Nov. 7, 1967 J. W. PAYNE ET AL 3,351,548

CRACKING WITH CATALYST HAVING CONTROLLED RESIDUAL COKE

Filed June 28, 1965 2 Sheets-Sheet 1

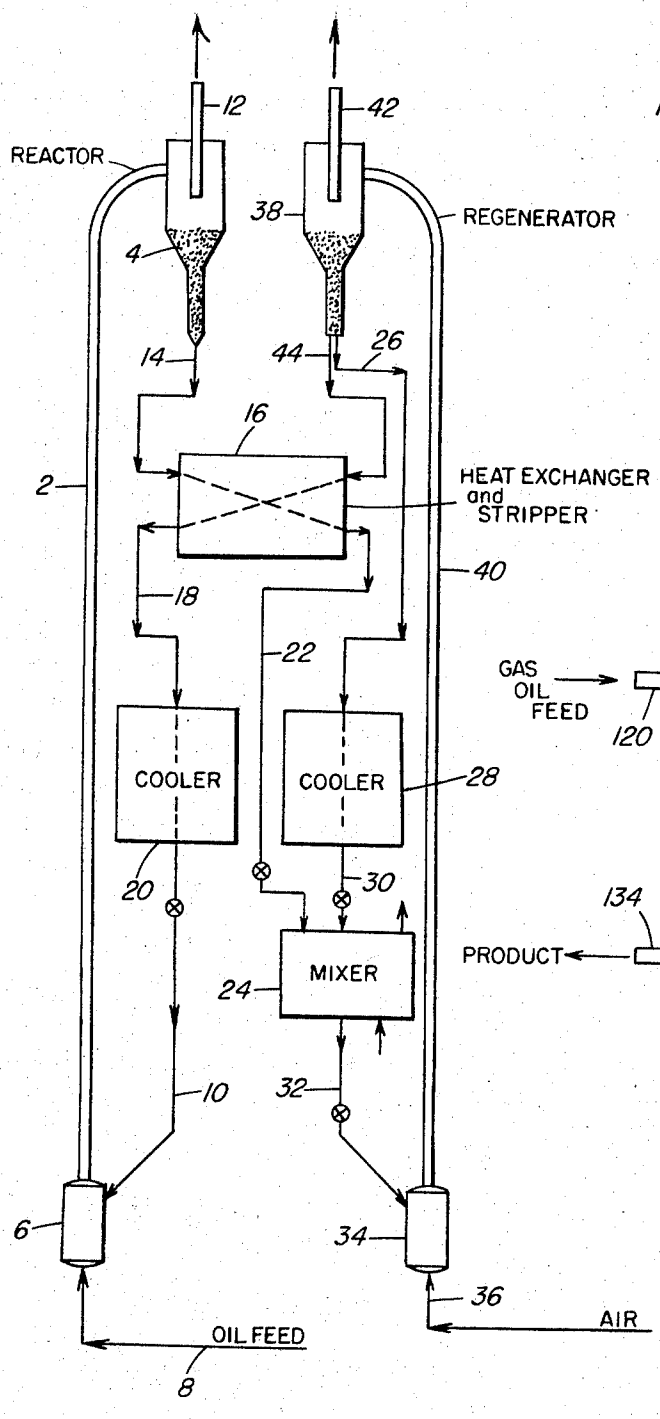
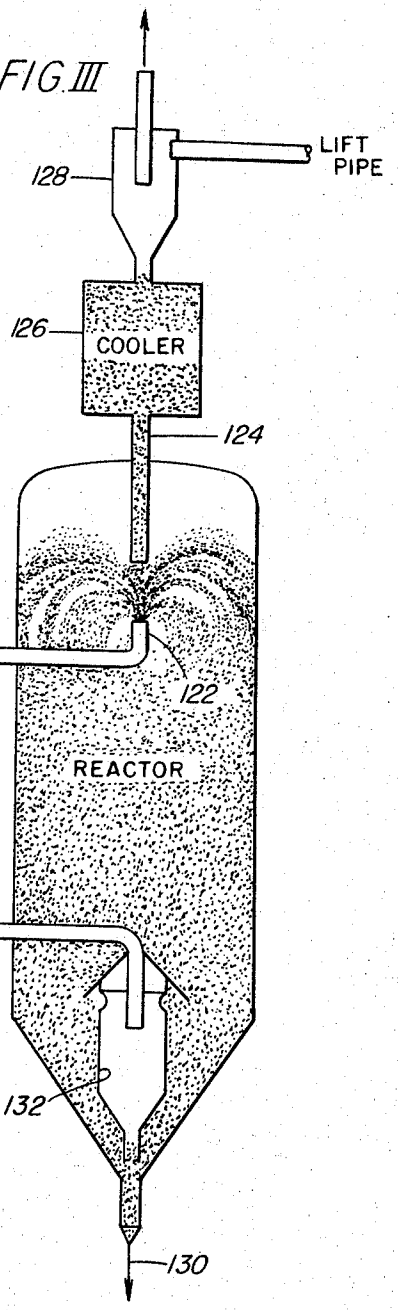


FIG. I

FIG. III



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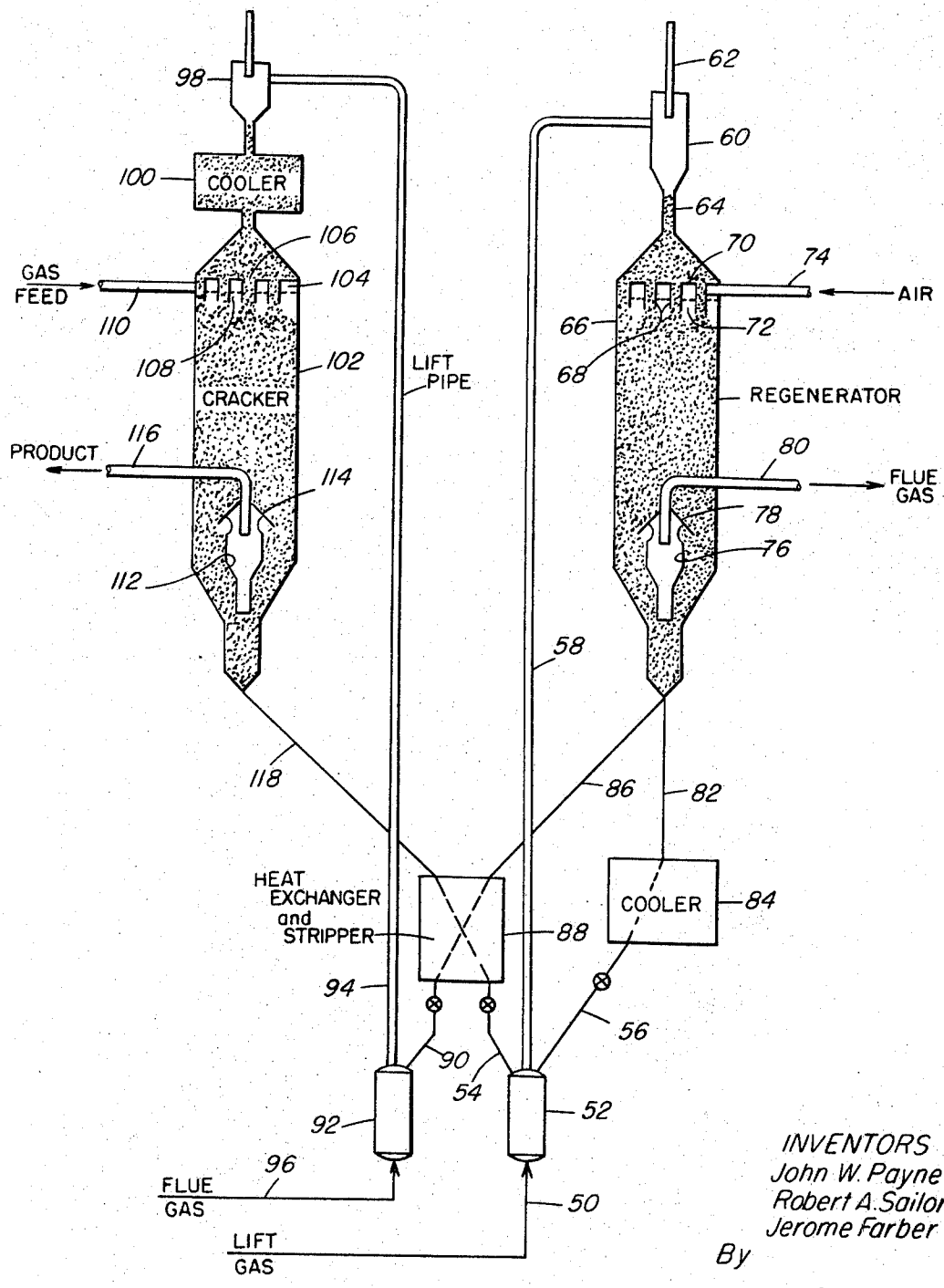
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CRACKING WITH CATALYST HAVING CONTROLLED RESIDUAL COKE

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FIG. II



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3,351,548

CRACKING WITH CATALYST HAVING CONTROLLED RESIDUAL COKE

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2 Claims. (Cl. 208—120)

This invention relates to the conversion of hydrocarbons in the presence of finely divided solid particle material having cracking activity. More particularly, the invention relates to the method for cracking hydrocarbons in the presence of an active alumino-silicate cracking component having an initial activity substantially above that obtainable with an amorphous silica-alumina catalyst. In another aspect, the present invention is concerned with the method of operating a catalytic conversion-regeneration system at substantially elevated temperatures in the presence of a catalyst of controlled activity.

In the cracking of hydrocarbons using the fluidized catalytic cracking technique, the catalyst in the form of a fine powder is circulated through a reaction-cracking zone and then through a regeneration zone for the removal of carbonaceous material deposited on the catalyst during the cracking step. The removal of carbonaceous material by burning heats the catalyst to an elevated temperature suitable for recycle to the regeneration step and use in the cracking step. The amount of catalyst recycled to the hydrocarbon conversion step is generally quite large in fluid systems, being in a range of from about 5 to about 20 times the amount of oil passed to the conversion step on a weight basis and is usually in a quantity sufficient to supply a large portion, if not a major portion of the reaction heat required in the conversion step.

In the catalytic cracking of hydrocarbon oils utilizing the fluid catalyst technique, one of the major problems in such an operation is concerned with regeneration of the catalyst. Regeneration of the catalyst is accomplished by burning carbonaceous deposits from the catalyst with air or oxygen supplemented gaseous material in one or more separate regeneration vessels. Accordingly, the spent catalyst containing deposited carbonaceous material is continuously supplied to a regeneration zone of a sufficient size which can become quite enormous depending upon the quantity of cokey material to be burned. For example, coke burned quantities of the order of about 20,000 and as high as 50,000 pounds of coke per hour are not uncommon in the industry. Therefore, the coke removal from catalyst particles of these magnitudes in a relatively short length of time, has in the past required relatively large and expensive regenerator equipment. Generally the regeneration system holds a major portion of the total catalyst inventory in the catalytic cracking-regeneration system.

In the method and system of this invention, many of the above mentioned and undesired factors have been taken into account so that catalyst inventory, equipment size and actual cost could be significantly reduced for the conversion of the quantity of hydrocarbon feed equal to or above that previously required in prior art systems.

An object of this invention relates to providing an improved system for the conversion of hydrocarbons in the presence of catalytic material having a high activity cracking component.

Another object of this invention relates to providing a system for the conversion of hydrocarbons in the presence of a cracking catalyst comprising a catalytically active crystalline alumino-silicate.

A further object of this invention relates to the method of converting hydrocarbons in a dispersed phase catalytic cracking regeneration system wherein the catalyst inventory and regeneration heat output are significantly below that normally produced.

Other objects of this invention will become more apparent from the following discussion.

This invention relates to forming a dilute suspension of granular catalyst containing residual coke in hydrocarbon vapors at a temperature of at least about 800° F. which suspension is then passed through an elongated reaction zone under conditions to achieve at least about 50% conversion of fresh feed. Spent particles are separated from hydrocarbon vapors and combined with sufficient freshly regenerated catalyst to form a mixture at a temperature of at least 1000° F. and thereafter the catalyst is regenerated under conditions to retain up to about 1.0% by weight, more usually up to about 0.5% by weight of residual coke. The catalyst is thus regenerated and under conditions not to exceed heat damaging temperatures or temperatures substantially above about 1500° F.

In a more specific embodiment, the present invention relates to the method and system for upgrading gas oil and higher boiling hydrocarbons by conversion thereof in the presence of a catalytic material of a particle size avoiding substantial undesired diffusion limitations and comprising an activity monitored crystalline alumino-silicate in combination with selective regeneration of the catalytic material in one or more catalyst contact zones. The contact zones may be in parallel or sequential hydrocarbon flow arrangement for effecting catalytic cracking of hydrocarbons and sequential catalyst flow arrangement for regeneration of the catalyst employed in the conversion steps.

The method and systems of this invention relate to a combination of processing steps which permits a limited and desired removal of carbonaceous material from the hydrocarbon conversion catalyst in one or more regeneration steps by an amount previously determined to maintain the activity of the catalyst within a desired range. Thereafter the thus regenerated catalyst is used for the conversion of hydrocarbons at a catalyst-oil ratio significantly lower than that generally employed in the prior art processes to achieve a conversion of fresh feed of at least 50% and as high as about 65%.

The catalysts useful in a present invention are those comprising catalytically active crystalline alumino-silicates which have an initial relatively high activity substantially above that attributable to an amorphous silica-alumina catalyst and maybe catalysts such as described in copending application Ser. No. 208,512, filed July 9, 1962. It has been found as a result of considerable experimental evidence that the catalyst comprising crystalline alumino-silicates in a catalytically active form are advantageous in view of product selectivity obtained by their use. It has also been noticed that when properly controlled, the gasoline yield to coke make in gas oil cracking has been very substantially more attractive than that obtainable with a more conventional cracking catalyst. Accordingly, the crystalline alumino-silicate catalysts suitable for use in the method and system of this invention are materials of ordered internal structure in which atoms of alkali metal, alkaline earth metal, or metals in replacement thereof are arranged in a definite and consistent crystalline or ordered pattern. These structures in one form or another contain a large number of small cavities interconnected by a number of still smaller openings. However, these cavities and openings are precisely uniform in size. The interstitial dimensions of openings in the crystal lattice of some of the zeolites limit the size and shape of a molecule (hydrocarbon) that can enter the interior of the alumino-silicate and it is such characteristics of crystalline zeolites that has led to their designation "Molecular Sieves."

Zeolites having the above characteristics include both natural and synthetic materials—for example, chabazite,

gmeilinite, mesolite, ptiliolite, mordenite, natrolite, nepheline, sodalite, scapolite, lazurite, leucrite, and cancrinite. Synthetic zeolites may be of the A type, X faujasite type, Y faujasite type, T type, or other well known form of molecular sieve including ZK zeolites such as those described in copending application Ser. No. 134,841 filed Aug. 30, 1961, now Patent No. 3,314,752. Preparation of zeolites of some of these types is well known, having been described in the literature—for example, A type zeolite in U.S. 2,882,243; X faujasite type zeolite in U.S. 2,882,-244; other types of materials in Belgium Patent No. 577,-642 and in U.S. 2,950,952. As initially prepared, the metal of the alumino-silicate is an alkali metal usually sodium. Such alkali metal is subject to base-exchange with a wide variety of other metal ions. The molecular sieve materials so obtained are usually porous, the pores having highly uniform molecular dimensions, generally between about 3 and possibly about 15 Angstrom units in diameter. Each crystal of molecular sieve material contains literally billions of tiny cavities or cages interconnected by openings of unvarying diameter. The size, valence, and amount of the metal ions in the crystal can control the effective diameter of the interconnecting channels.

At the present time, there are commercially available materials of the A series and of the X faujasite series. A synthetic zeolite known as "Molecular Sieve 4A" is a crystalline sodium alumino-silicate having openings of about 4 Angstroms in diameter. In the hydrated form, this material is chemically characterized by the formula:

$$Na_{12}(AlO_2)12(SiO_2)_{12}.27H_2O$$

The synthetic zeolite known as "Molecular Sieve 5A" is a crystalline alumino-silicate salt having openings about 5 Angstroms in diameter and in which substantially all of the 12 ions of sodium in the immediately above formula are replaced by calcium, it being understood that calicum replaces sodium in the ratio of one calcium for two sodium ions. A crystalline sodium alumino-silica having pores approximately 10 Angstroms in diameter is also available commercially under the name of "Molecular Sieve 13X." The letter X is used to distinguish the interatomic structure of this zeolite from that of the A crystals mentioned above. As prepared, the 13X material contains water and has the unit cell formula:

$$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].267H_2O$$

The 13X crystal is structurally identical with faujasite, a naturally occurring zeolite. The synthetic zeolite known as "Molecular Sieve 10X" is a crystalline alumino-silicate salt having openings about 10 Angstroms in diameter and in which a substantial proportion of the sodium ions of the 13X material have been replaced by calcium.

Molecular sieves of the X faujasite series are characterized by the formula:

$$M_{86/n}[(AlO_2)_{86}(SiO_2)_{106}].267H_2O$$

Where M is Na+, Ca++ or other metal ions introduced by replacement thereof and n is the valence of the cation M. The structure consists of a complex assembly of 192 tetrahedra in a large cubic unit cell 24.95 A. on an edge. Both the so-called X and the so-called Y type crystalline alumino-silicates are faujasites and have essentially identically crystal structures. They differ from each other only in that type Y alumino-silicate has a higher SiO_2/Al_2O_3 ratio than the X type alumino-silicate.

The alkali metal generally contained in the naturally occurring or synthetically prepared zeolites described above may be replaced by other metal ions. Replacement is suitably accomplished by contacting the initially formed crystalline alumino-silicate with a solution of an ionizable compound of the metal ion which is to be zeolitically introduced into the molecular sieve structure for a sufficient time to bring about the extent of desired introduction of such ion. After such treatment, the ion exchanged product is water washed, dried and calcined. The extent to which exchange takes place can be controlled. It is essential that the alumino-silicate undergoing activation be a metal containing alumino-silicate.

Naturally occurring or synthetic crystalline alumino-silicates may be treated to provide the superactive alumino-silicates employed in this invention by several means, such as base exchange to replace the sodium with rare earth metal compounds, by base exchange with ammonium compounds followed by heating to drive off NH_3 ions, leaving an H or acid form of alumino-silicates by treatment with mineral acid solutions to arrive at a hydrogen or acid form, and by other means. These treatments may be followed by activity-adjusting treatments, such as steaming, calcining, dilution in a matrix and other means. Explanation of the methods of preparing such catalysts is made in copending application Ser. No. 208,512, filed July 9, 1962, now abandoned.

It should be noted that the catalyst used in this invention may be a composite of the superactive alumino-silicate and a relatively inert matrix material, it may be a mechanical mixture of superactive material particles and matrix material particles, or it may consist only of the superactive catalyst. If the catalyst consists of a composite, it may be produced in the form of relatively small granules. The matrix material may be any hydrous oxide gel, clay or the like. The matrix material used must have a high porosity in order that the reactants may obtain access to the active component in the catalyst composite. A high porosity matrix of the hydrous oxide type may be used in these composite catalysts, such as silica-alumina complexes, silica-magnesia, silica gel, or high porosity clay, alumina, and the like.

The systems of this invention and methods of operation will be more specifically described with reference to the accompanying drawings. The drawings illustrate diagrammatically the major components of the systems and will be described in conjunction with an arrangement designed to process about 30M b.p.d. (30,000 barrels per day), of gas oil feed at a single pass conversion level up to about 65%. By percent conversion we mean 100—volume of insufficiently converted material boiling above gasoline boiling material.

In the arrangement of FIGURE I, the catalyst with hydrocarbon feed or regeneration gas is introduced to the bottom or lower portion of a lift type contact zone through which the catalyst is passed in a relatively dispersed phase condition. Velocities above about 5 feet per second for a contact time in the range of from about 1 to about 30 seconds are used and under conditions which avoid unstable flow of catalyst through the contact zones. Generally, the velocities employed in the conversion zone will be maintained as low as possible, in the range of from about 10 to about 50 feet per second, and high enough to avoid unstable catalyst flow conditions. In the method of this invention it is preferred to employ low catalyst to oil ratios in the range of from about 2 to about 4 pounds of catalyst per pound of oil in the dispersed phase conversion zone under conversion inlet temperature conditions generally above about 900° F. and preferably at least about 950° F. but below about 1050° F. Under these conditions employing a temperature of at least about 900° F. a conversion per pass up to about 60% and preferably about 65% will be obtained of the gas oil feed.

By unstable catalyst flow is meant a condition of catalyst refluxing resulting in excessive catalyst attrition, and/or excess erosion of equipment when operating with finely divided solid particle material. It is preferred in the method and system of this invention to employ a particle size sufficiently small to be suspended in a gasiform material and sufficiently small to avoid undesired diffusion limitations with respect to the cracking and regeneration operations but large enough to flow with mechanical aids. Accordingly, it is preferred to employ a catalyst particle size falling in the range of from about 60 to about 150 mesh size and/or mixtures thereof since particle material

in this size range pours relatively freely and handles in a manner similar to granular contact material.

The catalyst particles recovered from products of conversion and separated from the dispersed phase conversion zone are passed through one or more controlled stages of catalyst regeneration maintained under conditions to effect a limited removal of deposited carbonaceous material from the catalyst particles in any one stage. It is proposed to retain on the catalyst particles from about 0.1% to about 0.5% weight of residual coke. The coke retained on the catalyst particles has been successfully employed to snub the initial relatively high activity of alumino-silicate containing catalyst of the type herein described without substantially reducing the activity to an undesired level. In addition, the regeneration technique employed in accordance with this invention permits operating under conditions and in a manner providing significantly higher burning rates per unit volume of regenerator capacity thereby significantly contributing to reduced regeneration costs and equipment.

The burning rates obtainable in the method and systems of this invention are further enhanced by maintaining the regenerator system under elevated pressure conditions. However the pressure relationship between the reactor and regenerator should be selected which will avoid unduly long seal legs therebetween. It is significant that elevated pressures in the hydrocarbon conversion section can also be used to advantage for causing separated hydrocarbon conversion product vapors to pass from the hydrocarbon conversion zone to and through suitable product recovery equipment. Therefore, it is contemplated employing pressures in the regenerator-conversion sections sufficiently above atmospheric pressure to cause flow of hydrocarbon products from the conversion zone up to about 100 p.s.i.g. and preferably pressures of at least about 10 p.s.i.g.

The regeneration section of the system herein described and its method of operation departs rather significantly from the prior art since it includes among other things the recycle of a portion of the hot regenerated catalyst at substantially its maximum temperature to the inlet of the regeneration section in admixture with spent catalyst rather than the recycling of cooled regenerated catalyst as is well known in the prior art. That is, the regeneration technique herein employed includes the mixing of a sufficient excess of hot regenerated catalyst with spent catalyst recovered from the hydrocarbon conversion step to obtain a mixed catalyst temperature of at least about 1000° F. and preferably at least about 1150° F. It is preferred, therefore, whether employing one or more dispersed phase regeneration zones to limit the upper temperature of the catalyst particles to about 1300° F. even when employing a catalyst mixed temperature passed to the inlet of the regenerator in the range of from about 1150° F. to about 1200° F. In a specific embodiment it is contemplated mixing of the order of about 3 volumes of hot regenerated catalyst containing residual coke thereon with about 1 volume of catalyst recovered from the hydrocarbon conversion step to provide a mixture having a temperature of about 1200° F. The thus formed catalyst mixture is passed to the inlet of the regeneration section and subjected to coke burning conditions in the presence of an oxygen containing gas stream. The catalyst to be regenerated may be passed through a plurality of dispersed phase coke burning zones in the presence of an oxygen containing gas and maintained under conditions limiting the temperature rise encountered in any one zone below about 100° so that an upper catalyst temperature of about 1500° F. will not be exceeded. The regenerated catalyst with residual coke remaining thereon of a desired range is recovered from the regeneration section at a temperature not substantially above about 1500° F. and preferably not substantially above about 1300° F. The recycled regenerated catalyst serves a dual function in the method of this invention which includes providing a desired regenerator inlet temperature and the absorption of heat during burning of cokey deposits on the catalyst particles.

As suggested herein the system and method of operation of this invention may be regarded as a heat deficient operation because of the catalyst selectively employed therein. The hydrocarbon conversion conditions employed limits the coke on catalyst from the conversion operation that is available to heat the catalyst during regeneration to a desired regeneration temperature. However, by mixing a sufficiently large volume of hot regenerated catalyst with a desired amount of preheated and coked catalyst particles obtained from the conversion zone under suitable condition, the regeneration section inlet temperature will be sufficiently elevated to permit achieving a desired high burning rate. To accompiish the above, it was found that the spent conversion catalyst should be heat exchanged indirectly with regeneration catalyst to raise the temperature of the spent catalyst sufficiently so that when it is mixed with the hot regenerated catalyst a mixed temperature of about 1200° F. is obtained. Stripping of the spent conversion catalyst of entrained hydrocarbon vapors can be accomplished also during the indirect heat exchange step. Accordingly, an inert gaseous material is employed to remove varporizible hydrocarbons from the catalyst separated from the dispersed phase hydrocarbon conversion zone and this stripping may be accomplished separately or during the indirect heat exchange step as discussed above.

Having thus provided a general description of the improved method and systems of this invention, reference is now had to the drawing by way of examples which show specific arrangements of up flow and down flow dilute phase catalyst contact sections for practicing the method of this invention.

FIGURE 1 diagrammatically represents in elevation an arrangement of apparatus comprising a system for practicing the method of this invention in a dispersed phase elongated up flow confined contact zones.

FIGURE 2 diagrammatically represents in elevation an arrangement of apparatus comprising a system for practicing the method of this invention which includes dispersed phase down flow contact zones.

FIGURE 3 presents diagrammatically a modification of the contact zones of FIGURE 2 directed to countercurrent impingement contact of reactant and solid particle material.

Referring now to FIGURE 1 by way of example, an arrangement of apparatus is shown comprising an elongated up flow dilute phase confined conversion zone 2 or lift pipe discharging into a separation zone 4 for separating finely divided granular solid contact material from vaparous materials such as vaporous hydrocarbon product material obtained in the conversion step. It is contemplated employing in the arrangement of FIGURE 1 more than 1 elongated confined reaction zone or lift pipe in substantially parallel flow arrangement for freshly regenerated catalytic contact material and sequential flow of insufficiently converted hydrocarbon material. Accordingly, the hydrocarbon conversion products of one conversion stage may be separated in suitable equipment including a product fractionator to recover material boiling above gasoline boiling hydrocarbons which higher boiling material are passed through the second stage of hydrocarbon conversion. That is, an arrangement comprising parallel catalyst flow conversion zones may be employed under conditions for completing conversion in one zone the insufficiently converted hydrocarbons separated from the products of conversion in the adjacent hydrocarbon conversion stage. The hydrocarbon conversion products obtained in the conversion section are passed to and through suitable product recovery processing equipment not shown.

In the specific arrangement and embodiment of FIGURE 1, a hydrocarbon feed such as a gas oil boiling range hydrocarbon feed, is introduced by conduit 8 into

a vaporous hydrocarbon catalyst engaging or contacting zone 6 positioned at the bottom of an elongated conversion zone or lift pipe 2. The hydrocarbon feed is heated to a sufficiently elevated temperature of the order of about 915° F. before entering zone 6. Regenerated catalyst containing a desired amount of residual coke averaging about 0.25% by weight is passed by conduit 10 to the engaging zone 6 wherein a dispersed suspension of catalyst in hydrocarbon vapors is formed and passes upwardly through the conversion lift pipe. In the method of this invention a suspension having a catalyst to oil ratio of about 2:1 and at a mixed inlet temperature at about 950° F. is thereafter passed upwardly through the elongated confined lift pipe conversion zone 2 at a velocity sufficiently high to avoid undesired flow conditions but sufficient to provide a catalyst particle residence time of about 7 seconds. To accomplish the above conversion of hydrocarbon feed and obtain a single pass conversion of the order of about 65%, it is found that an elongated lift pipe about 6 feet in diameter and approximately 97 feet high is sufficient to provide the desired hydrocarbon-catalyst contact time. In this specific embodiment and operating under the above conditions, a catalyst composition is used comprising about 50% rare earth exchange Y type crystalline alumino-silicate combined with a suitable inert binder material to form granular particles of a desired size. A suspension comprising product vapors, insufficiently converted hydrocarbons and catalyst particles is discharged from the elongated conversion zone at a elevated temperature at about 880° F. into a suitable separation zone 4. Since the particle size of the catalytic contact material employed is in the range of from about 60 to about 150 mesh size, elaborate cyclone separator equipment can be substantially avoided to achieve suitable separation and recovery of catalyst particles from hydrocarbon vapors. Accordingly, separation zone 4 may be one or more sequentially connected cyclone separators which will effectively achieve the desired separation of catalyst particles from the hydrocarbon conversion product vapors. Hydrocarbon vapors thus separated and substantially free of entrained catalyst particles are removed from the upper portion of the separation zone 4 by conduit 12. The catalyst particles separated and recovered from the suspension introduced to separator 4 are removed from the lower portion of the separation zone 4 by conduit 14 and passed to a suitable heat exchanger-stripping zone 16. Zone 16 diagrammatically represents means for passing hot regenerated catalyst in indirect heat exchange with catalyst particles recovered from the hydrocargon conversion step. In conjunction with this heat exchange step, it is contemplated providing for stripping of the catalyst with a suitable relatively inert stripping gas to effect more complete removal of any entrained and adsorbed vaporous hydrocarbons remaining with the catalyst particles. Accordingly, the function of zone 16 comprises cooling of regenerated catalyst to a desired lower temperature by giving up heat to the spent or used catalyst passing therethrough before the spent stream of catalyst enters the regeneration section. As suggested above, heating of the used or spent catalyst before entering the regenerating zone is accomplished to provide a necessary and desired temperature level in the system. The stripping gas in indirect heat exchanger 16 also agitates the catalyst thereby improving heat exchange and horizontal flow of catalyst therein.

In the event that zone 16 does not accomplish sufficient cooling of the regenerated catalyst prior to entering the conversion section, the catalyst may be passed by conduit 18 to an additional cooling step identified as cooler 20. In cooler 20 the catalyst is cooled to a temperature more suitable for mixing with the hydrocarbon feed introduced to the inlet of riser 2. In the system of FIGURE 1 it is desired in one preferred embodiment to employ catalyst inlet temperatures to zone 6 not substantially above about 1000° F. and the catalyst cooling steps 16 and 20 when employed together are sufficient to provide desired optimum temperatures. It is contemplated in another embodiment, however, of passing the catalyst in conduit 44 at the elevated regeneration temperature directly to zone 6 thereby by-passing zones 16 and 20.

The contaminated catalyst stripped and subjected to preheating conditions in zone 16 raises the temperature of this catalyst stream to about 900° F. and is thereafter passed by conduit 22 to a mixer zone 24. In mix zone 24, the contaminated catalyst is intimately mixed with a sufficient quantity of freshly regenerated catalyst introduced thereto by conduit 30 to provide a catalyst mixture having a temperature of about 1200° F. Generally, the quantity of freshly regenerated catalyst combined with the contaminated catalyst will be about three-fold greater in order to obtain a desired mixed temperature sufficiently elevated for introduction to the inlet of the regenerated section. In the specific embodiment of FIGURE 1 approximately 1163 tons per hour of regenerated catalyst is combined with about 387 tons per hour of 900° F. spent catalyst to provide approximately 1550 tons per hour of 1200° F. catalyst going to the inlet of the regenerator. In order to obtain desired mixing and adjustment of the catalyst temperature, it is proposed to maintain the catalyst in mixing zone 24 in a relatively dense boiling bed condition prior to withdrawal of the catalyst by conduit 32 for passage to engaging zone 34 at the inlet of the regeneration zone 40. In one embodiment of this invention it is contemplated employing a plurality of relatively dispersed phase regeneration zones arranged for sequential flow of catalytic material therethrough to provide a desired residence time and controlled removal of carbonaceous deposits from the catalyst by burning in an oxygen containing atmosphere. Accordingly, it is proposed to effect the dispersed phase regeneration of the catalyst at velocities of at least about 10 feet per second and preferably at least about 20 feet per second. In any event, whether one or more stages of regeneration is employed, the regeneration of the catalyst is to be conducted with an oxygen containing gas introduced to the inlet of each regeneration stage by a conduit similar to conduit 36. Furthermore, as discussed hereinbefore regeneration of the catalyst is to be effected under conditions which leave a desired residual quantity of coke on the catalyst particles so that the catalyst passed to the inlet of the hydrocarbon conversion stage will have in one specific embodiment an average value of about 0.25% by weight residual coke on the catalyst. The regenerated catalyst whether passed through one or a plurality of stages of dilute phase regeneration is separated from regeneration flue gas at an elevated temperature of about 1300° F. in a suitable separation zone such as zone 38 of FIGURE 1. It is to be understood that separation zone 38 may comprise one or more suitably connected cyclone separators for the recovery of regenerated catalyst from regeneration flue gases. The separated flue gas is thereafter removed from separator zone 38 by conduit 42. The regenerated catalyst collected in the lower portion of separator 38 is withdrawn in desired quantities for passage to mix zone 24 and mix zone 16 by conduits 26 and 44 respectively. This then completes the circulation of catalyst particles within this system in a manner which permits converting hydrocarbons in accordance with at least one method of this invention.

In the event that the regenerated catalyst withdrawn by conduit 26 is at an elevated temperature higher than that desired for introduction to mix zone 24 a cooler 28 is provided to reduce the temperature of the recycled regenerated catalyst to a desired level before being passed by conduit 30 to mix zone 24. By "desired" is meant the temperature, which when mixed with the spent catalyst results in a mixed temperature of about 1200° F. The amount is the quantity which will hold the temperature rise in the regenerator to about 100° F.

FIGURE 2 on the other hand, although suitable for accomplishing the hydrocarbon conversion operation thus described with respect to FIGURE 1, differs therefrom by

the use of a dispersed phase down flow hydrocarbon conversion zone; the use of inert gas such as flue gas to lift regenerated catalyst to the upper portion of the hydrocarbon conversion zone; and a down flow dispersed phase regenerated zone is used in combination with an up flow dispersed phase regeneration stage. In the system of FIGURE 2 an oxygen containing lift gas such as air is introduced by way of conduit **50** to mix zone **52** wherein preheated spent or contaminated catalyst is introduced by conduit **54** and hot regenerated catalyst is introduced by conduit **56** to form a mixture of catalyst particles having a temperature of about 1100° F. Thereafter the regeneration gas containing catalyst particles dispersed therein is passed upwardly from mix zone **52** through the elongated up flow dilute phase regeneration zone **58** under conditions to effect at least partial regeneration of the catalyst therein. The suspension of gaseous materials and catalyst passing upwardly through regenerator **58** is permitted to attain an incremental temperature rise less than about 100° F. before being discharged into separation zone **60**. The partially regenerated catalyst is separated from flue gas in separator **60** and separated flue gas is removed from the upper portion thereof by conduit **62**. Separation zone **60** may comprise a plurality of suitably connected cyclone separators for the separation of solid particle material from gaseous material.

The partially regenerated catalyst at an elevated temperature of the order of about 1200° F. is introduced to the top of a second stage regeneration zone **66** and thereafter caused to shower down through the zone in a relatively dilute phase conditioned by a catalyst distributor arrangement across its upper cross section. The distributor comprises a plurality of open end vertically positioned passageways **68**. The passageways extend through a regeneration gas distributor or plenum chamber **70** also positioned in the upper portion of the regeneration zone adjacent the catalyst distributor means. A partition member or means forming the lower portion of the plenum chamber is a foraminous or perforated baffle member containing openings **72** through which re generation gas is passed after introduction to the plenum chamber by conduit **74**. The thus introduced regeneration gas contacts the catalyst particles discharged from the bottom open end of passageways **68**. The thus discharged partially regenerated particles in admixture with an oxygen containing regeneration gas are maintained under elevated temperature regeneration conditions during dispersed phase down flow to the lower portion of the regeneration zone.

Positioned in the lower portion of the regeneration zone is a flue gas recovery means **76** provided for separating regeneration flue gas from solid particle material. The flue gas recovery means **76** may be substantially any suitable equipment arrangement or means which will effectively recover particles of a size in the range of 60–150 mesh from the recognition flue gases. The separator means **76** specifically shown includes a conical deflector baffle means **78** arranged in a manner to deflect catalyst particles from a separator **76** positioned therebelow. This arrangement will be effective in obtaining the separation of solid particle material from gaseous material prior to the gaseous material being removed from separator means **76**. It is to be understood that separator means **76** may comprise a plurality of suitably arranged cyclone separators. Flue gas is withdrawn from separator means **76** by conduit **80**. The solids separated from the flue gas by baffle **78** and separator means **76** are collected in the bottom lower portion of the regeneration zone as regenerated catalyst particles for future use in the process as herein described. In accordance with this invention the regenerated catalyst particles contain residual coke thereon and are at elevated temperature of the order of about 1300° F. brought about by burning a portion of the deposited cokey material on the catalyst particles. A portion of the thus obtained hot regenerated catalyst particles is withdrawn from the bottom of the regeneration zone by conduit **82**, cooled in cooler **84** if desired, and thereafter passed by conduit **56** to an engaging zone **52**. Another portion of the regenerated catalyst comprising another portion thereof is passed by conduit **86** to an indirect heat exchanger **88**. Heat exchanger zone **88** may be similar in function to zone **16** described with respect to FIGURE 1. On the other hand, it is contemplated in an embodiment of this arrangement of passing catalyst directly from the regeneration zone to an engaging zone **92** thereby bypassing zone **88**. In the arrangement specifically shown in FIGURE 2 the regenerated catalyst passes through heat exchanger **88** and conduit **90** before entering engaging zone **92** about the inlet of riser **94**. In engaging zone **92** there is shown introducing a suitable inert gas such as flue gas by conduit **96**. The flue gas is combined with regenerated catalyst in engaging zone **92** to form a suspension which is thereafter passed upwardly through lift zone or conduit **94** to a suitable separation zone **98** at the discharge end of the lift conduit **94**. In separator zone **98** the regenerated catalyst at a desired elevated temperature is separated from the lift gas employed in lift conduit **94**. The lift gas used may be a cooling gas which is effective in achieving a partial cooling of the regenerated catalyst passed in contact therewith. It is also contemplated employing insufficiently converted vaporous hydrocarbons in place of flue gas under conditions which will effect a desired conversion of the hydrocarbons with simultaneous cooling of the catalyst as herein discussed. Positioned beneath separator zone **98** is a trim cooler zone **100** provided to effect further cooling of the catalyst and/or stripping in the event that vaporous hydrocarbons are employed in lift conduit **94**. Accordingly trim cooler **100** is positioned adjacent separator **98** and may be used as desired to regulate the temperature of the catalyst particles being passed to the conversion zone **102** hereinafter discussed. It is to be understood that separator **98** may be a plurality of separation zones similar to that discussed hereinbefore with respect to separator **60**, **38** and **4**. A plenum chamber **104** is provided across the upper cross sectional area of reactor chamber **102**. In order to achieve a desired distribution of catalyst particles flowing downwardly through reactor **102** in a dispersed phase condition, a plurality of open end passageways **106** are provided which extend through plenum chamber **104** in a manner similar to that described with respect to passageways **68**. Furthermore, the bottom of the plenum chamber **104** is provided with a perforated distributor plate containing openings **108** provided for distributing hydrocarbon vapors in contact with catalyst particles to form a down flowing dispersed phase mixture of catalyst in hydrocarbon vapors. The oil vapors are introduced to plenum chamber **104** by conduit **110**. A separator means **112** provided with baffle **114** similar in configuration to that described with respect to separator **76** in the regenerator is provided in the lower portion of the reactor zone for effecting separation of catalyst particles from hydrocarbon product vapors. Hydrocarbon conversion product vapors are withdrawn from separator **112** by conduit **116** for passage to suitable fractionating equipment not shown. Catalyst particles separated by deflector baffle **114** and separator zone **112** are collected in the bottom lower portion of the reactor zone as a relatively dense mass of catalyst particles. It is to be understood that a suitable stripping gas may be introduced to the lower portion of the reactor to effect at least partial removal of entrained and adsorbed vaporous hydrocarbons from the catalyst particles. Catalyst particles thus collected in the lower portion of reactor **102** are conveyed by conduit **118** to indirect heat exchange and stripping zone **88** which functions in a manner similar to that described with respect to zone **16**, FIGURE 1. Thereafter, the spent catalyst is conveyed to engaging zone **52** thereby completing the cyclic flow of catalyst particles through the system of FIGURE 2.

In the arrangement of FIGURE 2, it is to be understood that catalyst flow to the down flow dispersed phase reactor **102** and regenerator **66** may be controlled by varying the back pressure on the cyclone. Mechanical means may also be employed if preferred.

FIGURE 3 on the other hand presents an arrangement of means which may be more suitable than that specifically described with respect to FIGURE 2 for bringing reactant material in contact with solid particle material. That is, the contact zone of FIGURE 3 which may be employed either as a regeneration zone or a hydrocarbon conversion zone employs the principal of impinging a stream of hydrocarbon vapors of air against a down flowing stream of discharged catalyst particles to provide at least the initial contact therebetween. Experimenting with this method of contacting was found to be very effective for obtaining contact of gasiform material with solid contact material to form a desired dispersion for down flow through the contact zone. Accordingly, FIGURE 3 is similar to FIGURE 2 except for the manner that the gas oil feed is brought in contact with the catalyst. Conduit **120**, the gas oil feed conduit, terminates in an upwardly discharging L shaped nozzle arrangement **122** coaxially aligned with the bottom open end of catalyst conduit **124** extending downwardly from a cooler **126**. Cooler **126** is similar to cooler **100** described with respect to FIGURE 2. The rate of catalyst flow in conduit **124** may be controlled by mechanical means such as a valve either above or in conjunction with a pressure control on the reaction zone. Separator **128** above cooler **126** is similar to separator **98** of FIGURE 2 and catalyst particles are withdrawn from the bottom of the vessel by a conduit **130** which is similar to conduit **118** in FIGURE 2. A separator assembly **132** with gasiform withdrawal conduit **134** is positioned in the lower portion of the vessel and functions in a manner similar to that described with respect to **112** and **114** of FIGURE 2.

Although the arrangement specifically described herein shows different methods for effecting initial contact of gasiform material with solid particle material, there are other methods and means which may be successively employed and it is contemplated employing any one of these known arrangements in the systems of this invention to achieve the desired initial mixing or reactant material with solid particle material. Similarly, many different arrangements are known for separating solid particle material from gasiform material and it is contemplated employing these arrangements, where suitable, in the systems of this invention.

The methods and systems hereinbefore described are of a nature permitting considerable flexibility in their operation. Therefore, it is intended to take advantage of this flexibility in various operating embodiments thereof to obtain, for example, per pass conversion (recycle operations) in a range up to about 30 or 40%. Furthermore, the catalyst regeneration conditions are susceptible to wide variations in operating conditions to permit an exothermic temperature rise of as much as about 200 degrees without causing heat damage to the catalyst. This, therefore, permits considerable variation in the amount of recycled regenerated catalyst for the purpose herein discussed and this variation affects the permissible temperature in the system. It is also contemplated taking advantage of the catalyst heating and/or mixing zones external to the conversion and regeneration zones to achieve desired stripping of catalyst particles to recover, for example, hydrocarbon vapors from the spent catalyst.

It will be immediately recognized from the above discussion that many modifications and permutations may be made to the methods and systems of this invention without departing from the spirit and scope thereof and such variations may not be properly regarded as major departures therefrom.

Having thus provided a description of the methods and systems of this invention and discussed specific embodiments thereof, it is to be understood that no undue restrictions are to be imposed by reason thereof except as defined by the claims.

We claim:

1. A method for cracking hydrocarbons in the presence of finely divided solid crystalline aluminosilicate catalytic material which comprises forming a relatively dilute suspension of crystalline aluminosilicate catalytic material in hydrocarbon vapors at a temperature of at least about 850° F., passing the thus formed suspension through an elongated confined reaction zone under conditions to achieve at least about 50% conversion of fresh feed, separating spent catalytic material with carbon deposits thereon from said conversion products, combining separated spent crystalline aluminosilicate catalytic material with a quantity of hot regenerated catalytic material in an amount sufficient to provide a mixture of catalytic material at a temperature of at least about 1000° F., regenerating all of said mixture of catalytic material with oxygen containing gaseous material under conditions to retain up to about 0.5% by weight of residual coke on said catalytic material without exceeding a temperature of about 1500° F., recycling a sufficient portion of said regenerated catalytic material to form the above mixture with spent catalytic material at a temperature of at least about 1000° F., cooling a portion of said regenerated catalytic material, and employing the thus cooled catalytic material to form said relatively dilute suspension at a temperature of at least about 850° F.

2. A method for cracking hydrocarbons which comprises forming a suspension of hydrocarbon vapor with catalyst particles at a catalyst to oil ratio less than about 4, said catalyst comprising a rare earth exchanged crystalline alumino-silicate combined with from about 0.1% to about 0.5% by weight of residual coke, said suspension being initially formed at a temperature of at least about 950° F. and maintained in a dispersed phase reaction zone for a time sufficient to obtain at least 65% conversion of the fresh feed hydrocarbon vapors, separating said suspension after removal from said reaction zone into hydrocarbon vapors and catalyst particles, recovering said hydrocarbon vapors, combining said separated catalyst particles with sufficient hot regenerated catalyst particles in a dense aerated bed under condition to form a mixture at a temperature of at least about 1200° F., regenerating all of said mixture under conditions to limit the catalyst temperature increase to not substantially more than about 100 degrees, particularly cooling a portion of said regenerated catalyst particles, to form said suspension at a temperature of at least about 950° F. with said partially cooled catalyst particles.

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