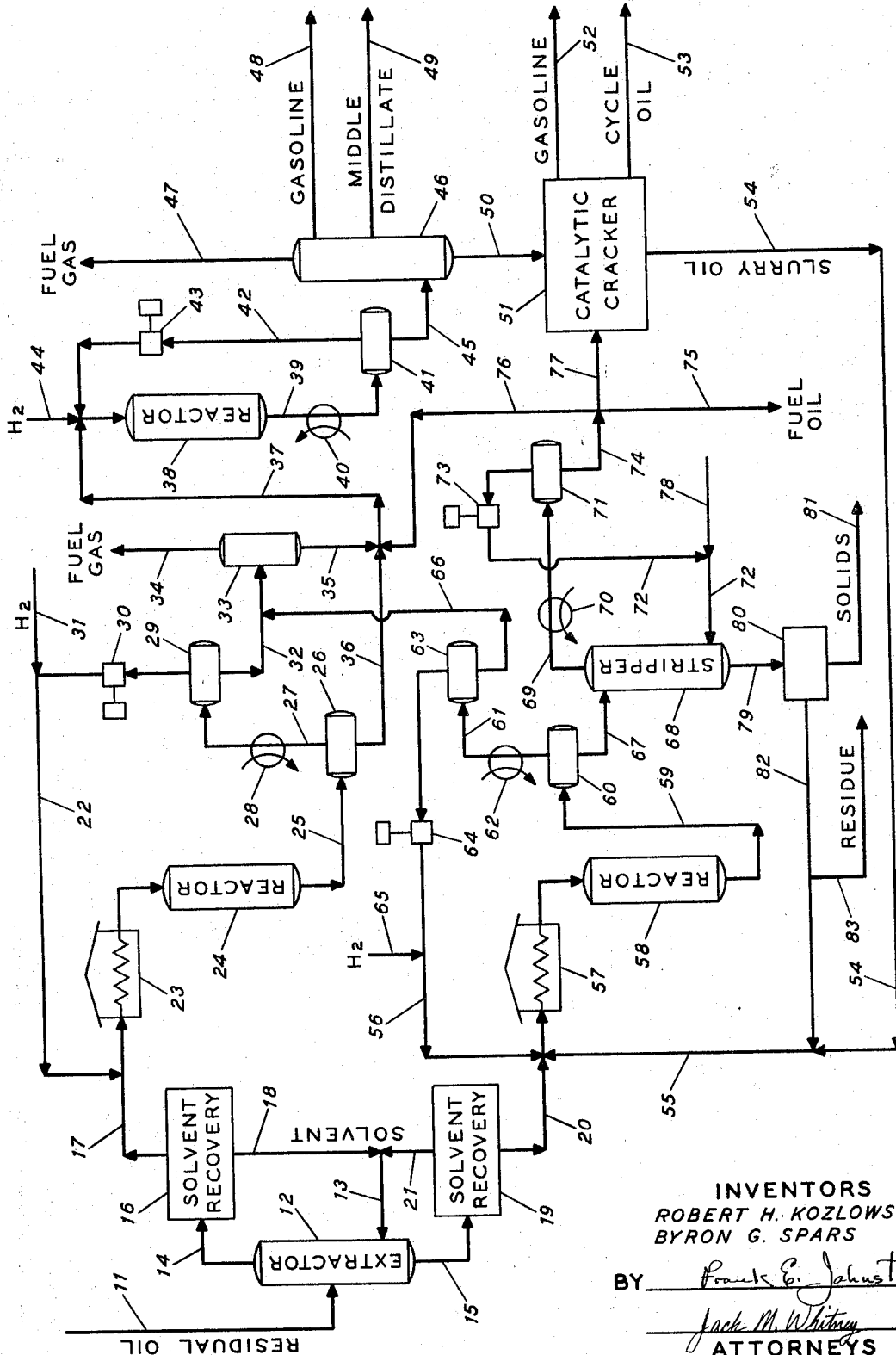


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CONVERSION OF RESIDUA TO PRODUCE MIDDLE
DISTILLATE OILS AND GASOLINE
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INVENTORS
ROBERT H. KOZLOWSKI
BYRON G. SPARS

BY Frank E. Johnston
Jack M. Whitney
ATTORNEYS

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CONVERSION OF RESIDUA TO PRODUCE MIDDLE DISTILLATE OILS AND GASOLINE

Robert H. Kozlowski, Berkeley, and Byron G. Spars, Mill Valley, Calif., assignors to Chevron Research Company, a corporation of Delaware
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This application is a continuation-in-part of our copending application Serial No. 372,448, filed June 6, 1964.

This invention relates to processes for converting the highest boiling portions of crude petroleum and like hydrocarbonaceous materials to lower boiling distillate oils. More particularly, the invention relates to processes for converting high boiling oils to lower boiling oils by the combined actions of hydrogen and elevated temperature.

Since crude petroleum and similar oils derived from carbonaceous deposits of ancient origin are composed primarily of materials boiling above about 700° F., but the materials boiling below about 700° F. have the greatest economic value, it is desired to convert the higher boiling materials to lower boiling materials. Many methods are available for converting the distillate portion, i.e., hydrocarbon oils boiling up to an end point of about 1000° F., to lower boiling distillates, but the problem remains how to convert efficiently the asphaltic residuum or remainder boiling above about 1000° F. This residuum generally contains asphaltenes, metal compounds, and other nonhydrocarbon contaminants.

In our aforementioned copending application there is disclosed a thermal hydrocracking process employing an active hydrogenation catalyst, whereby whole residuum, deasphalted residuum, or the asphaltic residue from deasphalting can be nearly completely converted to distillates without forming coke or oil-insoluble solids. It is found, however, that if the feed contains large amounts of metal compounds the catalyst bed can be rapidly plugged with metal deposits unless guard chambers or other means are provided for preremoval of metals. Where guard chambers containing metal-collecting particles are used, the frequency with which the collected metals must be cleaned out makes the process less attractive for treating high metal content residuums.

This invention is concerned with providing a process whereby a greater portion of residuum can be converted to distillates in a new and more effective manner.

Briefly, in accordance with the present invention, hydrocarbon residuum is first separated by solvent extraction into nonasphaltic residual oil and asphaltic residue. Hydrogen and the nonasphaltic residual oil are passed through a first hydrocracking reaction zone at elevated temperature and pressure, while hydrogen and the asphaltic residue are passed through a second, separate, thermal hydrocracking reaction zone at elevated temperature and pressure. Normally liquid distillate oils having gaseous hydrocarbons dissolved therein are separated from the hydrogen-rich vapor effluents of the respective zones. After freeing the distillate oils of dissolved normally gaseous hydrocarbons, at least a portion of the distillates are passed to a catalytic hydroconversion reaction zone with hydrogen to contact therein a sulfactive hydrogenation catalyst at elevated temperature and pressure. Hydrofined distillate oils are recovered from the catalytic hydroconversion zone.

In addition to the hydrogen-rich vapor effluents of each of the hydrocracking reaction zones, there are obtained liquid residual oil effluents. The liquid residual oil effluent of the first hydrocracking zone, wherein the nonasphaltic residual oil feed was treated, is also passed to the catalytic hydroconversion zone. The liquid residual oil effluent of

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the second, thermal, hydrocracking zone, wherein the asphaltic residue was treated, is not passed to the catalytic hydroconversion zone, but additional distillate oil may be stripped from this liquid residual oil effluent to obtain distillate oil which is also passed to the catalytic hydroconversion zone. In these latter cases there is obtained a hydrofined residual oil which can be recovered from the catalytic hydroconversion zone in addition to the hydrofined distillates, and the hydrofined residual oil is passed to a catalytic cracking process.

Where the catalytic cracking process employs a circulating powdered or fluidized cracking catalyst, there is obtained a slurry oil comprising heavy cracked oil containing entrained catalyst fines effluent of the cracking process. It is found highly advantageous to pass this heavy cracked oil containing entrained cracking catalyst fines also through the second thermal hydrocracking reaction zone for treating along with the asphaltic residue. The entrained cracking catalyst fines can then be removed from a liquid residual oil recycle stream in the second thermal hydrocracking zone, or from the bottoms product thereof.

In the attached drawing is shown a flow diagram illustrating a preferred mode of carrying out the invention, which will be described in more detail hereinafter.

The feed to the process of this invention may be any residual oil, by which is meant oil boiling at least in large part above 1000° F. and containing asphaltic and other contaminants including metal compounds. Thus, the feed may be crude petroleum, atmospheric or vacuum reduced crude, residuum stripper bottoms, or similar materials. Preferably, however, the feed oil is a vacuum reduced crude from which the maximum amount of metal-free distillate oil has already been recovered, so that the oil boils substantially entirely above about 900° F.

The feed is separated by solvent extraction in a known manner with solvents selective on the basis of polarity and/or molecular weight so as to obtain a nonasphaltic residual oil, which should not contain more than about 40 p.p.m. of metals, and an asphaltic residue in which metal compounds are concentrated. Thus, the extraction can be carried out by using a liquid lower alkane such as propane, butane, pentane, and mixtures thereof, at elevated temperature and at near the critical pressure of the solvent or mixed solvents to obtain an extract phase, comprising most of the solvent and the nonasphaltic residual oil, and a raffinate phase comprising the asphaltic residue and a minor amount of solvent. The separation achieved by lower alkane solvents is in large measure on the basis of polarity, but a separation based on molecular weight is also accomplished. Accordingly, while the extracted nonasphaltic oil will generally be lighter than the asphaltic residue, it will still contain residual materials boiling above 1000° F. which cannot be recovered by vacuum distillation.

Other solvent systems may be used to accomplish the separation, including solvents which will preferentially dissolve the asphaltenes and similar condensed aromatics, and also metal compounds, so that the asphaltic residue is obtained in the extract phase and the nonasphaltic residual oil is the raffinate. In any case, extraction conditions including solvent-to-oil ratio are controlled so that the nonasphaltic residual oil has a relatively low metal content, the metal compounds being concentrated in the asphaltic residue. Also, the solvent or solvents will be recovered from the respective phases and recycled for reuse.

The hydrocracking zones in which the nonasphaltic residual oil and the asphaltic residue are separately treated may be operated in substantially the same manner, but advantages are obtained if the thermal hydrocracking zone through which the asphaltic residue is passed is op-

erated in a somewhat different manner, as indicated hereinafter. In each case the oils are treated with a large excess of from 1,000 to 15,000 s.c.f. of hydrogen per barrel, at elevated temperatures of 750–900° F. and elevated pressures of 500–5,000 p.s.i.g., with a relatively long contact time of 0.1–2 LHSV based on reactor volume and residual oil volume. Each reaction chamber may be an empty cylinder or may be comprised of multiple series or parallel tubes, or it may contain inert refractory contacting materials for vapor and liquid distribution and contacting. The first hydrocracking reaction zone, through which the nonasphaltic residual oil is passed, may be operated in accordance with the procedures disclosed in our aforementioned copending application, using an active hydrogenation catalyst, or a nitrogen-and-sulfur-insensitive hydrocracking catalyst, in which cases high conversions of 80 to 95% may be achieved. The reaction zone through which the asphaltic residue is passed is best operated without any hydrogenation catalyst. It is found preferable that the conversion of the asphaltic residual oils to distillates boiling below 1000° F. be limited to less than about 60 volume percent, preferably to in the range 30–50 volume percent, and conversion of the nonasphaltic oil should be similarly limited if a catalyst is not used. The units can then be operated continuously without danger of plugging by the coke formation which can occur at excessively high conversions. The oil and hydrogen may be passed upwards or downwards through the respective reaction chambers, or in opposite directions, but in any event there will be obtained from each zone both a hydrogen-rich vapor effluent and a liquid residual oil effluent, as complete conversion of the residual oils is not achieved.

The hydrogen-rich vapor effluents of the respective hydrocracking zones are separately cooled to condense the normally liquid distillates contained therein, which distillates will accordingly dissolve normally gaseous hydrocarbons present. There are thereby obtained separate hydrogen-rich gas streams which can be recycled to the respective reaction zones, with additional makeup hydrogen added. The provision of separate hydrocracking zones applied to the separated portions of the residual oil feed is particularly advantageous in this respect in that the purity of hydrogen-rich recycle gas to the respective hydrocracking zones can be independently regulated to obtain optimal operation in each zone. Thus, in the hydrocracking zone wherein the nonasphaltic residual oil is converted a high per-pass conversion can be accomplished, which results in the production of greater amounts of normally gaseous by-products, but the reduced hydrogen purity in that zone does not have as adverse an effect as compared to in the thermal hydrocracking zone wherein the asphaltic residue is treated. In the thermal hydrocracking zone wherein the asphaltic oil is treated it appears that greater amounts of olefinic and other deleterious light hydrocarbon by-products are produced at high conversions, which material is included in the recycle gas and adversely affects the hydrocracking so as to cause undesired coke formation. Accordingly, in the second thermal hydrocracking zone a lower per-pass conversion may be taken so as to obtain higher purity recycle hydrogen.

The normally liquid distillates condensed from the vapor effluents of the respective hydrocracking zones are combined, freed of dissolved light hydrocarbons, and then passed through a catalytic hydroconversion reaction zone along with the liquid residual oil effluent of the first hydrocracking zone. The catalytic hydroconversion zone is operated primarily for hydrogenation at lower temperatures of 550–800° F. as compared to the higher temperatures used in the hydrocracking zones, and employs a sulfative hydrogenation catalyst. The catalyst usable comprise Group VI metals and compounds thereof, such as the oxides and sulfides, together with Group VIII metals or compounds thereof, such as the oxides or sulfides, associated with porous refractory oxides acting as a support,

such as alumina, silica-alumina or silica-magnesia. Especially suitable catalysts comprise nickel and molybdenum or tungsten intimately dispersed in refractory oxide carriers. The oils are passed with excess hydrogen in the amount of 1,000–15,000 s.c.f. per barrel at elevated pressure of 1,000–4,000 p.s.i.g. through a reaction zone containing the catalyst at space velocities of 0.2–10 LHSV. The purposes of this contacting include to convert hetero-organic compounds of oxygen, sulfur, and nitrogen to the by-products H_2O , H_2S , and NH_3 , and to hydrogenate unsaturated by-products of the thermal hydrocracking. The contacting may also accomplish substantial catalytic hydrocracking of the residual oil to distillates. Additionally, the small amount of metal compounds in the residual oil is desirably converted, the metals depositing on the catalyst, whereby the product hydrogenated residual oil is an improved feed for catalytic cracking. The amount of metals permissible in the feed to the catalytic hydrogenation zone, however, is limited to less than 30 p.p.m. and desirably to not over 10 p.p.m. because the metals will deposit on the catalyst. It is desirable that the process be carried out continuously for a long on-stream time of at least 1,000 hours, and desirably of 2,000 hours, which is not possible if excessive amounts of metals deposit in and around the catalyst particles so as to plug up the pores and interstices.

Thus, while the distillate oils contained in the vapor effluents of both the first and second hydrocracking zones, and the residual oil effluent of the first hydrocracking zone, are passed to the catalytic hydroconversion zone, the residual oil effluent of the second hydrocracking zone is differently treated. A portion of this residual oil effluent of the second, thermal, hydrocracking zone may be recycled to that zone, or may be withdrawn as a fuel oil product, but in accordance with the preferred mode of the present invention the residual oil is passed to a stripping zone wherein additional distillate oil is stripped from the liquid effluent at elevated temperature and pressure substantially as used in the thermal hydrocracking zone, employing at least 2,000 s.c.f. of hydrogen-rich stripping gas per barrel of liquid. It is found that substantial amounts of additional distillate oil having an end boiling point of up to 950° F. can be recovered from the liquid residual oil effluent of the second thermal hydrocracking zone in this manner. The distillate oils so recovered can be condensed from the hydrogen-rich stripping gas, which is recycled for reuse as stripping gas with additional makeup hydrogen as required, and the recovered distillate oil can then be further treated in several ways. The distillate oil has improved fuel oil properties as compared to the original residual oil feed, and accordingly a portion thereof may be recovered directly as fuel oil. Also, it is found that the metal compounds present in the asphaltic residue treated in the second thermal hydrocracking zone are effectively cracked at the elevated temperature and pressure conditions used therein, forming nonvolatile or less volatile metal compounds which do not readily vaporize with distillate oil in the stripping zone. Accordingly, the distilled oil recovered by stripping can also be passed to the catalytic hydroconversion zone. If desired, the distillate oil can instead be passed directly to the catalytic cracking zone when its metal content does not exceed a few parts per million, or at least when its metal content is low enough so that when blended with the other feedstocks to the catalytic cracking zone it does not increase the metal content of the gross feed to above 2 p.p.m.

A low metal content in the distillates produced in the second thermal hydrocracking zone applied to the asphaltic residue feed may be obtained more readily by means of a preferred embodiment of the invention wherein the slurry oil derived from the catalytic cracking process, containing entrained catalyst fines, is passed to said thermal hydrocracking zone in admixture with the feed thereto. It appears that the cracking catalyst particles

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can act as acceptors of the metals freed by hydrocracking of the metal compounds present in the asphaltic residue so that there is less tendency toward the formation of other metal compounds which might otherwise volatilize during the stripping operation. The unvaporized bottoms from the stripping zone will thus contain the cracking catalyst particles, which will have an adherent coating of coke and metals, and the solid cracking catalyst can be separated from the unvaporized bottoms by filtration, settling, or equivalent means. At least a portion of the unconverted residual oil will be withdrawn from the system for disposal, for example by blending into heavy fuel oil, but another portion thereof may be recycled to the thermal hydrocracking zone for further conversion therein.

The effluent of the catalytic hydroconversion or hydrogenation zone is separated into a hydrogen-rich recycle gas portion and a liquid portion composed of the normally liquid distillates and any unconverted residual oil remaining. The liquid oil is then fractionated in one or more stages to separate light normally gaseous by-products from distillates such as gasoline, middle distillates, and gas oils, and a residual portion which is passed to the catalytic cracking zone in accordance with the preferred mode of the present invention. The products may be further worked up in a variety of known ways, as by reforming, hydrofining, hydrocracking, etc. The operation of the catalytic cracking zone will be substantially as in accordance with prior art practice except that it is found that the portion of the feed thereto prepared in accordance with the present invention cracks readily and rapidly with a high yield of gasoline and minimal light gas production.

Referring now to the drawing, by way of example, a residual oil such as a short (vacuum) residuum in line 11 is passed to deasphalting tower or extractor 12 wherein it is contracted, countercurrently, with from 4 to 10 volumes, per volume of residual oil, of a mixed propane-butane solvent introduced through line 13. The more saturated and lower molecular weight portions of the residual oil dissolve in the solvent and are withdrawn overhead through line 14, while the less soluble components including asphaltenes are withdrawn through bottom line 15. In solvent recovery zone 16, comprising flash and distillation zones, solvent is recovered for reuse in line 18 and nonasphaltic residual oil is recovered in line 17. Similarly, the solvent entrained with the asphaltic residue in line 15 is removed in recovery zone 19 for return to the system via line 21, and the asphaltic residue is recovered in line 20. Thus, for example, by extraction of 10 volumes of vacuum residuum mainly of California origin, boiling 90% above 900° F., with 70 volumes of propane-butane at 500 p.s.i.g. and 220°–240° F., there is obtained 6 volumes of deasphalted residual oil containing about 30 p.p.m. metals and 4 volumes of asphaltic residue containing about 400 p.p.m. metals.

The nonasphaltic residual oil in line 17 and 2,000–10,000 s.c.f./bbl. hydrogen-rich gas provided via line 22 are preheated in furnace 23 and passed downward through hydrocracking reaction zone 24, containing a supported nickel sulfide-molybdenum sulfide hydrogenation catalyst, at elevated pressure of 1,000–4,000 p.s.i.g. and LHSV of 0.2–2. The temperature reaches 825–900° F., where thermal hydrocracking occurs, and unsaturated components are hydrogenated. The effluent of this first hydrocracking zone in line 25 is separated in separator 26 without cooling or depressuring to obtain a vapor-portion in line 27 and a liquid portion in line 36. The vapor is cooled in condenser 28 to condense the normally liquid distillates contained therein, which separate out in separator 29, from which hydrogen-rich recycle gas is withdrawn by compressor 30 and returned for reuse through line 22 with additional makeup hydrogen provided via line 31. The distillates recovered in line 32 then pass to flash zone 33, which operates at a

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lower pressure, to release dissolved normally gaseous constituents through line 34. The liquid distillate recovered passes via line 35 and then line 37 into catalytic hydroconversion zone reactor 38. The liquid residual oil recovered in line 36 also passes via line 37 to reactor 38. At typical thermal hydrocracking conditions of 830° F., 3,000 p.s.i.g., and 0.3 LHSV, using the catalyst in reactor 24, there is obtained from the 6 volumes of nonasphaltic residual oil 4.5 volumes of distillate with an end point of 950° F. and 1.5 volume of residual oil. The residual oil contains less than 10 p.p.m. metals. If hydrocracking zone 24 is operated without the use of any catalyst or other absorptive solid contact, conversion should be kept below 60%, and the oil in line 36 will contain all of the metals originally present in the nonasphaltic residual oil.

The asphaltic residue in line 20 is similarly treated by passing with 2,000–10,000 s.c.f./bbl. hydrogen supplied via line 56 through furnace 57 into the second thermal hydrocracking reaction zone 58 at 800–900° F., 1,000–4,000 p.s.i.g., and 0.2–2 LHSV. Reactor 58 contains only catalytically inert liquid distributing surfaces. The effluent of this zone in line 59 is separated without cooling or depressurizing into vapor and liquid in separator 60, the vapor passing via line 61 through condenser 62 to separator 63. Hydrogen-rich recycle gas is withdrawn from vessel 63 by compressor 64 for return via line 56 with makeup hydrogen introduced through line 65. The normally liquid distillate oils condensed from the vapor effluent of the thermal hydrocracking zone are passed via line 66 into the same low pressure flash separator 33 as utilized for recovery of dissolved normally gaseous by-products in line 34, as was the case in connection with the first hydrocracking zone. For example, at 825° F., 3,000 p.s.i.g., and 0.3 LHSV, there is obtained from the 4 volumes of asphaltic residue about 0.75 volume of distillate with an end point of 950° F. Thus, the oils passed to catalytic hydroconversion reactor 38 comprise the 4.5 volumes of distillate produced by hydrocracking of the nonasphaltic residual oil, the 0.75 volume of distillate produced by thermal hydrocracking of the asphaltic residue, and the 1.5 volumes of nonasphaltic residual oil effluent of the first thermal hydrocracking zone which was not converted to vaporized distillate. These oils are of sufficiently low metal content that they are readily hydrogenated in reactor 38 without fouling the catalyst used therein.

As illustrated, the effluent of the catalytic reactor 38 is worked up by withdrawing through line 39 and passing through cooler-condenser 40 to separator 41. Hydrogen-rich recycle gas is withdrawn through line 42 by compressor 43 and returned to the reactor with makeup hydrogen provided by line 44. The condensed liquid portion in line 45 passes to distillation facilities as illustrated by 46 to separate the light gaseous by-products in line 47, a gasoline boiling range product in line 48, a middle distillate or gas oil product in line 49, and a higher boiling oil in line 50 which may still contain residual components which do not distill below 1000° F. This oil, however, is essentially metal-free and is accordingly a prime feedstock for passing to catalytic cracker 51.

In the catalytic cracking there is produced predominantly gasoline, recovered through line 52, a minor portion of cycle oils which may boil up to 850° F., in line 53, and a smaller amount of slurry oil in line 54 obtained by washing product gas streams to remove entrained cracking catalyst fines. The slurry oil in line 54 is returned via line 55 for admixture with the asphaltic residue feed to the second thermal hydrocracking zone 58. The cracking catalyst particles pass through the reactor and are withdrawn from separator 60 with the unvaporized residual oil in line 67 and passed to stripping zone 68. Therein the oil is contacted with hydrogen-rich stripping gas introduced through line 72 to vaporize additional portions of distillate oils which pass overhead

with the hydrogen through line 69, containing condenser 70, to separator 71 wherein they are separated out as liquid and recovered in line 74. The hydrogen-rich recycle gas is withdrawn by compressor 73 and recycled for reuse through line 72 together with makeup hydrogen added through line 78. The amount of makeup hydrogen needed at this point is nominal, as only a minor amount of conversion occurs in the stripping zone. The distillate oils recovered in this manner in line 74 may be withdrawn as fuel oil through line 75, or all or another portion of the oil may be passed via line 77 to the catalytic cracker 51.

More desirably, a portion of the distillate in line 74 is passed through line 76 for passage through line 37 to catalytic hydroconversion reactor 38. The feed to reactor 38 will then include an additional 0.75 volume of distillate oil having an end point of 950° F. and of low metal content, when all the distillate recovered by stripping with 15,000 s.c.f. of H₂/bbl. at 850° F. and 3,000 p.s.i.g. is so passed. When the oils are passed through reactor 38 containing a nickel sulfide and tungsten sulfide on silica-magnesia catalyst having hydrogenation and moderate hydrocracking activity, at 750° F. and 2,500 p.s.i.g. with 6,000 s.c.f. H₂/bbl., metal compounds are nearly completely removed, most of the nitrogen and sulfur are removed, and very little of the product still boils above 950° F. Most of the product, about 85%, boils between 400° F. and 750° F. and is readily converted to gasoline by hydrocracking. The portion boiling above 750° F. is readily converted to gasoline by catalytic cracking along with conventional cracker feeds.

From the bottom of stripping zone 68 unvaporizable residual oil containing cracking catalyst fines is withdrawn through line 79 and passed to solids separation zone 80. Therein the solid particles may be removed, for example by filtration of the hot liquid, and discarded through line 81. Other methods may be used, for example by diluting with a solvent for asphaltenes and settling out solids (not illustrated). The recovered unconverted asphaltic residual oil in line 82 may be recycled to reactor 58 via line 55, and a lower per-pass conversion be taken therein by lowering the temperature somewhat, but in the embodiment exemplified by the yields and operating conditions just described it was assumed that the remaining 2.5 volumes of residual oil is withdrawn through line 83 for disposal in heavy fuel oil, or for asphalt manufacture, or as a feed for hydrogen manufacture.

To illustrate some of the advantages obtainable by means of the invention, it will be observed that in accordance with the above example about 75% of the short residuum can be converted to distillates, continuously, without danger of plugging the reactors or catalyst with coke or metals. When the short residuum was converted directly by thermal hydrocracking in a reactor devoid of catalyst, only about 60% conversion could be obtained without plugging by coke occurring. When an active hydrogenation catalyst was used at thermal hydrocracking conditions with the short residuum feed, higher conversion could be obtained without coke formation but the catalyst became plugged with metal deposits. When a guard chamber was used to remove the metals ahead of the catalyst, the guard chamber had to be changed or cleaned out about every 30 days. The guard chambers needed to enable continuous operation would cost nearly as much as the reactors for a commercial scale unit, and they do not remove the various metal species present completely enough to prevent the catalyst ultimately being fouled.

We claim:

1. The process which comprises: separating residuum by solvent extraction into non-asphaltic residual oil and asphaltic residue; passing hydrogen and nonasphaltic residual oil through a hydrocracking reaction zone at elevated tempera-

ture and pressure effective to convert at least 30% of said residual oil to distillates boiling below 1000° F.;

passing hydrogen and asphaltic residue through a separate thermal hydrocracking reaction zone at elevated temperature and pressure effective to convert from 30 to 60% of said asphaltic residue to distillates boiling below 1000° F.;

separating from the hydrogen-rich vapor effluents of said zones normally liquid distillate oils having normally gaseous hydrocarbons dissolved therein; freeing said distillate oils of dissolved normally gaseous hydrocarbons, and then passing at least a portion of the distillate oils to a catalytic hydroconversion reaction zone with hydrogen to contact therein a sulfactive hydrogenation catalyst at elevated temperature and pressure;

also passing liquid residual oil effluent of the first-mentioned hydrocracking zone to said catalytic hydroconversion zone;

recovering hydrofined distillate oils and hydrofined residual oil from said catalytic hydroconversion zone; and passing hydrofined residual oil so recovered to a catalytic cracking process employing a circulating powder cracking catalyst.

2. The process of claim 1 wherein additional distillate oil is stripped from liquid residual oil effluent of said thermal hydrocracking zone at elevated temperature and pressure employing at least 2,000 s.c.f. of H₂-rich stripping gas per barrel of liquid, and distillate oil so obtained is also passed to said catalytic hydroconversion zone.

3. The process which comprises:

separating residuum by solvent extraction into non-asphaltic residual oil and asphaltic residue;

passing hydrogen and nonasphaltic residual oil through a hydrocracking reaction zone at elevated temperature and pressure;

passing hydrogen, asphaltic residue, and heavy cracked oil containing entrained cracking catalyst fines effluent of a catalytic cracking process through a separate thermal hydrocracking reaction zone at elevated temperature and pressure;

separating from the hydrogen-rich vapor effluents of said zones normally liquid distillate oils having normally gaseous hydrocarbons dissolved therein;

freeing said distillate oils of dissolved normally gaseous hydrocarbons, and then passing at least a portion of the distillate oils to a catalytic hydroconversion reaction zone with hydrogen to contact therein a sulfactive hydrogenation catalyst at elevated temperature and pressure;

and recovering hydrofined distillate oils from said catalytic hydroconversion zone.

4. The process of claim 3 wherein liquid residual oil effluent of said separate thermal hydrocracking zone is treated to remove entrained cracking catalyst fines, and at least a portion of residual oil so treated is returned to said zone.

5. The process which comprises:

separating residuum by solvent extraction into non-asphaltic residual oil and asphaltic residue;

passing hydrogen and nonasphaltic residual oil through a hydrocracking reaction zone at elevated temperature and pressure;

passing hydrogen and asphaltic residue through a separate thermal hydrocracking reaction zone at elevated temperature and pressure;

separating from the hydrogen-rich vapor effluents of said zones normally liquid distillate oils having normally gaseous hydrocarbons dissolved therein;

freeing said distillate oils of dissolved normally gaseous hydrocarbons, and then passing at least a portion of the distillate oils to a catalytic hydroconversion reaction zone with hydrogen to contact therein a sul-

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factive hydrogenation catalyst at elevated temperature and pressure;
 passing liquid residual oil effluent of the first-mentioned hydrocracking zone to said catalytic hydroconversion zone, recovering hydrofined distillate oils and hydrofined residual oil from said catalytic hydroconversion zone;
 stripping additional distillate oil from liquid residual oil effluent from said separate thermal hydrocracking reaction zone at elevated temperature and pressure employing at least 2000 s.c.f. of hydrogen-rich stripping gas per barrel of liquid, and passing distillate oil so obtained and hydrofined residual oil so recovered to a catalytic cracking process employing a circulating powder cracking catalyst.

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References Cited by the Examiner

UNITED STATES PATENTS

2,972,313	2/1961	Pevere et al.	208—86
3,089,843	5/1963	Eastman et al.	208—58
3,098,029	7/1963	Snyder	208—63
3,147,206	9/1964	Tulleners	208—111
3,175,966	3/1965	Burch	208—111

References Cited by the Applicant

UNITED STATES PATENTS

3,132,088	5/1964	Beuther et al.
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DELBERT E. GANTZ, *Primary Examiner.*A. RIMENS, *Assistant Examiner.*