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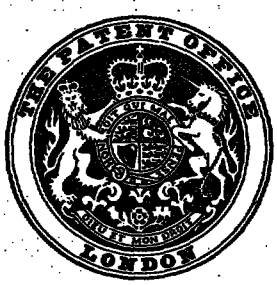

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(54) HYDROCARBON CONVERSION WITH GRAVITY-FLOWING CATALYST PARTICLES

(71) We, UOP INC., a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin and Mt. Prospect Roads, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is directed toward an improved technique for effecting the catalytic conversion of a hydrocarbonaceous charge stock in a multiple-stage reaction system in which (1) the charge stock and hydrogen flow serially through a plurality of catalytic reaction zones and (2) catalyst particles move through each reaction zone via gravity-flow. More particularly, the described process technique is adaptable for utilization in vaporphase systems where the conversion reactions are principally endothermic, especially those where the flow of the hydrocarbonaceous reactant stream, with respect to the direction of movement of the catalyst particles, is cocurrent, and essentially radial.

Various types of multiple-stage reaction systems have found widespread utilization throughout the petroleum and petrochemical industries for effecting multitudinous reactions, especially hydrocarbon conversion reactions. Such reactions are either exothermic or endothermic and may be hydrogen-producing or hydrogen-consuming. Multiple-stage reaction systems are generally of two types: (1) side-by-side configuration with intermediate heating between the reaction zones, in which the reactant stream or mixture flows serially from one zone to another zone; and, (2) a stacked design wherein a singe reaction chamber, or more than one, contains the multiple catalytic contact stages. Such systems, as applied to petroleum refining, have been employed to effect numerous hydrocarbon conversion reactions including those which are prevalent in catalytic reforming, alkylation, ethylbenzene dehydrogenation to produce styrene and other dehydrogenation processes. Our invention is specifically intended for utilization in processes where the conversion reactions are effected in vapor-phase, and where the reaction system exists in side-by-side relation, or where two or more catalytic contact zones are "stacked", and where one or more additional reaction zones may be disposed in side-by-side relationship with the stack. Since catalytic particles which are moving through a reaction system by way of gravity-flow are necessarily moving in a downwardly direction, the present process contemplates the withdrawal of catalyst particles from a bottom portion of one reaction zone and the introduction of fresh or regenerated catalyst particles into the top portion of a second reaction zone. Our invention is also intended to be applied to those reaction systems wherein the catalyst is disposed as an annular bed and the flow of the reactant stream, serially from one zone to another reaction zone, is perpendicular, or radial to the movement of catalyst particles. In the interest of brevity, the following discussion will be directed toward those systems wherein a downwardly moving bed of catalyst particles is employed in the conversion of a hydrocarbonaceous reactant stream, with the catalyst particles being disposed in the form of an annular bed, through which the reactant stream flows laterally and radially.

A radial-flow reaction system generally consists of tubular-form sections, of varying nominal cross-sectional areas, vertically and coaxially disposed to form the reaction vessel. Briefly, the system comprises a reaction chamber containing a coaxially disposed catalyst-retaining screen, having a nominal, internal cross-sectional area less than said chamber, and a perforated centerpipe having a nominal, internal cross-sectional area less

than the catalyst-retaining screen. The reactant stream is introduced in vapor-phase, into the annular-form space created between the inside wall of the chamber and the outside surface of the catalyst-retaining screen. The latter forms an annular-form, catalyst-holding zone with the outside surface of the perforated centerpipe; vaporous reactant flows laterally and radially through the screen and catalyst zone into the centerpipe and out of the reaction chamber. Although the tubular-form configuration of the various reactor components may take any suitable shape—i.e., triangular, square, oblong, diamond, etc.—many design, fabrication and technical considerations indicate the advantages of using components which are substantially circular in cross-section.

Illustrative of a multiple-stage stacked reactor system, to which the present invention is particularly adaptable, is that shown in U.S. Patent No. 3,706,536. As indicated, the transfer of the gravity-flowing catalyst particles from one reaction zone to another, as well as introduction of fresh catalyst particles and withdrawal of "spent" catalyst particles, is effected through the utilization of a plurality of catalyst-transfer conduits. Experience in the use of such systems, as well as those where the reaction zones are disposed in a side-by-side relationship indicates that the high vapor flow through the annular-form catalyst-holding sections result in catalyst particles being pinned in the vicinity of the perforated centerpipe thus creating stagnant catalyst areas where the catalyst particles are prevented from assuming the gravity-flow pattern.

It would be desirable to prevent catalyst "pinning" in a hydrocarbon conversion system in which catalyst particles are movable via gravity-flow, to provide an improved processing technique for use in a multiple-stage, stacked reactor system in wich catalyst particles in each reaction zone move via gravity-flow, and catalyst particles flow from one zone to the next succeeding zone by way of gravity-flow, and/or to provide for the advantageous distribution of the overall heat of reaction in a multiple-stage, substantially endothermic hydrocarbon conversion system effected in vapor-phase and wherein the catalyst particles are downwardly movable via gravity-flow.

According to the present invention there is provided a method of converting a hydrocarbonaceous charge stock in a multiple-stage catalytic conversion system, in which (1) a heated hydrocarbonaceous charge stock and hydrogen flow serially through a plurality of catalytic reaction zones maintained at hydrocarbon conversion conditions; (2) the reaction product effluent from each reaction zone (except the last) is heated prior to the introduction thereof into the next succeeding reaction zone; and (3) catalyst particles move through each reaction zone via gravity-flow, which method comprises the steps of: (a) introducing the heated charge stock and hydrogen into a first reaction zone; (b) heating the effluent from the first reaction zone in admixture with added hydrogen, and then introducing the resulting heated mixture into the second reaction zone; (c) separating the effluent from the last reaction zone to provide (i) a normally liquid product stream and (ii) a hydrogen-rich vaporous phase; (d) admixing a first portion of the hydrogen-rich phase with the charge stock prior to heating (e) admixing a second portion of the hydrogen-rich phase with the effluent from the first reaction zone prior to heating and introduction into the second reaction zone; (f) at least periodically withdrawing catalyst particles from one of the reaction zones; and (g) at least periodically introducing fresh or regenerated catalyst particles into another of the reaction zones.

A specific, preferred embodiment of the present invention is a multiple-stage hydrocarbon catalytic reforming process which comprises the steps of: (a) introducing a heated hydrocarbon charge stock and hydrogen into a first catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow; (b) heating the effluent from the first reaction zone in admixture with added hydrogen and then introducing the heated mixture into a second catalytic reaction zone maintained at reforming conditions; and in which catalyst particles move via gravity-flow; (c) heating the effluent from the second reaction zone in admixture with added hydrogen and then introducing the heated mixture into a third catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow; (d) heating the effluent from the third reaction zone and then introducing the heated effluent into a fourth catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow; (e) separating the effluent from the fourth reaction zone to provide (i) a normally liquid product stream and (ii) a hydrogen-rich vaporous phase; (f) admixing a first portion of the vaporous phase with the charge stock prior to heating, a second portion with the effluent from reaction zone prior to heating and a third portion with the effluent from the second reaction zone prior to heating; (g) at least periodically withdrawing catalyst particles from the fourth reaction zone; and, (h) at least periodically introducing fresh or regenerated catalyst particles into the first reaction zone.

Desirably, the four catalytic reaction zones are disposed as a vertical stack having a

common vertical axis, and catalyst particles move from one reaction zone to the next succeeding reaction zone via gravity-flow.

Candor compels recognition of the fact that various types of hydrocarbon conversion processes utilize multiple-stage reaction systems, either in side-by-side configuration, as a vertically-disposed stack, or a combination of a stacked system in side-by-side relation with one or more separate reaction zones. As applied to petroleum refining, such systems may be employed in a wide variety of hydrocarbon conversion reactions. While our inventive concept is adaptable to many conversion reactions and processes, through the reaction system of which the catalyst particles move via gravity-flow, the same will be additionally described in conjunction with the well-known endothermic catalytic reforming process. Historically, the catalytic reforming process was effected in a non-regenerative, fixed-bed system comprising a plurality of reaction zones in side-by-side relation. When the catalytic composite had become deactivated to the extent that continuous operation was no longer economically feasible, the entire unit was shut-down and the catalyst regenerated in situ. Of more recent vintage is the so-called "swing bed" system in which an extra reactor is substituted for one which is due to be placed off-stream for regeneration purposes. Still more recently, multiple-stage reactor systems have been provided in which the catalyst particles flow, via gravity, through each reaction zone. In a "stacked" system, the catalyst particles also flow downwardly from one catalyst-containing zone to another and ultimately transfer to a suitable regeneration system also preferably functioning with a downwardly moving bed catalyst particles. In effect, the catalyst particles are maintained from one section to another in a manner such that the flow of catalyst particles is continuous, at frequent intervals, or at extended intervals, with the movement being controlled by the quantity of catalyst withdrawn from the last of the series of individual reaction zones.

U.S. Patent No. 3,470,090 illustrates a multiple-stage, side-by-side reaction system with intermediate heating of the reactant stream which flows serially through the individual reaction zones. Catalyst withdrawn from any one of the reaction zones is transported to suitable regeneration facilities. A system of this type can be modified to the extent that the catalyst particles withdrawn from a given reaction zone are transported to the next succeeding reaction zone, while that catalyst withdrawn from the last reaction zone may be transported to a suitable regeneration facilitiy. The necessary modifications can be made in the manner disclosed in U.S. Patent No. 3,839,197, involving an inter-reactor catalyst transport method. Catalyst transfer from the last reaction zone in the plurality to the top of the catalyst regeneration zone is possible through the technique illustrated in U.S. Patent No. 3,839,196.

A stacked reaction configuration is shown in U.S. Patent No. 3,647,680 as a two-stage system having an integrated regeneration facility which receives that catalyst withdrawn from the bottom reaction zone. Similar stacked configurations are illustrated in U.S. Patent No. 3,692,496 and U.S. Patent No. 3,725,249.

U.S. Patent No. 3,725,248 illustrates a multiple-stage system in side-by-side configuration with gravity-flowing catalyst particles being transported from the bottom of one reaction zone to the top of the next succeeding reaction zone, those catalyst particles being removed from the last reaction zone being transferred to suitable regeneration facilities.

As hereinbefore stated, general details of a three reaction zone, stacked system are presented in U.S. Patent No. 3,706,536, which illustrates one type of multiple-stage system to which the present inventive concept is applicable. It should be noted, as generally practiced in a catalytic reforming unit, that each succeeding reaction zone contains a greater volume of catalyst, and that the annular-form catalyst-holding zone is greater in cross-sectional area.

These illustrations are believed to be fairly representative of the art which has developed in the multiple-stage conversion systems wherein catalyst particles are movable through each reaction zone via gravity-flow. Noteworthy is the fact that none recognize the existence of stagnant catalyst areas areas resulting when catalyst particles are pinned to the perforated centerpipe by the radial/lateral vapor flow across the annular-form catalyst bed. Likewise, it is readily ascertained that there is no recognition of splitting the hydrogen flow to alleviate these difficulties and remedy the problem.

U.S. Patent No. 3,864,240 is illustrative of the integration of a reaction system having gravity-flowing catalyst particles with a fixed-bed system. As stated in this reference, one of the advantages resides in revamping an existing three reaction zone, fixed-bed system to conform to the integrated system. In such a modification, it is suggested that a second compressor be added to permit the split-flow of hydrogen-rich recycle gas as also described in U.S. Patent No. 3,516,924. The use of the additional compressor would be to supply the necessary hydrogen recycle to the moving-bed portion of the system, while the original compressor supplies the hydrogen recycle to the plurality of fixed-bed reaction zones. Again, there is no recog-

nition of the difficulties attendant catalyst pinning in the zone where the catalyst particles are movable via gravity-flow. Quite obviously, this pinning problem is non-existent in a fixed-bed reaction system. Furthermore, the moving bed reaction zone must handle all the vaporous material in the system including the recycle hydrogen from its own compressor and the total effluent from the last fixed-bed reaction zone.

Split-flow hydrogen recycle is recognized in the literature directed toward conversion systems in which the reaction zones are of the fixed-bed configuration. For example, U.S. Patent No. 2,938,853 indicates that the separated hydrogen-rich phase may be recycled in part to all the reaction zones where desired. Similarly U.S. Patent No. 3,392,107 illustrates a four, fixed-bed reaction zone system in which the hydrogen recycle is split to the first and the fourth reaction zones in the series. No recycle hydrogen is added to the second and third reaction zones, and the split of the recycle hydrogen is such that approximately one-sixth is introduced into the first reaction zone and the remaining five-sixths is added to the effluent from the third reaction zone prior to the introduction thereof into the last reaction zone.

In brief summation, the prior art which is directed toward moving-bed catalytic conversion systems is not cognizant of the existence of a catalyst pinning problem and its attendant difficulties. Further, the split-flow hydrogen recycle solution, on which the present inventive concept is founded, is not recognized. In the same vane, while some of the prior art directed toward fixed-bed systems indicates an awareness of split-flow hydrogen recycle, in such systems the catalyst pinning problem does not exist.

As hereinbefore set forth, the process encompassed by our inventive concept is suitable for use in hydrocarbon conversion systems characterized as multiple-stage and in which catalytic particles move via gravity-flow in each reaction zone. Furthermore, the present invention is principally intended for utilization in systems where the principal reactions are endothermic, and are effected in vapor-phase operation. Although the following discussion is specifically directed toward catalytic reforming of naphtha boiling range fractions, there is no intent to so limit the present invention. Catalytic reforming, as well as many other processes, has experienced several phases of development currently terminating in a system in which the catalyst beds assume the form of a descending column in one or more reaction vessels. Typically, the catalysts are utilized in spherical form having a nominal diameter ranging from about 1/32-inch to about 5/32-inch in order to offer free-flow characteristics which will neither bridge, nor block the descending column, or columns of catalyst within the overall system. In one such multiple-stage system, the reaction chambers are vertically stacked, and a plurality (generally from 6 to 16) of relatively small diameter conduits are employed to transfer catalyst particles from one reaction zone to the next lower reaction zone (via gravity-flow) and ultimately as withdrawn catalyst from the last reaction zone. The latter are usually transported to the top of a catalyst regeneration facility, also functioning with a descending column of catalyst particles; regenerated catalyst particles are transported to the top of the upper reaction zone of the stack. In order to facilitate and enhance gravity-flow within each reaction vessel, as well as from one to another, it is particularly important that the catalyst particles have a relatively small nominal diameter, and one which is preferably less than about 5/32-inch. In a conversion system having the individual reaction zones in side-by-side relationship, catalyst transport vessels (of the type shown in U.S. Patent No. 3,839,197) are employed in transferring the catalyst particles from the bottom of one zone to the top of the succeeding zone, and from the last reaction zone to the top of the regeneration facility.

Catalytic reforming of naphtha boiling range hydrocarbons, a vapor-phase operation, is effected at conversion conditions which include catalyst bed temperatures in the range of 700°F. to 1020°F; judicious and cautious techniques generally dictate that catalyst temperatures should not substantially exceed a level of 1020°F. Other conditions include a pressure from 50 psig. to 1000 psig., a liquid hourly space velocity (defined as volumes of fresh charge stock per hour, per volume of total catalyst particles) of from 0.2 to 10 and a hydrogen to hydrocarbon mole ratio from 1:1 to 10:1. As those possessing the requisite skill in the refining art are aware, the described continuous regenerative reforming system offers numerous advantages when compared to the prior fixed-bed systems. Among these in the capability of efficient operation at lower pressures—e.g. 50 psig. to about 150 psig.—and higher liquid hourly space velocities—e.g. 3:1 to 8:1. Further, as a result of continuous catalyst regeneration, higher consistent inlet catalyst bed temperatures can be maintained—e.g. 950°F. to 1010°F. There can also exist a corresponding increase in both hydrogen production and hydrogen purity in the recycled vaporous phase from the product separator.

Catalytic reforming reactions are multifarious, and include the dehydrogenation of naphthenes to aromatics, the dehydrocyclization of paraffins to aromatics, the hydro-

cracking of long-chain paraffins into lower-boiling normally-liquid material and, to a certain extent, the isomerization of paraffins. These reactions are effected through the use of one or more Group VIII noble metals (e.g. platinum, irridium, rhodium) combined with a halogen (e.g. chlorine and/or fluorine) and a porous carrier material such as alumina. Recent investigations have indicated that more advantageous results are attainable and enjoyed through the cojoint use of a catalytic modifier; these are generally selected from the group of cobalt, nickel, gallium, germanium, tin, rhenium, vanadium and mixtures thereof. Regardless of the particular selected catalytic composite, the ability to attain the advantages over the common fixed-bed systems is greatly dependent upon achieving acceptable catalyst flow downwardly through the system. Not only must this be substantially uniform throughout the cross-section of the annular catalyst bed, but stagnant areas must be maintained at the most achievable minimum.

Catlytic reforming is a well known process which has been thoroughly described in the literature, having been a commercially important tool of the petroleum refining industry for more than a quarter of a century. One of the many things gleaned from the vast amount of reforming experience and resulting knowledge is the soundness of utilizing multiple stages, each of which contains a different quantity of catalyst, expressed generally as volume percent. The reactant stream, hydrogen and the hydrocarbon feed, flows serially through the reaction zones in order of increasing catalyst volume with, of course, interstage heating. In a three reaction zone system, typical catalyst loadings are: first, 10% to 30%; second, from 20% to 40%; and, third, from 40% to 60%. With respect to a four reaction zone system, suitable catalyst loading would be: first, 5% to 15%; second 15% to 25%; third, 25% to 35%; and, fourth, 35% to 50%. Unequal catalyst distribution, increasing in the serial direction of reactant stream flow, facilitates and enhances the distribution of the reactions and overall heat of reaction.

As hereinbefore stated, catalyst pinning stems primarily from high vapor velocity laterally across the annular-form catalyst-holding zone, this adverse effect increasing in degree as the cross-sectional area and length of the catalyst bed decreases. In multiple-stage catalytic reforming systems, therefore, the effect is most pronounced in the first and second reaction zones (having the smaller annular cross-sectional area), somewhat less in the third reaction zone and of minor consequence in the fourth reaction zone as a result of its length and larger cross-sectional catalyst area. The current operating technique involves separating the effluent from the last reaction zone, in a high-pressure separator at a temperature of 60°F. to 140°F., to provide a normally liquid product stream and a hydrogen-rich vaporous phase. A portion of the latter (the remainder being vented on pressure control) is combined with the fresh charge stock for introduction into a heater to achieve reaction temperature and passed therewith into the first reaction zone. In accordance with the present procedure, not all of the recycled hydrogen-rich phase is introduced into the first reaction zone. A first portion is diverted, and admixed with the first zone effluent, and thet mixture is reheated to reaction temperature by means of an interheater and introduced into the second reaction zone; preferably a second portion is admixed with the second reaction zone effluent, and the mixture is reheated to reaction temperature by means of an interheater and introduced therewith into the third reaction zone. This decreases the total vapor flow in the first and second reaction zones to the extent that catalyst pinning is substantially alleviated.

It is not generally necessary to divert a portion of the recycled hydrogen-rich gas to enter the last or bottom reaction zone. However, this technique may be included as an additional tool for effecting the optimum utilization of the reaction zone interheaters such that the reaction zone inlet temperatures in the plurality of reaction zones can be made to exhibit a substantially equal profile which results in an ascending average catalyst bed temperture through the zones in the direction of reactant stream flow. Average catalyst bed temperatures are principally, but not totally dependent upon the catalyst bed inlet temperatures which are subject to control. An ascending average catalyst bed temperature, achieved via a substantially equal inlet temperature profile is preferred in order to improve selectivity.

When a catalytic reforming system is being designed, the principal considerations constitute a detailed charge stock analysis and the intended octane rating of the normally liquid product. Generally, based upon previous experience, an estimate is prepared which indicates the range of the various operating variables required to maximize the volumetric yield of the desired product. Important aspects of the estimate are, the overall heat of reaction to be anticipated, the recommended catalyst distribution among the plurality of reaction zones in the system and, ultimately, the design capacity of the charge heater and reaction zone interheaters. As hereinbefore stated, when a given unit is in operation, sound technical considerations dictate control of the inlet temperature profile (average catalyst bed temperature profile), consistent with the desired product distribution. These are con-

stantly affected by changes in the composition of the feed stream as well as fluctuations in the flow rate thereof. The added advantage of the present invention resides in the capability to adjust for such changes in feedstock properties, product requirements, and various operating conditions and thus maintain the desired reaction zone temperature profile.

In further describing the present invention, and the method of operation, reference will be made to the accompanying drawing. It is understood that the drawing is presented solely for the purposes of illustration, and the same is not intended to be construed as limiting upon the scope and spirit of our invention as defined by the appended claims. Therefore, miscellaneous appurtenances, not required for a complete understanding of the inventive concept, have been eliminated or reduced in number. Such items are well within the purview of one possessing the requisite skill in the appropriate art. The illustrated embodiment is presented as a simplified schematic flow diagram showing a four reaction zone, stacked catalytic reforming system 1, having a charge heater 12 and reaction zone inter-heaters 16, 20 and 24.

The stacked, gravity-flowing catalyst system 1 is shown as having four individual reaction zones 2, 3, 4 and 5. These are sized both as to length and cross-sectional annular catalyst area such that the distribution of the total catalyst volume is 10%, 15%, 25% and 50%, respectively. In a normal, substantially problem-free operation, fresh or regenerated catalyst particles are introduced through inlet port 6 into the uppermost zone 2, and flow via gravity therefrom into reaction zone 3, from zone 3 into zone 4, from zone 4 into zone 5, and are ultimately withdrawn from the system through a plurality of outlet ports 7. Catalyst particles so removed may be transported to a continuous regeneration zone (not illustrated), or may be stored until a sufficient quantity is available for batchwise regeneration. The rate of catalyst flow through the system, or the period of time required for catalyst particles to be introduced into the system, traverse the four reaction zones and be withdrawn for regeneration is determined by the rate at which the latter is effected. By monitoring various operating parameters while the system is in continuous operation, the catalyst withdrawal rate, or regeneration load can be controlled.

For illustration purposes, it will be presumed that a catalyst pinning problem as hereinbefore described has developed, principally in reaction zones 2 and 3, and somewhat less severe in reaction zone 4. Further, that the distribution of the overall heat of reaction has become detrimental to the optimum operation as a result of both composition change and flow rate of the feed stock introduced through conduit 8. As a result, charge heater 12 is functioning as if it were underdesigned, while interheaters 16 and 20 are performing as if they were overdesigned. With respect to reaction zone 5 and interheater 24, it will be additionally presumed that such difficulties are minimal and do not, therefore, exert a serious detrimental effect upon the operation.

The naphtha boiling range charge stock is introduced via line 8, admixed with a first portion of a hydrogen-rich gaseous phase from line 9 and is introduced into heat exchanger 10. The thus heated mixture continues through line 11 into charge heater 12, wherein the temperature is further elevated to the level necessary to provide the temperature desired at the inlet to the first catalyst bed. The combined charge stock and hydrogen enters the stacked reaction zone system by way of line 13.

The reaction product effluent from catalyst zone 2 is introduced via conduit 14, in admixture with a second portion of hydrogen-rich vaporous phase in line 15, into inter-heater 16 wherein the temperature is increased; the heated mixture is introduced into reaction zone 3 through line 17. Reaction product effluent from zone 3 is withdrawn through conduit 18, admixed with a third portion of hydrogen-rich recycle gas in line 19 and passed into inter-heater 20; the heated mixture is passed via conduit 21 into reaction zone 4. Conduit 22 carries the effluent from reaction zone 4, in admixture with another portion of the hydrogen-rich gaseous phase from line 23, into interheater 24, and the heated mixture is introduced via line 25 into lowermost reaction zone 5. As hereinbefore stated, the catalyst pinning problem is seldom found in the lowermost reaction zone; however, conduit 23 which supplies the hydrogen-rich gas to inter-heater 24 is provided to afford, where needed, an additional tool for maintaining the proper distribution of the overall heat of reaction.

The product effluent from lowermost reaction zone 5 is withdrawn via line 26 and introduced as the heat-exchange medium into heat-exchanger 10. Exiting by way of line 27, the effluent is passed into condenser 28, wherein the temperature is further decreased to a level within the range of about 60°F. to about 140°F., the condensed material passing via line 29 into separator 30. The condensed material is removed through line 31 and transported thereby to suitable fractionation facilities designed to recover the normally liquid product.

A portion of the hydrogen-rich vaporous phase recovered in line 9 is removed from the reforming system through line 32, generally on pressure control. This excess

hydrogen is of value for use in other units of the refinery, particularly those processes in which hydrogen is consumed. A portion of the remaining hydrogen-rich recycle gas in line 9 is diverted through line 15 in an amount to satisfy the total introduced into inter-heaters 16, 20 and 24 through lines 15, 19 and 23, respectively.

Through the implementation of the present invention, as above described, the catalyst pinning problem which adversely affects uniform catalyst flow throughout the system is substantially alleviated, and the entire operation is optimized as a result of the technique which affords utilization of inter-heater duty capacities available as a result of distribution changes in the heat of reaction.

WHAT WE CLAIM IS:—

1. A method of converting a hydrocarbonaceous charge stock in a multiple-stage catalytic conversion system, in which (1) a heated hydrocarbonaceous charge stock and hydrogen flow serially through a plurality of catalytic reaction zones maintained at hydrocarbon conversion conditions; (2) the reaction product effluent from each reaction zone (except the last) is heated prior to the introduction thereof into the next succeeding reaction zone; and (3) catalyst particles move through each reaction zone via gravity-flow, which method comprises the steps of:

(a) introducing the heated charge stock and hydrogen into the first reaction zone;

(b) heating the effluent from the first reaction zone in admixture with added hydrogen, and then introducing the resulting heated mixture into the second reaction zone;

(c) separating the effluent from the last reaction zone to provide (i) a normally liquid product stream and (ii) a hydrogen-rich vaporous phase;

(d) admixing a first portion of the hydrogen-rich phase with said charge stock prior to heating;

(e) admixing a second portion of the hydrogen-rich phase with the effluent from the first reaction zone prior to heating and introduction into the second reaction zone;

(f) at least periodically withdrawing catalyst particles from one of the reaction zones; and

(g) at least periodically introducing fresh or regenerated catalyst particles into another of the reaction zones.

2. A method as claimed in claim 1 wherein the reaction zones are disposed in side-by-side relationship.

3. A method as claimed in claim 1 wherein the reaction zones are stacked and have a common vertical axis.

4. A method as claimed in claim 3 wherein catalyst particles are at least periodically withdrawn from the lowermost reaction zone in said stack and fresh or regenerated catalyst particles are at least periodically introduced into the uppermost reaction zone in said stack.

5. A method as claimed in claim 3 or 4 wherein catalyst particles flow via gravity from one reaction zone to the next lower reaction zone in said stack.

6. A method as claimed in any of claims 1 to 5 wherein portions of the hydrogen-rich phase are admixed with the effluent from each reaction zone, except the last, prior to heating and introduction into the next reaction zone.

7. A method as claimed in any of claims 1 to 5 wherein there are three reaction zones.

8. A method as claimed in any of claims 1 to 5 wherein there are four reaction zones and a portion of the hydrogen-rich phase is admixed with the effluent from the second reaction zone prior to heating and introduction into the third reaction zone.

9. A multiple-stage hydrocarbon catalytic reforming process which comprises the steps of:

(a) introducing a heated hydrocarbon charge stock and hydrogen into a first catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow;

(b) heating the effluent from the first reaction zone in admixture with added hydrogen and then introducing the heated mixture into a second catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow;

(c) heating the effluent from the second reaction zone and then introducing the heated effluent into a third catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow;

(d) separating the effluent from the third reaction zone to provide (i) a normally liquid product stream and (ii) a hydrogen-rich vaporous phase;

(e) admixing a first portion of the vaporous phase with the charge stock prior to heating, and admixing a second portion of the vaporous phase with the effluent from the first reaction zone prior to heating;

(f) at least periodically withdrawing catalyst particles from the third reaction zone; and

(g) at least periodically introducing fresh or regenerated catalyst into the first reaction zone.

10. A multiple-stage hydrocarbon catalytic reforming process which comprises the steps of:

(a) introducing a heated hydrocarbon charge stock and hydrogen into a first catalytic reaction zone maintained at reforming

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hydrogen is of value for use in other units of the refinery, particularly those processes in which hydrogen is consumed. A portion of the remaining hydrogen-rich recycle gas in line 9 is diverted through line 15 in an amount to satisfy the total introduced into inter-heaters 16, 20 and 24 through lines 15, 19 and 23, respectively.

Through the implementation of the present invention, as above described, the catalyst pinning problem which adversely affects uniform catalyst flow throughout the system is substantially alleviated, and the entire operation is optimized as a result of the technique which affords utilization of inter-heater duty capacities available as a result of distribution changes in the heat of reaction.

WHAT WE CLAIM IS:—

1. A method of converting a hydrocarbonaceous charge stock in a multiple-stage catalytic conversion system, in which (1) a heated hydrocarbonaceous charge stock and hydrogen flow serially through a plurality of catalytic reaction zones maintained at hydrocarbon conversion conditions; (2) the reaction product effluent from each reaction zone (except the last) is heated prior to the introduction thereof into the next succeeding reaction zone; and (3) catalyst particles move through each reaction zone via gravity-flow, which method comprises the steps of:

(a) introducing the heated charge stock and hydrogen into the first reaction zone;

(b) heating the effluent from the first reaction zone in admixture with added hydrogen, and then introducing the resulting heated mixture into the second reaction zone;

(c) separating the effluent from the last reaction zone to provide (i) a normally liquid product stream and (ii) a hydrogen-rich vaporous phase;

(d) admixing a first portion of the hydrogen-rich phase with said charge stock prior to heating;

(e) admixing a second portion of the hydrogen-rich phase with the effluent from the first reaction zone prior to heating and introduction into the second reaction zone;

(f) at least periodically withdrawing catalyst particles from one of the reaction zones; and

(g) at least periodically introducing fresh or regenerated catalyst particles into another of the reaction zones.

2. A method as claimed in claim 1 wherein the reaction zones are disposed in side-by-side relationship.

3. A method as claimed in claim 1 wherein the reaction zones are stacked and have a common vertical axis.

4. A method as claimed in claim 3 wherein catalyst particles are at least periodically withdrawn from the lowermost reaction zone in said stack and fresh or regenerated catalyst particles are at least periodically introduced into the uppermost reaction zone in said stack.

5. A method as claimed in claim 3 or 4 wherein catalyst particles flow via gravity from one reaction zone to the next lower reaction zone in said stack.

6. A method as claimed in any of claims 1 to 5 wherein portions of the hydrogen-rich phase are admixed with the effluent from each reaction zone, except the last, prior to heating and introduction into the next reaction zone.

7. A method as claimed in any of claims 1 to 5 wherein there are three reaction zones.

8. A method as claimed in any of claims 1 to 5 wherein there are four reaction zones and a portion of the hydrogen-rich phase is admixed with the effluent from the second reaction zone prior to heating and introduction into the third reaction zone.

9. A multiple-stage hydrocarbon catalytic reforming process which comprises the steps of:

(a) introducing a heated hydrocarbon charge stock and hydrogen into a first catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow;

(b) heating the effluent from the first reaction zone in admixture with added hydrogen and then introducing the heated mixture into a second catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow;

(c) heating the effluent from the second reaction zone and then introducing the heated effluent into a third catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow;

(d) separating the effluent from the third reaction zone to provide (i) a normally liquid product stream and (ii) a hydrogen-rich vaporous phase;

(e) admixing a first portion of the vaporous phase with the charge stock prior to heating, and admixing a second portion of the vaporous phase with the effluent from the first reaction zone prior to heating;

(f) at least periodically withdrawing catalyst particles from the third reaction zone; and

(g) at least periodically introducing fresh or regenerated catalyst into the first reaction zone.

10. A multiple-stage hydrocarbon catalytic reforming process which comprises the steps of:

(a) introducing a heated hydrocarbon charge stock and hydrogen into a first catalytic reaction zone maintained at reforming

conditions and in which catalyst particles move via gravity-flow;

(b) heating the effluent from the first reaction zone in admixture with added hydrogen and then introducing the heated mixture into a second catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow;

(c) heating the effluent from the second reaction zone in admixture with added hydrogen and then introducing the heated mixture into a third catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow;

(d) heating the effluent from the third reaction zone and then introducing the heated effluent into a fourth catalytic reaction zone maintained at reforming conditions and in which catalyst particles move via gravity-flow;

(e) separating the effluent from the fourth reaction zone to provide (i) a normally liquid product stream and (ii) a hydrogen-rich vaporous phase;

(f) admixing a first portion of the vaporous phase with the charge stock prior to heating, a second portion with the effluent from the first reaction zone prior to heating and a third portion with the effluent from the second reaction zone prior to heating;

(g) at least periodically withdrawing catalyst particles from the fourth reaction zone; and

(h) at least periodically introducing fresh or regenerated catalyst particles into the first reaction zone.

11. A process as claimed in claim 10 wherein the four catalytic reaction zones are disposed as a vertical stack having a common vertical axis, and catalyst particles move from one reaction zone to the next succeeding reaction zone via gravity-flow.

12. A method as claimed in claim 1, 9 or 10 carried out substantially as hereinbefore described or as illustrated with reference to the accompanying drawing.

13. A reformate when obtained by a reforming method as claimed in any of claims 1 to 12.

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