June 9, 1964 R. P. VAN DRIESEN 3,136,712

HYDROCRACKING OF HEAVY HYDROCARBON OILS WITH THE USE OF A THERMAL HYDROCRACKING-MULTISTAGE FRACTIONATION ZONE

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Fig 1

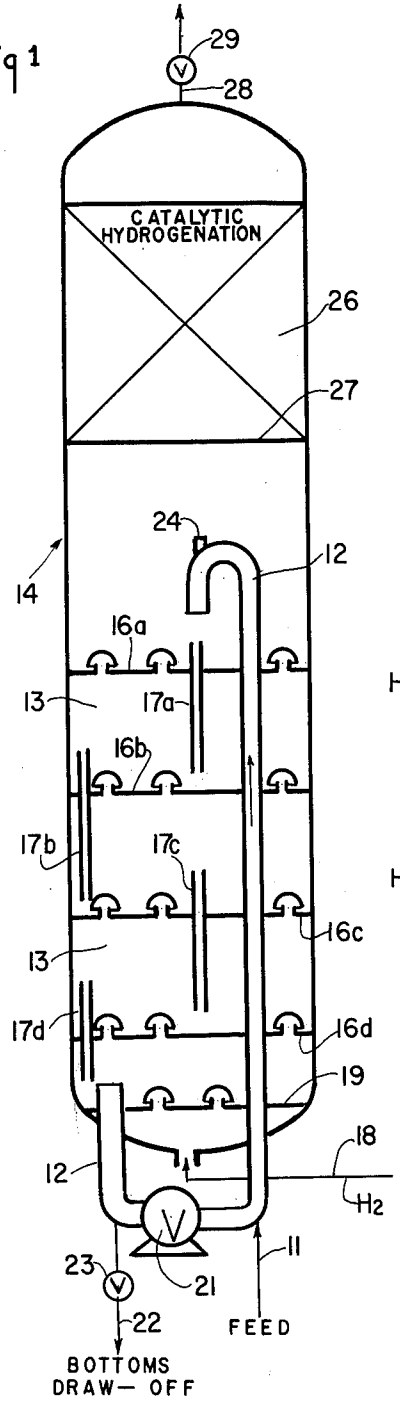
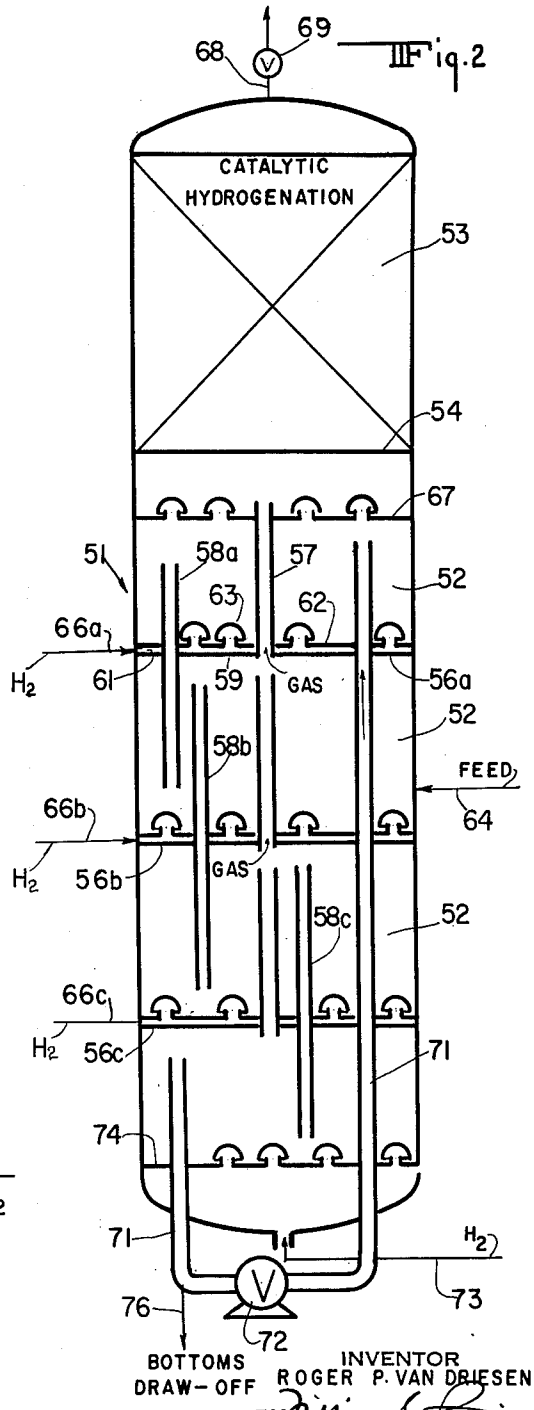


Fig 2



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HYDROCRACKING OF HEAVY HYDROCARBON OILS WITH THE USE OF A THERMAL HYDROCRACKING - MULTISTAGE FRACTIONATION ZONE

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4 Claims. (Cl. 208—58)

This invention relates to the conversion of hydrocarbon oil and more particularly to an improved process for the hydrogenation of relatively high boiling hydrocarbon oils.

Considerable difficulty has been experienced previously in developing processes suitable for the hydrogenation of relatively heavy hydrocarbon oils. For instance, in processes in which the total feed is contacted with a hydrogenation catalyst various impurities in the feed frequently cause premature poisoning of the catalyst and consequently a considerable shortening of the effective life of the catalyst. In order to avoid this difficulty it has previously been suggested that the feed and hydrogen should be passed cocurrently through a thermal hydrogenation zone with the thermal hydrogenation treatment being followed by separation of a relatively light fraction which is then passed through a catalytic hydrogenation zone. These processes, while in some cases avoiding the above mentioned difficulty of catalyst poisoning, have introduced additional difficulties. For instance, when hydrogen and heavy feed oils are passed co-currently through a thermal hydrogenation zone, the lighter fractions of the feed are degraded by being subjected to excessively high temperatures for too long a period of time. This, of course, has an adverse effect on product quality. Also, previously known hydrogenation treatments are not operable with some residual oils and other heavy feeds. A common problem in previously known thermal hydrogenation treatments has been material depositing out in recycle lines. These deposits are due mostly to incompatibility between the lighter fractions present and heavier materials which is immiscible with the lighter fractions. Such deposits are further aggravated if solids such as catalyst or contact material are present. In this case, heavy, immiscible material causes severe agglomeration of the solids particles and may plug recycle lines or reactors. This problem is especially severe at high conversion rates.

It is an object of the present invention to provide an improved process for the hydrogenation of heavy hydrocarbon oils in which the above mentioned difficulties are substantially eliminated.

It is a further object of the invention to provide an improved process for hydrocracking heavy hydrocarbon oils.

This application is a continuation in part of my copending application Serial No. 839,256, filed September 10, 1959, now abandoned, for Counter-Current Two Stage Hydrocracking.

According to a preferred embodiment of the present invention a heavy hydrocarbon oil is subjected to a two stage hydrogenation process. In the first stage the feed oil is passed downwardly through a thermal hydrogenation-fractionation zone which is substantially free of solids. Hydrogen is passed upwardly through the hydrogenation-fractionation zone in countercurrent contact with the feed to partially hydrogenate and vaporize the feed oil. Due to the fractionating effect of the thermal hydrogenation zone as well as the hydrogenating reactions, a heavy liquid fraction collects in the lower portion of the hydrogenation zone. At least a portion of this heavy fraction is recycled from the lower portion of the thermal hydrogenation zone to the upper portion thereof. Vaporous material is passed from the thermal hydrogenation zone to a catalytic hydrogenation zone in which it is contacted with hydrogenation catalyst to further hydrogenate the vaporous material. Product vapors may be withdrawn from the catalytic hydrogenation zone.

For a better understanding of the invention reference should be had to the accompanying drawings in which FIGURE 1 is a somewhat diagrammatic illustration in which equipment is shown in elevation of a suitable arrangement of apparatus for treating hydrocarbon oil in accordance with a preferred embodiment of the invention and FIGURE 2 is a somewhat diagrammatic illustration in which equipment is shown in elevation of another suitable arrangement of apparatus for treating hydrocarbon oil in accordance with another preferred embodiment of the invention.

Referring to FIGURE 1, heavy hydrocarbon feed oil entering through a conduit **11** passes through a conduit **12** into the upper portion of a thermal hydrogenation-fractionation zone **13** of a reaction vessel **14**. In the thermal hydrogenation-fractionation zone **13** the feed oil passes downwardly over a series of conventional bubble cap plates such as **16***a–d* with liquid being passed from one tray to the next by suitable means such as downcomers **17***a–d*. Hydrogen, introduced as through a conduit **18** passes upwardly through the bubble cap plates thereby partially hydrogenating and vaporizing the liquid feed oil. Hydrogen may be distributed within the reaction vessel **14** by suitable means such as a bubble cap plate **19** which allows hydrogen to pass upwardly but has no downcomer for passage of liquid. Recycle liquid is withdrawn from the lower portion of the thermal hydrogenation-fractionation zone **13** through the conduit **12** and recycled to the upper portion of the thermal hydrogenation-fractionation zone as by a recycle pump **21**. A bottom draw off stream is preferably withdrawn as through a conduit **22** and valve **23** and a vent **24** is preferably provided for release of vapors from the recycle conduit **12** as shown in FIGURE 1.

From the thermal hydrogenation-fractionation zone **13** hydrogen and vaporous hydrocarbons preferably pass upwardly through a catalytic hydrogenation zone **26** located in the upper portion of the reaction vessel **14** and containing suitable hydrogenation catalyst, preferably in the form of a fixed catalyst bed supported by a suitable means such as a screen **27**. Operating conditions in the catalytic hydrogenation zone **26** are preferably such that the predominate reaction taking place in the zone **26** is hydrogen addition with relatively little hydrocracking taking place. Various products may be withdrawn as through a conduit **28** and valve **29** for use in any suitable manner.

It should be understood that the operating conditions maintained in the thermal hydrogenation-fractionation zone **13** and the catalytic hydrogenation zone **26** of the reaction vessel **14** may vary widely depending upon the feed and the particular type of hydrogenation reaction desired in each of these zones. Such hydrogenation reactions may include for instance hydrocracking (cracking with hydrogen addition), hydrodesulfurization (desulfurization with hydrogenation), or combinations of these or other hydrogenation reactions. Also, of course, the various operating conditions are to a large extent interdependent and may vary in accordance with well known relationships without adversely affecting reactions taking place in the respective hydrogenation zones of the reaction vessel.

While the present invention is suitable for the treatment of a wide variety of heavy hydrocarbon feed oils, it is

especially advantageous in the hydrocracking of feed oil a substantial part of which boils above about 975° F. at high rates of conversion, e.g., conversion of at least about 75% of such high boiling feed oil into material boiling less than about 975° F. It is in the treatment of such heavy feed oils at such high rates of conversion that previously known hydrogenation processes have encountered particularly serious difficulties of the type described above. For instance, attempts to subject such heavy feed oils to hydrocracking at high rates of conversion in the presence of solid catalyst or contact particles have resulted in severe agglomeration of solids due to the presence in the hydrocracking zone of both solids and immiscible heavy material of the type described above. As discussed in greater detail below, the present invention substantially reduces or eliminates the presence of such immiscible material and where such immiscible material is present, its adverse effect is substantially reduced due to the absence of solids.

For hydrocracking heavy residual hydrocarbon oils of the type described above, it is usually preferred that the predominate reaction in the thermal hydrogenation-fraction zone **13** be hydrocracking together with vaporization of a portion of the feed, while the predominate reactions in the catalytic hydrogenation zone **26** should be hydrogen addition and hydrodesulfurization without excessive amounts of hydrocracking taking place. While any suitable operating conditions may be employed, it is extremely desirable as discussed above to maintain the thermal hydrogenation-fractionation zone substantially free of solids. To do this, the thermal hydrogenation-fractionation zone **13** should preferably be operated under non-coking conditions because the formation of coke would provide solids particles which would agglomerate badly with immiscible heavy material when heavy feed such as that boiling above about 975° F. is used. For this purpose the thermal hydrogenation-fractionation zone is preferably maintained at a temperature below about 900° F., such as between about 800° F. and about 875° F., under a hydrogen partial pressure between about 1500 and about 4000 p.s.i. Temperatures below about 900° F. are necessary to avoid coking if feed boiling above about 975° F. is used. The catalytic hydrogenation zone **26** is preferably maintained at a temperature of between about 600° F. and about 900° F. and is normally maintained at approximately the same total pressure as the thermal hydrogenation-fractionation section as a matter of convenience. An suitable space velocity may be used with space velocities between about 1 and about 10 volumes of feed per volume of reactor space per hour being preferred. Likewise, any suitable rate of hydrogen addition may be used such as between about 2500 and about 10,000 standard cubic feet per barrel of feed. The recycle rate of liquid being recycled from the lower portion of the thermal hydrogenation-fractionation zone to the upper portion thereof may also widely vary with recycle ratios of about 1 to 100, more usually between about 3 and about 40, based on feed being preferred.

The hydrogenation catalyst employed in the catalytic hydrogenation zone **26** may be any suitable hydrogenation catalyst such as cobalt, cobalt-molybdate, tungsten, nickel, molybdenum, iron or the oxides or sulfides of these materials. Such materials may, if desired, be used in conjunction with suitable carriers such as alumina or silica. Such catalysts may be positioned in the catalytic hydrogenation zone by any suitable means but are preferably present in the form of a conventional fixed bed of catalyst pellets.

By introducing the feed into the upper portion of the thermal hydrogenation-fractionation zone **13** as described above and passing hydrogen upwardly in general countercurrent contact with such feed liquid, the lighter fractions of the feed are flashed into vapor at the upper portion of the hydrogenation-fractionation zone and are further stripped from the liquid as it progresses downwardly through this zone by contact with the upwardly flowing hydrogen. By stripping the light ends in this manner the residence time of olefinic materials in the thermal hydrogenation-fractionation zone is substantially decreased and these materials do not achieve as high temperatures as they would in normal operation of previously known hydrogenation processes. Since these olefinic materials are believed to contribute to the formation of the above mentioned immiscible material by initiating condensation and polymerization reactions, the net effect is to substantially reduce the quantities of such immiscible material and thereby allow treatment of heavier feeds at higher conversion rates than would otherwise be possible.

The use of the zone **13** as a combination thermal hydrogenation-fractionation zone in the manner described above has several distinct advantages over hydrogenation followed by fractionation in the manner previously suggested. In addition to providing improved distribution of liquid and vapors within the thermal hydrogenation zone, use of fractionating equipment such as bubble cap plates or perforated plates in such a zone allows direct recycle of a relatively heavier, high boiling fraction than would otherwise be possible without external fractionation. Since hydrocracking is an exothermic reaction, the heat generated in the thermal hydrogenation-fractionation zone (in which hydrocracking is the desired hydrogenation reaction) may be used to advantage to supply the heat of fractionation for fractionating the feed without recourse to pumping or heat exchangers. Also, because of the dual use of the thermal hydrogenation zone for both hydrogenation and fractionation, the hydrogen not only supplies reaction material for the hydrogenation reactions but also serves as stripping gas for gas stripping of the light ends in a manner similar to steam stripping. A further advantage in this mode of operation is that the heavy, unconverted feed material has a relatively long residence time while the lighter materials have a very short residence time once they have been converted to the desirable boiling range by hydrocracking. In addition, the use of a combination thermal hydrogenation-fractionation zone allows application of the highest temperature to the lower portion of the thermal hydrogenation zone where the heaviest material is present and hence where the most severe hydrocracking is desired. In such a hydrogenation-fractionation zone, such as the zone **13** described above, the recycled oil also serves as reflux for the fractionation operation.

In hydrogenating heavy hydrocarbon oil in accordance with this invention a unique and desirable thermal distribution is established. The upper portion of the thermal hydrogenation-fractionation zone is operated at the temperature desired for entrance of hydrocarbon vapors and hydrogen to the catalytic hydrogenation zone. This temperature may be controlled by any suitable means such as by control of the preheating of fresh feed or by temperature control of the recycle stream. As the oil passes downwardly through the thermal hydrogenation-fractionation zone, endothermic vaporization, endothermic cracking and exothermic hydrogenation occur. The exothermic effects are largest near the lower portion of the thermal hydrogenation-fractionation zone since the relatively lighter portions of the fresh feed have been removed by endothermic vaporization in the upper portions of this zone. Also, the hydrogen partial pressure is highest near the lower portion of the thermal hydrogenation-fractionation zone. As a result the feed heats up as it descends through the thermal hydrogenation-fractionation zone and reaches a maximum temperature near the lower portion of this zone. This is highly desirable because hydrocracking requires a higher temperature than non-cracking thermal hydrogenation and a relatively high conversion of heavy feed into lighter products by hydro-

cracking is desired in the lower portion of the thermal hydrogenation-fractionation zone.

The present process provides for withdrawal of a bottoms drawoff stream if desired and, by thus permitting withdrawal of impurities, insures that such impurities do not pass into the catalytic hydrogenation zone. Since only hydrogen and light hydrocarbon fractions pass to the catalytic hydrogenation zone and since, as mentioned above, the hydrocarbon vapors being passed to the catalytic hydrogenation zone have not been subjected to high temperatures for long periods of time, the life of the catalyst is substantially extended. Also, the product produced by the present process is superior to that produced by previous processes in which the light fractions were subject to relatively higher temperatures for relatively longer periods of time.

The apparatus shown in FIGURE 2, while basically similar to that shown in FIGURE 1, is suitable for operation in accordance with another embodiment of the present invention and has certain advantages (described below) over the method and apparatus described above in connection with FIGURE 1.

Referring to FIGURE 2, a reaction vessel **51** is provided having a lower thermal hydrogenation-fractionation zone **52** and an upper catalytic hydrogenation zone **53**. The catalytic hydrogenation zone contains suitable hydrogenation catalyst, preferably in the form of a fixed catalyst bed supported by suitable means such as a screen **54**. The hydrogenation-fractionation zone **52** is provided with a series of trays such as **56***a–c*. Each of these trays is designed in a suitable manner to permit upward passage of gas only through one or more gas conduits, such as a central gas conduit **57**, while permitting downward flow of liquid only through suitable means such as downcomers **58***a–c*. For instance, the tray **56***a* may include a bottom plate **59**, a central open area **61** and a top plate **62** provided with perforations or bubble caps such as **63**. It is readily apparent that such an arrangement will permit passage of gas from the open area **61** upwardly through the bubble caps such as **63** but will not permit passage of gas or liquid through the bottom plate **59** except through the various conduits and downcomers described separately.

In the operation of the apparatus shown in FIGURE 2 heavy hydrocarbon feed oil enters the upper portion of the thermal hydrogenation-fractionation zone **52**, preferably below the upper fractionation stage thereof, as through a conduit **64**. By introducing feed below the uppermost fractionation stage of the thermal hydrogenation-fractionation zone, the uppermost stage may be maintained at a higher temperature by introduction of recycle liquid as described below and more efficient flashing of the light ends from the feed will be obtained. Hydrogen is introduced into the central areas of the fractionating trays **56***a–c* through suitable conduits such as **66***a–c*. Hydrogen from each fractionation tray passes upwardly through the liquid on that tray and then enters the central gas conduit **57** through which all vapors from each fractionation stage of the hydrogenation-fractionation zone **52** are passed to the upper portion of such zone. Such gas, together with vapors formed in the hydrogenation-fractionation zone **52**, may pass through a conventional bubble cap tray **67** and thence upwardly through the catalytic hydrogenation zone **53** described above. From the catalytic hydrogenation zone **53** product vapors may be withdrawn as through a conduit **68** and valve **69**.

Liquid from each fractionating stage of the hydrogenation-fractionation zone **52** passes downwardly through the downcomers **58***a–c* to the lower portion of the zone **52** from which recycle liquid is preferably passed to the upper portion of the thermal hydrogenation-fractionation zone **52** as through a recycle conduit **71** and pump **72**. Additional hydrogen may be introduced into the lower portion of the thermal hydrogenation zone **52** as through a conduit **73** and distributed by suitable means such as a conventional bubble cap plate **74**. A bottom draw off stream is preferably removed as through a conduit **76**.

Apparatus of the type described above in connection with FIGURE 2 is especially advantageous where it is desired to pass a relatively higher boiling fraction of feed materials from the thermal hydrogenation-fractionation zone to the catalytic hydrogenation zone as vapor. By introducing hydrogen separately to each of the fractionation stages in the thermal hydrogenation-fractionation zone and passing vapors from each fractionation stage directly to the catalytic hydrogenation zone, as through the central gas conduit **57**, material which is vaporized in the lower portions of the thermal hydrogenation-fractionation zone does not have the opportunity to recondense in the upper portions of the thermal hydrogenation-fractionation zone as might occur to some extent in the apparatus shown in FIGURE 1. If such vapors should condense out in the gas conduit **57** they would be swept along by entrainment because of the gas velocity in the conduit.

Example

The following specific example illustrates a practical application of the present invention using the process described above and the apparatus shown in FIGURE 1.

In this example a West Texas long residual feed oil is introduced through the conduit **11**. This feed oil has a gravity of 16.8° API and contains 2.5 weight percent sulfur. The Ramsbottom carbon residue test shows 8.6 weight percent carbon and the hydrogen to carbon ratio is 1.6. The upper portion of the thermal hydrogenation-fractionation zone **13** is at a temperature of 800° F. while the lower portion thereof is at a temperature of 850° F. This relatively large temperature difference is, of course, made possible by the use of this zone as a combination hydrogenation-fractionation zone with the use of the bubble cap plates **15***a–d*. The hydrogen partial pressure in the reaction vessel **14** is 2,000 p.s.i., the space velocity 2 volumes per hour per volume and the hydrogen rate 3,000 standard cubic feet per barrel of feed. The catalytic hydrogenation zone **26** contains cobalt-molybdate hydrogenation catalyst on an alumina base. This catalyst is present in the form of a fixed bed of ⅛ inch pellets. The temperature in the catalytic hydrogenation zone **26** is 800° F. Liquid is recycled through the conduit **12** at a rate three times the feed rate. The total collected liquid product from this process has a gravity of 33° API and contains 0.3 weight percent sulfur with the Ramsbottom carbon residue test indicating 1.2 weight percent carbon. The hydrogen to carbon ratio is 1.9 and the volume yield is 107% based on feed with 80% conversion of feed boiling above 975° F. to material boiling below 975° F.

The invention has been shown and described above in connection with preferred embodiments thereof. It will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention and it is intended to cover all such changes and modifications in the appended claims.

I claim:

1. The process for treating heavy hydrocarbon oil which comprises passing said oil downwardly from stage to stage through a thermal hydrogenation-multistage fractionation zone maintained substantially free of solid particles, introducing hydrogen separately into the lower portion of each of the fractionation stages of the thermal hydrogenation-multistage fractionation zone and allowing the same to flow upwardly through the liquid in each of such stages to thereby partially hydrogenate and vaporize the liquid oil in each said stages, withdrawing liquid hydrocarbon from the lower portion of said thermal hydrogenation-multistage fractionation zone and recycling at least a portion of same to the upper portion of said zone, and withdrawing the entire vaporous product from

at least a majority of the fractionation stages of said thermal hydrogenation-multistage fractionation zone without allowing such vaporous product to contact liquid in any other fractionation stage of said zone.

2. The process for hydrogenating heavy hydrocarbon oil boiling about 975° F. which comprises passing said oil downwardly from stage to stage through a thermal hydrocracking-multistage fractionation zone substantially free of solids and maintained under non-coking conditions, separately introducing hydrogen to the lower portion of each of the fractionation stages of said thermal hydrocracking-multistage fractionation zone, allowing said hydrogen to pass upwardly through the hydrocarbon oil in each of said fractionation stages to thereby partially hydrocrack and vaporize said oil and convert at least about 75% of said oil boiling above 975° F. to material boiling below 975° F., withdrawing liquid hydrocarbon from the lower portion of said thermal hydrocracking-multistage fractionation zone and recycling at least a portion of the same to the upper portion of said zone, and separately withdrawing the entire vaporous product from the upper portion of at least a majority of the fractionation stages of said thermal hydrocracking-multistage fractionation zone without allowing such vaporous product to contact liquid in any of the other fractionation stages of the thermal hydrocracking-multistage fractionation zone.

3. The process for hydrogenating heavy hydrocarbon oil boiling above 975° F. which comprises passing said oil downwardly from stage to stage through a thermal hydrocracking-multistage fractionation zone substantially free of solids, separately introducing hydrogen to the lower portion of each of the fractionation stages of said thermal hydrocracking-multistage fractionation zone, allowing said hydrogen to pass upwardly through the hydrocarbon oil in each of said fractionation stages to thereby partially hydrocrack and vaporize said oil and convert at least about 75% of said oil boiling above 975° F. to material boiling below 975° F., withdrawing liquid hydrocarbon from the lower portion of said thermal hydrocracking-multistage fractionation zone and recycling at least a portion of the same to the upper portion of said zone, separately withdrawing the entire vaporous product from the upper portion of at least a majority of the fractionation stages of said thermal hydrocracking-multistage fractionation zone and passing such vaporous product to a catalytic hydrogenation zone without allowing it to contact liquid in any of the other fractionation stages of the thermal hydrocracking-multistage fractionation zone, in said catalytic hydrogenation zone contacting said vaporous material with hydrogenating catalyst to thereby hydrogenate and hydrodesulfurize said vaporous material, and withdrawing vaporous products from said catalytic hydrogenation zone.

4. The process for hydrocracking heavy hydrocarbon oil boiling above 975° F. which comprises passing said oil downwardly from stage to stage through a thermal hydrocracking-multistage fractionation zone susbtantially free of solids and maintained under non-coking conditions, including a temperature of less than 900° F., said feed oil being introduced into the upper portion of said zone below the uppermost fractionation stage thereof, separately introducing hydrogen to the lower portion of each of the fractionation stages of said thermal hydrocracking-multistage fractionation zone, allowing said hydrogen to pass upwardly through the hydrocarbon oil in each of said fractionation stages to thereby partially hydrocrack and vaporize said oil and convert at least about 75% of said oil boiling above 975° F. to material boiling below 975° F., withdrawing liquid hydrocarbon from the lower portion of said thermal hydrocracking-multistage fractionation zone and recycling at least a portion of such vaporous product to a fractionation stage in the upper portion of said zone above the fractionation stage into which the feed oil is introduced, separately withdrawing the entire vaporous product from the upper portion of each of the fractionation stages of said thermal hydrocracking-multistage fractionation zone and passing same to a catalytic hydrogenation zone without allowing it to contact liquid in any of the other fractionation stages of the thermal hydrocracking-multistage fractionation zone, in said catalytic hydrogenation zone contacting said vaporous material with hydrogenating catalyst to thereby hydrogenate and hydrodesulfurize said vaporous material, and withdrawing vaporous products from said catalytic hydrogenation zone.

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CERTIFICATE OF CORRECTION

Patent No. 3,136,712 June 9, 1964

Roger P. Van Driesen

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, lines 22 and 23, for "hydrogenation-fraction" read -- hydrogenation-fractionation --; line 48, for "An" read -- Any --; column 8, line 26, for "such" read -- same --; line 27, strike out "vaporous product --; line 32, for "same" read -- such vaporous product --.

Signed and sealed this 20th day of October 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents