and catalyst containing adsorbed residual material which is returned directly to said dense bed, introducing stripping gas into said second dense bed to strip the catalyst mixture, and passing stripped catalyst upwardly as a confined stream within said second dense bed into said regeneration zone.

8. The method of claim 7 in which catalyst is flowed downwardly from said second dense bed and passed through a baffled catalyst stripping zone prior to passage of such catalyst upwardly into said regeneration zone.

9. The method for catalytically converting relatively high boiling hydrocarbons to lower boiling products in a heat balanced conversion system which comprises: maintaining a first relatively dense fluidized bed of catalyst undergoing regeneration in a regeneration zone superimposed vertically above a second relatively dense bed of catalyst participating in conversion in a reaction zone, flowing regenerated catalyst downwardly from said regeneration zone exclusively into the second dense bed to provide a catalyst mixture having reduced activity and a temperature which is substantially lower than that of the freshly regenerated catalyst, contacting solid material consisting of said catalyst mixture with inert gaseous material to produce an upflowing confined suspension of catalyst and inert material, contacting such confined upflowing suspension with relatively high boiling hydrocarbon, and maintaining hydrocarbon conversion conditions within said suspension while maintaining a catalyst to oil ratio between about 25 and about 50:1, discharging said suspension adjacent the upper level of said second dense bed under conditions to separate vaporous material which is withdrawn overhead and catalyst containing adsorbed residual oil material which is returned directly to said dense bed, stripping said catalyst mixture and passing such stripped catalyst upwardly into said regeneration zone.

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