

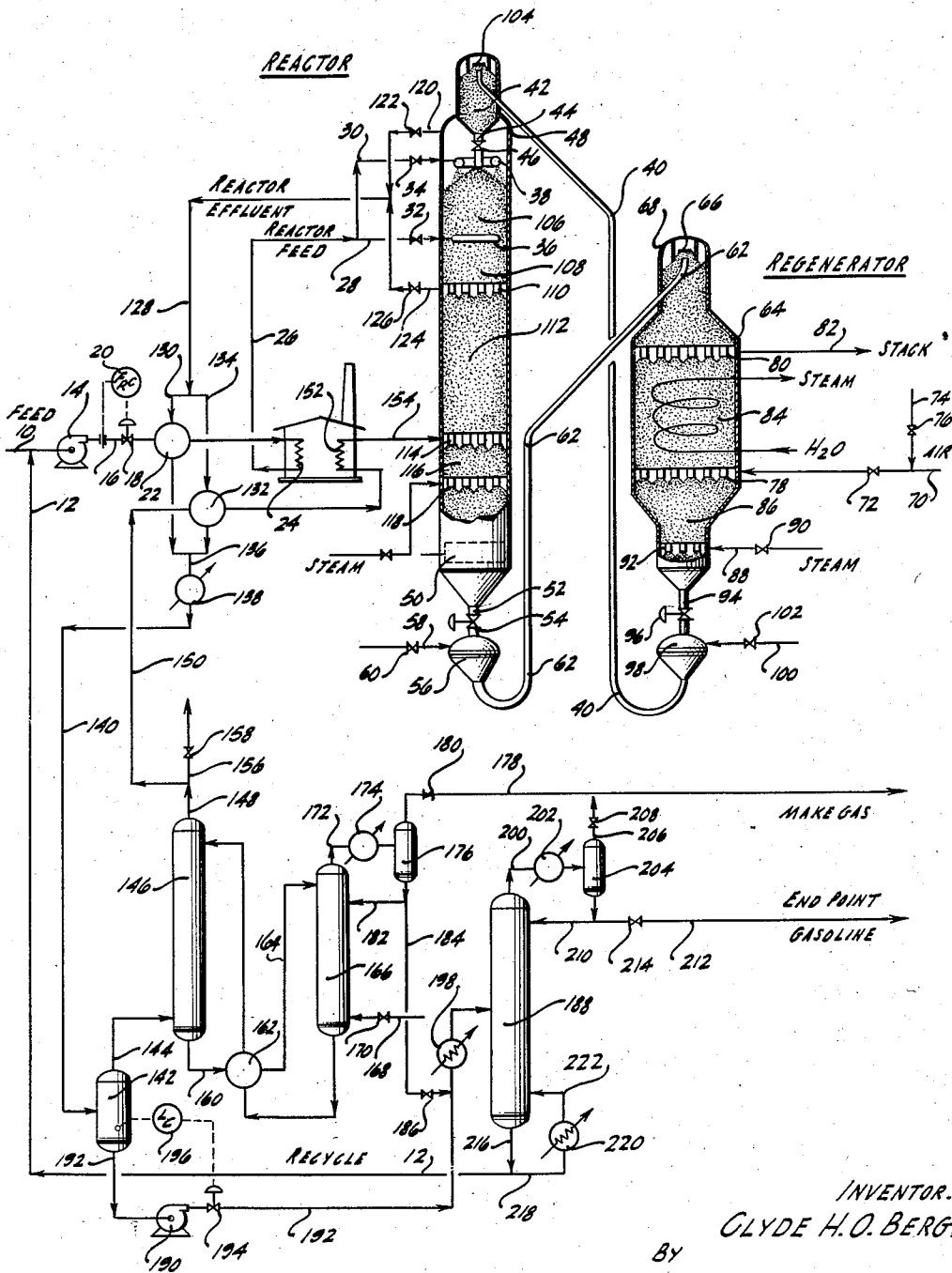
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
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PROCESS FOR HYDROCARBON BOILING POINT REDUCTION

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PROCESS FOR HYDROCARBON BOILING POINT REDUCTION

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This invention relates generally to the conversion of hydrocarbons and in particular relates to a hydrocarbon contacting process to effect a boiling point reduction simultaneously with, if desired, other hydrocarbon conversion processes. Specifically, it relates to an improved process and apparatus for the treatment of hydrocarbons boiling above about 400° F. to effect a maximum production of hydrocarbon products boiling in the gasoline range, and minimum production of coke and gas and which may also simultaneously effect reforming, desulfurization, denitrogenation, aromatization, isomerization, hydrogenation, dehydrogenation, or other hydrocarbon treating reactions.

Hydrocarbon boiling point reduction processes are well-known and include the thermal and catalytic hydrocarbon cracking processes, heavy oil coking processes and others and which may involve contacting the hydrocarbon stream to be treated with a moving compact bed or a fluidized body of solids which may or may not have catalytic activity for hydrocarbon conversions. In the thermal processes a relatively heavy hydrocarbon fraction is heated to its reaction temperature by passage through a heater wherein at least a partial decomposition to more volatile products is effected and generally with the simultaneous production of heavy hydrocarbonaceous residual materials referred to as coke. In the catalytic processes the hydrocarbon feed is heated generally to a somewhat lower temperature and is contacted with granular solids having catalytic activity promoting the desired hydrocarbon conversion reaction.

In these conventional processes all of the materials introduced as feed and which are not converted to residual materials such as coke pass at substantially the same velocity through the reaction or conversion zone. Thus, any desired product which is formed initially is nevertheless subjected to further and unneeded treatment during its passage through the remainder of the reaction zone and whereby a partial degradation of these materials to undesirable products invariably takes place. In spite of the fact that the gasoline range hydrocarbons thermally decompose at roughly only half the rate at which a gas oil range hydrocarbon does, still a substantial proportion of the gasoline hydrocarbons are thus lost and an unduly high gas and coke production results.

In addition, even under recycling conditions, the unreacted fraction of the feed material becomes more and more aromatic or refractory in nature and becomes successively difficult to convert under the existing temperature and pressure conditions. Thus, a certain amount of the hydrocarbon feed cannot be converted into the products having the desired boiling range.

The principal disadvantages, therefore, of the conventional processes may be summarized as: first, a substantial proportion of the hydrocarbon feed is converted to coke and gas; second, the residual unreacted material becomes refractory precluding operations processing the hydrocarbon feed to extinction; third, desirable boiling range hydrocarbons initially formed are at least partially

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degraded before they can be removed from the reaction zone; and fourth, a selective removal of the desired products as formed is not possible.

The process and apparatus of the present invention successfully overcomes the afore-mentioned disadvantages and comprises an improved operation in which a given hydrocarbon feed stock of relatively high boiling point may be converted at high efficiency into a product fraction boiling in the gasoline hydrocarbon range with an absolute minimum of gas and coke production and which also may, if desired, simultaneously subject either the hydrocarbon feed or the desirable hydrocarbons formed as products or both to the other hydrocarbon conversion reactions such as those referred to above.

It is therefore a primary object of this invention to provide an improved process for effecting the boiling point reduction of hydrocarbons at improved efficiency wherein a relatively long concurrent contact of hydrocarbon feed and granular solids is effected under reaction conditions of temperature and pressure followed by a rapid removal of the hydrocarbon products boiling in the desired range effected by a relatively short countercurrent contact of such products with solids prior to removal from the reaction zone.

Another object of this invention is to provide an improved hydrocarbon boiling point reduction process which comprises concurrently contacting a moving bed of heated granular solids with a liquid hydrocarbon to be converted in a reaction zone while maintaining in this zone a countercurrent flow of gas which sweeps the hydrocarbon products of reduced boiling point countercurrently through the reaction zone for removal therefrom at high velocity to prevent the desired hydrocarbon fraction from being decomposed.

It is a further object of this invention to provide an improved process as stated in the foregoing objects in which the countercurrent flow of gas maintained in the reaction zone contains hydrogen to further enhance the increased yield of hydrocarbons boiling in the desired range and to inhibit the formation of undesired products such as coke and aromatic refractory residual hydrocarbons.

It is an additional object of this invention to provide the boiling point reduction process mentioned above in the foregoing objects in which a moving bed of granular hydrocarbon cracking catalyst is employed.

It is a further object of this invention to provide a process for hydrocarbon conversion which effects a hydrocarbon boiling point reduction according to the objects above simultaneously with an effective desulfurization, reforming, denitrogenation, isomerization, aromatization, hydrogenation, and/or dehydrogenation whereby either the feed hydrocarbons or the product hydrocarbons or both are further improved and upgraded.

It is an additional object to provide in such a process the use of a mixed catalyst whereby a hydrocarbon boiling point reduction and one or more of the named hydrocarbon conversion reactions are effected catalytically.

A further specific object of this invention is to provide a process for catalytically cracking petroleum hydrocarbon fractions and recycled unconverted hydrocarbons boiling above about 400° F. by contact with a hydrocarbon cracking catalyst in the presence of a recycle gas containing hydrogen and flowing countercurrent to the catalyst flow whereby the hydrocarbons thus treated may be converted to extinction to hydrocarbon products boiling in the gasoline range.

Another object of this invention is to provide an improved apparatus adapted to effect the foregoing objects.

Other objects and advantages of the present invention

will become apparent to those skilled in the art as the description and illustration thereof proceeds.

Briefly, the present invention comprises a continuous hydrocarbon-granular solids contacting process for the boiling point reduction of hydrocarbon fractions wherein a liquid hydrocarbon feed is contacted with a moving mass of granular solids and passes concurrently therewith at least part way through a reaction zone under reaction conditions of temperature and pressure and in the presence of a countercurrent flow of vapor containing the hydrocarbon products of the process. Liquid hydrocarbons are brought into contact by spraying, or are otherwise mixed with the moving bed of heated granular solids and are retained thereon by adsorption and/or wetting depending on the physical characteristics of the solid materials. The heated solids are thus at least partly "saturated" with liquid hydrocarbon feeds. The hydrocarbon feed in normal operation does not run down through the solids bed, especially at high solids to feed ratios, but it may to some extent at the lower ratios. Ordinarily the feed oil, at least partly saturating the solids, is carried by the moving bed of solids at least part way down through the reaction or soaking zone maintained under conversion conditions of pressure and temperature. During this time, the boiling point reduction and hydrocarbon cracking reactions take place on the saturated solids with the formation of hydrocarbon products of increased volatility and lower boiling point. Because of the increased volatility, the products are rapidly vaporized substantially as soon as they are formed in contact with the granular solids and are rapidly removed from the reaction zone by means of a counter-current gas and vapor flow maintained at a high velocity therein. Heat is introduced to the reaction zone in the heated granular solids and in the heated countercurrent flow of vapor passing through the solids bed whereby heat of product vaporization is supplied. The relatively heavy hydrocarbons introduced as feed remain in contact with the granular solids as long as is necessary to form products of sufficient volatility to escape from the liquid phase established on the granular solids. The granular solids move relatively slowly down through the reactor and the vapor phase can be made to move therethrough as fast as desired. The feed hydrocarbons of relatively high boiling point pass concurrently with the solids until more volatile products are formed and these products are swept rapidly countercurrent to the granular solids through the reaction zone and are removed therefrom at a rate sufficient to eliminate further boiling point reduction reactions.

In the case where additional hydrocarbon conversion reactions are desirable, the granular solids may be selected to catalytically enhance either one or both of the boiling point reducing reaction and the desired additional reaction and the rate at which the desired hydrocarbon products are passed countercurrently through the reaction zone may be further varied according to the required conditions of the additional conversion reaction.

The process employs a downwardly moving compact bed of granular solids which may or may not have catalytic activity. Preferably, a catalyst such as any one of the well-known hydrocarbon cracking catalysts is employed to increase the rate of the boiling point reduction reaction. However, in the treatment of hydrocarbon feed stocks catalytically inactive granular solids, such as coke, aluminum oxide, high melting point metals, etc., may be employed to effect a noncatalytic hydrocarbon conversion on the extended surface area provided by the heated granular solids. Following the passage of the granular solids through the reaction zone they are passed through a regeneration zone and subjected to the action of an oxygen-containing gas for reheating and regeneration in the case of catalysts and returned to contact further quantities of the hydrocarbon to be processed.

The simultaneous countercurrent and concurrent flow of hydrocarbons relative to the granular solids flow is

established by employing a liquid feed stream entering near the top of the reaction zone, the introduction of a recycle gas near the bottom and removal of the desired hydrocarbon products and the recycle gas in the vapor phase from near the top of the reaction zone. Thus, the hydrocarbon feed flows in the liquid phase concurrently with the solids through the reaction zone and the hydrocarbon products are removed in the vapor phase countercurrent to the solids flow. If desired, product removal may be effected above the feed inlet point thus subjecting the product to the action of fresh solids whereby the heavier or higher boiling fractions may be absorbed and returned for further reaction and/or the product may be reacted in the presence of the fresh catalyst.

The hydrocarbon product stream is removed from the reaction zone and fractionated for the separation of gas and liquid hydrocarbons boiling in the desired temperature range from the unreacted hydrocarbons having boiling points greater than the end point of the desired product. The unreacted hydrocarbons, which do not have the aromatic and refractory characteristics of conventional hydrocarbon boiling point reduction reactions for reasons described below, are recirculated for reintroduction with fresh feed into the reaction zone. At least part of the gas recovered from the reaction zone effluent may be fractionated if desired and a stream thereof, preferably containing hydrogen, is introduced into the bottom of the reaction zone to sweep out the hydrocarbon products countercurrently as they are formed. The desired hydrocarbons may be subject to further fractionation and are removed from the process as one or more product streams.

The recycle gas contains substantial quantities of hydrogen formed in the cracking and boiling point reduction reactions. Even in the absence of other hydrocarbon conversion processes such as aromatization, desulfurization, and other such reactions named above, this hydrogen has been found to have an extremely beneficial effect upon the boiling point reduction reactions in this process whereby highly increased liquid yields are obtained. First, this hydrogen recycle sweep gas represses to a large extent the formation of heavy non-volatile hydrocarbonaceous products in the reaction zone. Second, it represses the formation of aromatic refractory residual hydrocarbons which ordinarily prevent recycling hydrocarbons to extinction in the conventional cracking processes. Third, it effectively strips hydrocarbons from the granular solids just prior to their removal from the reaction zone keeping the liquid yield at a high value. Fourth, the hydrogen and the product hydrocarbons are exposed to countercurrent reaction conditions in the presence of a catalyst to further upgrade and improve the product hydrocarbons. Fifth, a rapid removal of the product hydrocarbons of desired boiling range results precluding product degradation. Sixth, the great difference in the boiling point between the hydrogen and the hydrocarbon products simplify hydrogen recovery and recirculation.

The present invention will be more clearly understood by reference to the accompanying drawing which is described in connection with the catalytic cracking of hydrocarbons boiling in the gas oil range in the presence of a cracking catalyst according to the principles of this invention.

Referring now particularly to the drawing, a flow diagram is given which also indicates in cross section elevation some of the structural details of the reactor and regenerator.

In the drawing, the hydrocarbon to be converted is passed through line 10 and combined with a recycle stream of incompletely converted hydrocarbons flowing through line 12. The combined stream of reactor feed is passed by means of pump 14 through line 16 at a rate controlled by valve 18 in accordance with flow recorder controller 20 through interchanger 22 in exchange with part of the reactor effluent whereby it is preheated and the effluent partly cooled. The thus preheated combined

feed stream is passed through heater coil 24 wherein it is further heated to a temperature for introduction into the reactor. The heated liquid reactor feed then flows through line 26 for introduction through either of lines 28 or line 30 controlled respectively by valves 32 and 34 into distributor members 36 or 38.

The reactor feed is in the liquid phase and is distributed onto and to at least partly saturate a downwardly moving bed of granular solid material circulated through the reactor and regenerator vessels in a continuous stream. Granular solids are introduced into the reactor via line 40 from the bottom of the regenerator. The granular solids subsequently pass downwardly through separator zone 42 through line 44 provided with solids flow control means 46. The solids pass downwardly through reactor vessel 48 as a compact moving bed. Near the bottom of the reactor 48 is provided reciprocating solids feeder means 50 whereby a uniform downward flow of solids is maintained throughout the cross sectional area of the reactor vessel. Granular solids are removed by means of line 52 controlled by valve 54 and are introduced into induction chamber 56. A conveyance fluid under pressure is introduced therein by means of line 58 controlled by valve 60. The granular solids flow by gravity and the forces generated by the depressuring conveyance fluid downwardly from chamber 56 into spent solids conveyance conduit 62. The conveyance fluid depressures through the conveyance conduit concurrently with a flow of compact unfluidized granular spent solids into the top of regenerator vessel 64. Thrust plate 66 within separator chamber 68 applies a thrust force to the discharge of solids from conduit 62 thereby maintaining the solids during conveyance in substantially compact unfluidized form, a condition wherein the bulk or apparent density in pounds of solids per cubic feet of occupied volume is the same during conveyance as the density of the granular solids in the moving beds passing through reactor vessel 48 or regenerator vessel 68.

The spent granular solids pass downwardly as a compact moving bed through the regenerator vessel 64 wherein the solids are contacted by an oxidizing regeneration gas thereby removing residual hydrocarbonaceous deposits on the granular solids forming regenerated and heated solids. Air is introduced through line 70 at a rate controlled by valve 72 together with recirculated flue gas flowing through line 74 controlled by valve 76. This regeneration gas mixture is introduced into regeneration gas engaging zone 78, passes in direct contact with the granular solids burning the hydrocarbonaceous deposit therefrom, and the flue gases formed are removed from flue gas disengaging section 80 through line 82. These gases may be partly disposed of to a stack and part thereof may be recirculated for dilution of the regeneration gases.

Regenerated solids pass downwardly from regeneration zone 84 into stripping zone 86 wherein they are countercurrently contacted by stripping steam introduced through line 88 controlled by valve 90 into stripping steam engaging zone 92. The stripping steam passes partly into regeneration zone 84 removing flue gas therefrom and partly with the regenerated solids from the regeneration column via line 94 at a rate controlled by valve 96.

The granular solids are then passed into regenerated solids induction chamber 98 into which is introduced a conveyance fluid under pressure through line 100 controlled by valve 102. The granular solids and the conveyance fluid flow concurrently through conveyance conduit 40, into separator zone 42. Thrust plate 104 applies a thrust force to the solids discharge therein from conduit 40 serving to maintain the granular solids in a compact and unfluidized condition so that the bulk or apparent density of the regenerated solids is the same as the bulk density of the solids moving downwardly through regenerator 64. Thus, a continuous recirculation of the

granular solids employed for contacting the hydrocarbons to be converted is established.

The conveyance conduits 40 and 62, being filled with moving compact porous masses of granular solids, have a relatively high pressure drop of greater than about 0.1 p. s. i. g. per foot of length, the actual value depending upon the physical characteristics of the solids. Thus, these conveyance conduits effectively seal the reactor and regenerator vessels from each other without requiring the lengthy sealing legs conventionally employed and the tall supporting structures therefore required.

Referring to reactor 48, the liquid hydrocarbon feed, introduced either to distributors 36 or 38, saturates the moving bed of hot catalyst with liquid hydrocarbons. The thus saturated solids pass downwardly through primary and secondary reaction zones 106 and 108 and through intermediate product disengaging zone 110 into tertiary reaction and soaking zone 112. The granular solids subsequently pass through recycle gas engaging zone 114, stripping zone 116, stripping gas engaging zone 118, and are subsequently removed as described from the bottom of the reactor.

In the operation of reactor 48 a number of modifications exist relative to the particular point or points of feed induction and reactor effluent removal. In all of these cases the reactor feed is a liquid which is introduced onto the downwardly moving bed of solids and moves concurrently therewith downwardly through the various zones of the vessel. Subsequently, upon conversion of the feed to lower boiling point materials, a countercurrent flow thereof together with the recycle gas is maintained upwardly through the reactor to one or more of the product outlet points. The reactor effluent is then treated in a manner described below.

In one modification, the entire reactor feed passes through line 30 controlled by valve 34 into distributor 38. The more volatile hydrocarbon products, formed deep in the moving bed of solids below the inlet point, are swept upwardly through the bed and removed from reactor 48 through line 120 controlled by valve 122.

In another modification with the feed totally introduced through line 30, the reactor effluent is withdrawn from disengaging zone 110 through line 124 controlled by valve 126. In this modification, a certain amount of reaction time is provided in primary and secondary reaction zones 106 and 108 before product withdrawal is made, thus decreasing somewhat the direct recycling of fluids from the inlet to the outlet of the reactor and also shortening the product-solids contact time. Any products formed in zones 106 and 108 are drawn concurrently therethrough and removed through line 124 with other products.

In another modification with the total feed being introduced through line 30, part of the product may be withdrawn through line 120 with the remainder of the product being withdrawn through line 124.

In another modification of the present invention, the reactor feed is totally introduced through line 28 and is brought into contact with the moving solids by means of distributor 36. The solids, saturated with feed, pass downwardly as a moving bed from distributor 36. The countercurrent flow of recycle gas carries the hydrocarbon products countercurrently through zones 112, 108 and 106 for removal through line 120 controlled by valve 122 at the top of the column. This type of operation permits the contacting of the hydrocarbon products and recycle gas with fresh solids in zone 106 effectively adsorbing and retaining the higher boiling and less effectively treated hydrocarbon fractions for return with the bed of solids into the lower source of the reactor. A minimum of feed bypassing results and is an operation which is particularly effective when an additional hydrocarbon conversion such as any one or more of those named above is simultaneously carried out.

In another modification with the reactor feed entering

through distributor 36, the reactor effluent is withdrawn from disengaging zone 110 through line 124. Such a procedure effectively reduces the contact time which is advantageous when treating certain hydrocarbon feed stocks which are relatively easy to process in an apparatus such as that shown in the drawing designed for treating a wide variety of materials.

In still another modification with the reactor feed entering through distributor 36, the reactor effluent may be partly withdrawn through line 124 and the remainder be removed through line 120.

The other modifications involving reactor feed introduction simultaneously through distributors 36 and 38 are obvious from the discussion above.

The reactor effluent passes, after removal from reactor 48 following any of the procedures or a combination thereof described above, through line 128. This stream is split and passed partly through reactor feed interchanger 22 by means of line 130, and the remaining part is passed through recycle gas interchanger 132 through line 134. The partially cooled reactor effluent, resulting from combining the split streams, is passed through line 36 through effluent cooler 138 which reduces the effluent to near atmospheric temperature. The partially condensed reactor effluent is introduced through line 140 into separator vessel 142. The uncondensed portion passes therefrom through line 144 and through recycle gas absorber 146 countercurrent to an absorption oil. The pressure conditions and the oil to gas ratio maintained in absorber 146 are sufficient to absorb normally liquid hydrocarbons present in the gas as well as the C_3 and C_4 hydrocarbons together with a substantial proportion of C_1 and C_2 hydrocarbons if desired. The unabsorbed lean gas, containing a substantial proportion of hydrogen, is removed from absorber 146 through line 148 and is recycled through line 150, preheated in interchanger 132, further heated in heater coil 152, and introduced through line 154 into recycle gas engaging zone 144 in the reactor to introduce heat and maintain the temperature of the soaking zone. Temperature conditions in the reactor are often such as to provide a net production of hydrogen and a sufficient amount of the recycle gas may be bled off through line 156 at a rate controlled by valve 158 thereby maintaining the desired quantity and rate of recycle gas in the system. In other cases, make-up hydrogen is added to the recycle.

The rich absorption oil is removed through line 160 from absorber 146, preheated in exchanger 162 and introduced through line 164 into rich oil stripper 166. Steam or other stripping gas may be introduced through line 168 controlled by valve 170 or the stripper may be reboiled. The absorbed materials recovered from the rich absorption oil flow through line 172 through overhead condenser 174 for cooling and partial condensation. The cooled mixture is passed into separator 176 from which the net make gas is removed through line 178 controlled by valve 180 which may be a back pressure regulator. The condensate may be partly returned through line 182 to stripper 166 for reflux and the remainder is passed through line 184 at a rate controlled by valve 186 into gasoline distillation column 188 as described below.

Returning to separator 142, the condensed portion of the reactor effluent is removed therefrom through line 90, is pumped therefrom by means of pump 190 through line 192 controlled by valve 194 which in turn is actuated by level controller 196. This liquid stream is combined with the condensate flowing in line 184 and the mixture is preheated in preheater 198 and is introduced for distillation into distillation column 188.

Distillation column 188 produces as an overhead product a hydrocarbon fraction having the desired maximum boiling point which, for example, may be 400° F. end point gasoline. The overhead vapor flows through line 200 through condenser 202 into separator 204. Any gases remaining uncondensed are removed through line

206 controlled by valve 208. The condensate is employed in part as reflux in column 188 flowing through line 210 while the remainder flows as a product from the process through line 212 controlled by valve 214.

Those hydrocarbon materials boiling above the desired end point are removed as bottoms from column 188 through line 216. Part of these materials are passed through line 218, vaporized in reboiler 220 and the vapors passed through line 22 into the bottom of column 188. The remaining part is recycled through line 12 and combined for retreatment with the fresh feed flowing through line 10.

Thus, a complete cyclical hydrocarbon conversion process having unique reaction and conversion features is provided. The major proportion of the feed is converted to a product having certain desired boiling range. A small amount of make gas is removed as a product through line 178 and a small quantity of coke is burned from the granular solids in regenerator 64.

Following the above general description of the process, operating data are given below indicating specific procedures and conditions for the various hydrocarbon conversion processes which may be carried out according to the principles of this invention.

The hydrocarbon feed stocks suitable for conversion to products having lower boiling points in the process of the present invention include hydrocarbon naphthas, gas oils, whether straight-run or cracked, and the heavier residual type oils etc. Specifically, straight-run and/or cracked gas oil boiling above 400° F. comprises an excellent feed stock for the production of gasoline range hydrocarbons.

Preferably, the feed stock is preheated to temperatures of the order of 500° F. to 750° F. but in those cases when higher catalyst to oil weight ratios of the order of from 3 to 15 are employed, cold liquid feed may be introduced directly onto the hot regenerated granular solids introduced into the reactor.

The type of granular solids employed in the process depends, of course, upon the process desired to be carried out. With catalytic cracking of heavy gasolines, gas oil and heavier hydrocarbons, cracking catalysts such as acid treated natural clay, silica-alumina synthetic bead catalyst, and especially the synthetic bead catalyst containing about 0.005% by weight of chromium constitute excellent catalysts in the process of this invention.

When a reforming or aromatization or dehydrogenation of the feed stock and/or the more volatile products produced therefrom is desired, a catalyst may be employed comprising chromium oxide, molybdenum trioxide, or cobalt molybdate. Catalysts comprising mixtures of CoO and MoO₃ or the other well-known catalysts for these reactions may be employed. These catalysts preferably are supported on a carrier such as aluminum oxide, or they may be impregnated directly upon the catalyst having the cracking activity, or a mixture of cracking and reforming catalysts may be used.

When a simultaneous desulfurization is to be carried out, the catalyst preferably comprises cobalt molybdate or mixtures of CoO and MoO₃. These catalysts are also satisfactory for the catalytic denitrogenation of the feed stock or the products produced.

The catalyst to oil ratio as measured from the relative weights of catalyst and oil introduced into the reactor vary, of course, according to the particular reaction to be carried out. In general, values of from about 0.5 to 15.0 may be employed with preferable values being between about 1.0 and 5.0 for catalytic cracking alone. The liquid hourly space velocity (LHSV) at which the product is removed in the recycle gas is below about 1.0, preferable values being between about 0.005 and 0.5. These catalyst to oil ratios and LHSV values also apply to the other processes named above.

One essential step in the process is the countercurrent gas recycle employed in the reactor. The quantity of this

recycle may be between about 50 and 10,000 s. c. f./barrel of feed. The actual values depend largely upon the nature of hydrocarbon conversion process carried out together with the boiling point reduction separation. Recycle rates of between 500 and 2,000 s. c. f./barrel are preferred for straight catalytic cracking, between about 1000 and 4000 s. c. f./barrel for simultaneous cracking and reforming, and between about 750 and 3000 s. c. f./barrel for simultaneous cracking and desulfurization.

The recycle gas employed preferably contains a substantial quantity of hydrogen. The actual concentration of hydrogen in the recycle gas varies with different processes and with different feed stocks. The recycle gas may contain as little as 10% hydrogen and as much as 95% or more hydrogen. With an unsaturated coker pressure distillate the recycle gas contains between about 25% and about 50% hydrogen when catalytic cracking alone is carried out. With saturated feed stocks, that is, for example, a straight-run gas oil, the recycle gas contains from 40% to 80% hydrogen. When the principles of this process are applied to thermal contact coking of heavy oils, the recycle gas desirably contains less hydrogen and may be treated for hydrogen removal. It may be predominately methane and lower boiling hydrocarbon gases.

The operation pressures may vary within wide ranges such as from atmospheric to about 5000 p. s. i. g. With straight catalytic cracking, pressures of the order of above 50 p. s. i. g. are preferred since increased liquid yields and decreased coke laydown is obtained. Pressures between about 100 p. s. i. g. and 250 p. s. i. g. are very effective. However, pressures as high as about 600 p. s. i. g. may be employed. When desulfurization or aromatization or hydrogenation are desired, higher operating pressures are preferable such as between about 500 p. s. i. g. and 2000 p. s. i. g., with pressures of the order of 1000 p. s. i. g. to 1500 p. s. i. g. being preferred.

Operation temperatures again vary depending upon the process and the feed stock. In general, catalysts are introduced into the reactor at temperatures between about 800° F. and 1200° F. and preferably of the order of from 100° F. to as high as 600° F. above the temperature at which the reactor feed is introduced. In straight catalytic cracking, temperatures of between about atmospheric and about 750° F. may be employed for the inlet feed temperature. Preferably, the reactor feed is introduced at about 700° F. with the cracking catalyst entering at from about 700° F. to 1000° F.

The reaction temperatures can only be given as averages since considerable temperature variation occurs within the bed of solids in the reactor as well as varying from one process to another within limits of between about 500° F. and about 1100° F. With catalytic cracking preferred temperatures lie between 750° F. and 950° F., with catalytic reforming preferred temperatures lie between 800° F. and 1000° F., in desulfurization preferred temperatures lie between 750° F. and 950° F., and when thermal contact coking is carried out according to this invention, the reaction temperatures are preferably between about 800° F. and 1100° F. These average reaction temperatures are the temperatures of the granular solids passing through the reaction zones 106 and 108 and the soaking and stripping zone 112 shown in the drawing and are not necessarily the temperatures at which the feed or solids are introduced.

The temperature at which the hydrogen recycle gas is introduced is preferably equal to or somewhat higher than the average reaction temperature within the reactor. Therefore, the recycle gas is preheated to temperatures of between about 700° F. and 1000° F. prior to being introduced into the reaction zone.

The following specific examples are illustrative of the principles of the present invention applied to straight catalytic cracking for the production of gasoline in a typical boiling point reduction process and to such a boiling point reduction process carried out simultaneously

with other hydrocarbon conversion processes listed above for the production of desulfurized products or products containing increased quantities of aromatic hydrocarbons of reduced boiling point.

Example 1

Data for the catalytic cracking of gas oil with synthetic bead cracking catalyst according to the present invention are given below. The feed has a 450° F. to 750° F. boiling range. The fresh feed, flowing at 10,000 barrels per day, is combined with 20,000 barrels per day of oil recycle and is preheated to a temperature of 835° F. and contacted with 460 tons per hour of synthetic alumina-silica bead catalyst for a catalyst to oil ratio of about 2.3. The catalyst is introduced at a temperature of 920° F. The average reaction temperature is about 860° F. The recycle gas rate is 2000 s. c. f./barrel of feed to the reactor. This recycle gas is preheated to a temperature of 900° F. prior to injection into the reactor. The recycle gas contains about 45% hydrogen. The reactor effluent is condensed and fractionated to recover a stream of 400° F. and point gasoline. An 81% by volume yield is obtained, the gasoline product being produced at a rate of 8100 barrels per day. The reactor pressure is maintained at a value of 185 p. s. i. g.

Example 2

A catalytic cracking process according to this invention may be carried out in the manner illustrated in Example 1 by employing 540 tons per hour of acid treated natural clay cracking catalyst. The gasoline yield is 7900 barrels per day under substantially the same reaction conditions as described in Example 1.

Example 3

An aromatization and reforming process may be carried out in the presence of a mixed reforming and cracking catalyst consisting of a silica-alumina carrier containing 10% molybdenum oxide (MoO_3) and synthetic bead catalyst as used in Example 1. The recycle gas rate is 2500 s. c. f./barrel of feed, the feed is a heavy naphthenic gas oil boiling between about 475° F. and 800° F., the average reaction temperature is about 950° F., and the reactor effluent is removed at a temperature of about 870° F. A catalyst to oil ratio on a weight basis of about 2 is employed. The pressure of operation is 225 p. s. i. g. Upon fractionation of the products, a 68% by volume yield of aromatic gasoline containing 6% olefins and 42% aromatics is obtained. A substantial degree of aromatization thus results simultaneously with the boiling point reduction to produce a high quality aromatic and olefin containing gasoline boiling range stock.

Example 4

Comparable results are obtained in the process of Example 3 wherein an acid treated natural clay cracking catalyst is impregnated with molybdenum oxide to promote aromatization reactions.

Example 5

By employing a catalyst having cracking properties and promoted with either about 15% of cobalt molybdate or from 2% to 3% cobalt oxide and from 8% to 12% molybdenum oxide, the continuous desulfurization, denitrogenation and boiling point reduction of 850° F. end point coker distillate containing 1.97% by weight of sulfur and 0.10% by weight of nitrogen is carried out. The operating pressure is 1100 p. s. i. g. and an average reactor temperature of 860° F. is used. The recycle gas rate is 3000 s. c. f./barrel of feed. The reactor effluent is fractionated and a 64% yield of 410° F. end point gasoline is obtained containing 0.13% sulfur and 0.005% nitrogen. The catalyst to oil ratio is 3.

Example 6

Results comparable to those of Example 5 are obtained when a mixed catalyst comprising acid treated natural clay or synthetic bead cracking catalyst and an alumina-cobalt molybdate impregnated desulfurization catalyst is substituted for the catalyst of Example 5.

Example 7

The principles of the present invention are applied to contact coking employing a bed of petroleum coke granules averaging from 0.2 inch to 0.75 inch in diameter and recirculated at 12 tons per hour. Residual oil having an A. P. I. gravity of 11° is heated to a temperature of 700° F. and directly contacted at a rate of 100 barrels per day with a moving bed of coke heated to a temperature of 1050° F. A recycle gas comprising methane and hydrogen is countercurrently recirculated through the coking zone which is maintained at an average temperature of 925° F. The coker distillate yield is 86% by volume and contains an increased proportion of coker gasoline due to the fact that the gasoline vapors produced are removed very rapidly from the reaction zone in the gas recycle.

A particular embodiment of the present invention has been hereinabove described in considerable detail by way of illustration and several specific applications of the principles of this invention have been given to illustrate the application of the invention in various modifications to a few specific processes. It should be understood that various other modifications and adaptations may be made in applying these same principles to other hydrocarbon conversion processes by those skilled in this particular art without departing from the spirit and scope of this invention as set forth in the appended claims.

I claim:

1. A process for the simultaneous boiling point reduction and catalytic conversion of hydrocarbons which comprises passing a moving compact nonfluidized granular adsorptive solid catalyst bed adapted to promote boiling point reduction and catalytic conversion of hydrocarbons downwardly through a reaction zone, at least partly saturating said adsorptive catalyst with liquid hydrocarbon feed whereby said moving bed of catalyst carries said hydrocarbons adsorbed thereon at least part way through said reaction zone in the absence of any substantial downward liquid flow therethrough maintaining a temperature within said reaction zone of between about 500° F. and about 1100° F., flowing a recycle gas containing hydrogen at a rate of between about 50 s. c. f. and about 10,000 s. c. f. per barrel of said hydrocarbon feed through said reaction zone countercurrent to the flow of catalyst therethrough whereby hydrocarbon products of reduced boiling point vaporizing from the liquid hydrocarbon phase contained on said catalyst are swept out of said reaction zone in the vapor phase at a rate sufficient to prevent any substantial degree of further boiling point reduction of the hydrocarbon vapor products after vaporization from said catalyst bed while countercurrently contacting said products and said recycle gas with said catalyst forming a reaction zone effluent, cooling and partially condensing said effluent to separate normally liquid from normally gaseous components thereof, separating said recycle gas containing hydrogen from the normally gaseous fraction, heating at least part of said recycle gas, recirculating the heated recycle gas to said reaction zone, fractionating a fraction of the desired boiling range from the normally liquid fraction of said effluent as a liquid product, and recirculating the higher boiling fraction with said liquid hydrocarbon feed to said reaction zone for retreatment.

2. A process according to claim 1 in combination with the step of passing spent catalyst from said reaction zone through a regeneration zone, contacting said catalyst therein with a regeneration gas containing oxygen to burn

hydrocarbonaceous deposits therefrom forming a regenerated catalyst, returning said regenerated catalyst to said reaction zone, conveying said catalyst between said zones through elongated conveyance and sealing zones therebetween as a moving mass having a bulk density substantially the same as the bulk density of said moving bed, concurrently flowing an inert conveyance fluid through said conveyance zones to generate a substantial pressure differential greater than about 0.1 p. s. i. g. per foot and convey said catalyst while applying a thrust force to catalyst discharging therefrom to prevent fluidization, the substantial pressure differential existing across said conveyance zones effectively sealing said reaction zone from said regeneration zone.

3. A process for simultaneously cracking and catalytically converting hydrocarbon liquids to form hydrocarbon products of lower boiling range and improved quality which comprises passing a moving bed of compact nonfluidized granular adsorptive solid cracking and hydrocarbon conversion catalyst downwardly through a reaction zone, contacting said moving bed of catalyst therein with a liquid stream of hydrocarbon feed in an amount controlled to at least partly saturate said catalyst therewith but insufficient to cause any of said liquid stream to flow downwardly through said catalyst bed moving through said reaction zone, maintaining reaction zone temperatures of between about 500° F. and about 1100° F., passing a countercurrent flow of hydrogen-containing recycle gas at a rate of between about 50 s. c. f. and about 10,000 s. c. f. per barrel of said hydrocarbon feed through said reaction zone whereby cracked hydrocarbons of decreased boiling range vaporizing from the liquid hydrocarbon feed-containing catalyst are passed therewith back through said reaction zone in the vapor phase countercurrent to the catalyst flow at a rate sufficiently high to prevent substantial further cracking of the cracked hydrocarbon vapor and are removed therefrom as a reactor effluent, cooling and partially condensing said effluent to separate normally liquid from normally gaseous components thereof, separating said recycle gas containing hydrogen from the normally gaseous fraction, heating at least part of said recycle gas, recirculating the heated recycle gas to said reaction zone, fractionating a fraction of the desired boiling range from the normally liquid fraction of said effluent as a liquid product, and recirculating the higher boiling fraction with said liquid hydrocarbon feed to said reaction zone for retreatment.

4. A process according to claim 3 wherein the weight ratio of catalyst to hydrocarbon feed is between about 0.5 and about 15.0, said hydrogen-containing recycle gas is introduced into said reaction zone at a temperature greater than the average reaction zone temperature, the reaction zone pressure is maintained between about atmospheric and about 5000 p. s. i. g., said liquid hydrocarbon feed is introduced at a temperature between about 500° F. and about 750° F., and said catalyst is introduced into said reaction zone at a temperature of between about 100° F. and about 500° F. above the feed temperature.

5. A process according to claim 3 wherein the weight ratio of catalyst to said hydrocarbon feed is between about 3.0 and 15, said catalyst is introduced at a temperature between about 800° F. and about 1200° F., and said hydrocarbon feed is introduced unheated.

6. A process according to claim 3 wherein said catalyst comprises a mechanical mixture of hydrocarbon cracking catalyst and a catalyst to promote at least one other hydrocarbon conversion reaction selected from the group consisting of catalytic desulfurization, denitrogenation, isomerization, aromatization, hydrogenation, dehydrogenation, and reforming of hydrocarbons.

7. A process for simultaneously cracking and catalytically desulfurizing hydrocarbon liquids to form a desulfurized hydrocarbon product of reduced boiling point which comprises passing a moving bed of compact non-

fluidized bed of granular adsorptive solid cracking and hydrocarbon desulfurization catalyst downwardly through a reaction zone, contacting said moving bed of catalyst therein with a liquid stream of hydrocarbon feed to adsorb on and at least partly saturate said catalyst with said hydrocarbon liquid prior to movement of the thus treated catalyst bed containing said adsorbed hydrocarbon liquid through said reaction zone, controlling the amount of said feed to prevent any substantial liquid flow downwardly through said adsorptive catalyst bed, maintaining reaction zone temperatures of between about 750° F. and about 950° F., passing a flow of hydrogen containing recycle gas at a rate of between about 750 s. c. f. and about 3000 s. c. f. per barrel of said hydrocarbon feed countercurrently through said reaction zone whereby cracked hydrocarbons of decreased boiling range vaporizing from the liquid hydrocarbon feed-containing catalyst are passed therewith back through said reaction zone in the vapor phase countercurrent to the catalyst flow at a rate sufficient to eliminate any further substantial boiling point reduction reaction and are removed therefrom as a reactor effluent containing a reduced sulfur content, cooling and partially condensing said effluent to separate normally liquid from normally gaseous components thereof, separating said recycle gas containing hydrogen from the normally gaseous fraction, heating at least part of said recycle gas, recirculating the heated recycle gas to said reaction zone, fractionating a fraction of the desired boiling range from the normally liquid fraction of said effluent as a liquid product, and recirculating the higher boiling fraction with said liquid hydrocarbon feed to said reaction zone for retreatment.

8. A process according to claim 7 wherein said desulfurization catalyst is selected from the group consisting of cobalt molybdate and mixtures of cobalt oxide and molybdenum trioxide.

9. A process for simultaneously cracking and catalytically reforming hydrocarbon liquids to form a reformed aromatic hydrocarbon containing product of reduced boiling point which comprises passing a moving compact nonfluidized bed of granular adsorptive solid cracking and hydrocarbon reforming catalyst downwardly through a reaction zone, contacting said moving bed of catalyst therein with a liquid stream of hydrocarbon feed to adsorb on and at least partly saturate said catalyst with said hydrocarbon feed prior to movement of the thus treated catalyst bed containing said adsorbed hydrocarbon liquid through said reaction zone, controlling the rate of liquid hydrocarbon introduction so as to prevent any substantial liquid flow downwardly through said adsorptive catalyst bed, maintaining reaction zone temperatures of between about 800° F. and about 1000° F., passing a flow of hydrogen-containing recycle gas at a rate of between about 1000 s. c. f. and about 4000 s. c. f. per barrel of said hydrocarbon feed countercurrently through said reaction zone whereby cracked hydrocarbons of decreased boiling range vaporizing from the liquid hydrocarbon feed-containing catalyst are passed therewith back through said reaction zone in the vapor phase countercurrent to the catalyst flow and are removed therefrom as a reactor effluent containing aromatic hydrocarbons, cooling and partially condensing said effluent to separate normally liquid from normally gaseous components thereof, separating said recycle gas containing hydrogen from the normally gaseous fraction, heating at least part of said recycle gas, recirculating the heated recycle gas to said reaction zone, fractionating a fraction of the desired boiling range from the normally liquid fraction of said effluent as a liquid product, and recirculating the higher boiling fraction with said liquid hydrocarbon feed to said reaction zone for retreatment.

10. A process according to claim 9 wherein said reforming catalyst is selected from the group consisting of molybdenum trioxide, cobalt molybdate, chromium

oxide, and mixtures of cobalt oxide and molybdenum trioxide.

11. A process for conversion of hydrocarbons in contact with a compact nonfluidized bed of granular adsorptive solids which comprises passing a moving bed of granular solids downwardly by gravity through a reaction zone, contacting said adsorptive solids with a liquid stream of hydrocarbons to be converted whereby said liquid hydrocarbon is adsorbed on and at least partially saturates said adsorptive solids and is carried thereby at least part way through said reaction zone, maintaining hydrocarbon conversion conditions of pressure and temperature within said reaction zone, and passing a countercurrent flow of gas through said reaction zone at a sufficiently high rate to sweep hydrocarbon conversion products of increased volatility escaping into the vapor phase from the liquid phase associated with the solids rapidly from said reaction zone without substantial further reaction thereof.

12. A process for conversion of hydrocarbons to produce products of reduced boiling temperature which comprises passing a moving bed of compact nonfluidized granular adsorptive solids downwardly by gravity through a reaction zone, contacting the moving bed of adsorptive solids with a liquid stream of hydrocarbons to be converted whereby said hydrocarbons are adsorbed thereon so as to at least partially saturate said adsorptive solids and be carried downwardly through said reaction zone by said moving bed in the absence of any substantial concurrent liquid flow therethrough, maintaining hydrocarbon conversion conditions of temperature and pressure therein, and rapidly sweeping hydrocarbon vapor products of reduced boiling temperature vaporizing from said moving bed by passing a flow of low molecular weight gas at a sufficiently high rate countercurrently through said reaction zone to prevent any substantial conversion of said hydrocarbon vapor products subsequent to their vaporization from said moving bed of solids.

13. An improved process for the cracking of liquid hydrocarbons to produce hydrocarbons of decreased boiling points which comprises passing a moving bed of heated nonfluidized granular adsorptive solids downwardly by gravity through a reaction zone, contacting said solids with a heated liquid stream of hydrocarbons to be cracked whereby said hydrocarbons are adsorbed thereon and carried at least part way thereby through said reaction zone, controlling the amount of said liquid stream to prevent any substantial liquid flow downwardly through said moving bed of adsorptive solids, maintaining hydrocarbon cracking temperature conditions within said reaction zone whereby cracked hydrocarbon products are vaporized from said solids and maintaining a sufficiently high rate of a low molecular weight recycle gas flow countercurrently through said moving bed to sweep hydrocarbon vapor products rapidly from said reaction zone to prevent substantial further cracking thereof.

14. A process for catalytic cracking of hydrocarbons which comprises passing a moving bed of nonfluidized adsorptive cracking catalyst downwardly by gravity through a reaction zone, contacting said catalyst with a controlled amount of liquid hydrocarbon feed to be cracked whereby said liquid hydrocarbon is adsorbed on said adsorptive catalyst and movement of said catalyst carries said feed adsorbed thereon downwardly through said zone and whereby no substantial flow of said liquid hydrocarbon through said moving bed results, maintaining a temperature of between about 750° F. and about 950° F. within said reaction zone, passing between about 500 s. c. f. and about 2000 s. c. f. per barrel of feed of a hydrogen-containing recycle gas therethrough countercurrent to said bed of catalyst at a rate sufficient to sweep cracked hydrocarbon vapors therefrom without substantial further cracking thereof, cooling and partially con-

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densing the reaction zone effluent, separating said hydrogen-containing recycle gas therefrom, and recirculating at least part thereof to said reaction zone.

15. A process according to claim 14 wherein said liquid hydrocarbon feed is brought into contact with said catalyst substantially at the point it is introduced into said reaction zone and said reaction zone effluent is removed as a vapor at substantially the same point.

16. A process according to claim 14 wherein said reactor effluent is removed as a vapor at a point adjacent the point at which said catalyst is introduced and said liquid hydrocarbon feed is introduced at an intermediate point within said reaction zone thereby permitting countercurrent contact of fresh cracking catalyst with said recycle gas and cracked hydrocarbons adjacent the reactor effluent removal point.

17. A process according to claim 14 wherein said liquid hydrocarbon feed is introduced adjacent the catalyst inlet into said reaction zone and said reactor effluent is removed at an intermediate point within said reaction zone.

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