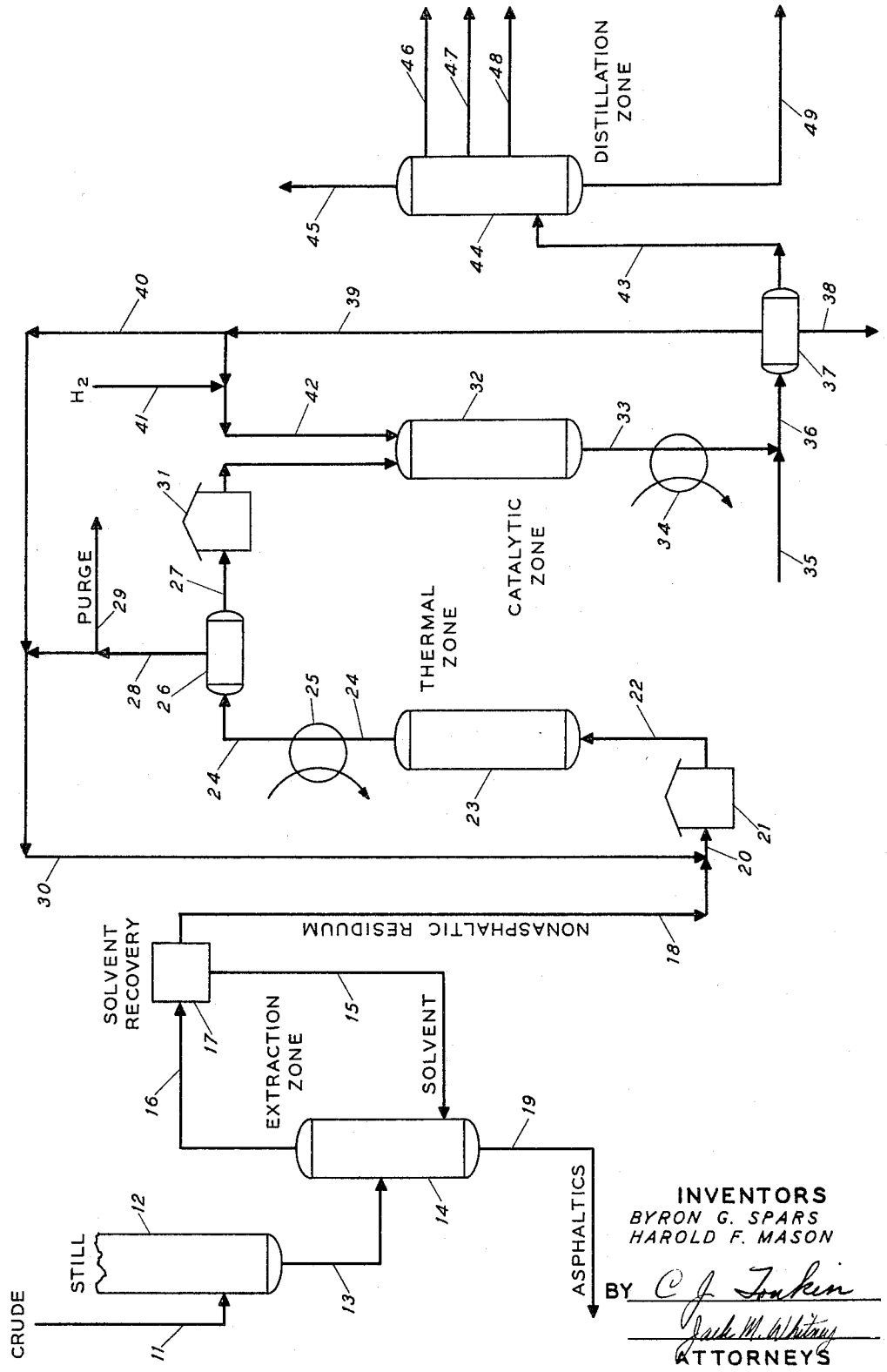
Nov. 29, 1966 B. G. SPARS ETAL 3,288,703

RESIDUUM CONVERSION PROCESS TO OBTAIN LOWER BOILING PRODUCTS BY HYDROCRACKING

Filed Jan. 2, 1964



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United States Patent Office 3,288,703 Patented Nov. 29, 1966

3,288,703

RESIDUUM CONVERSION PROCESS TO OBTAIN LOWER BOILING PRODUCTS BY HYDROCRACKING

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Filed Jan. 2, 1964, Ser. No. 335,109
13 Claims. (Cl. 208—86)

This invention relates to processes for the production of distillate oils from residua. More particularly, the invention relates to hydroconversion processes applied to the heaviest portions of crude oil.

Because crude petroleum and similar oils derived from carbonaceous deposits of ancient origin are composed primarily of materials boiling above about 700° F., but the hydrocarbon materials boiling primarily below about 700° F. have greatest economic value, many processes have been devised and proposed for converting the higher boiling materials to lower boiling materials. There are many commercial processes for upgrading the distillate portion, i.e., materials boiling up to an end point of about 1000° F., for example, by catalytic reforming, catalytic hydrocracking, and catalytic cracking. The problem remains, however, what to do with the residual remainder boiling above about 1000° F.

Recently, new catalytic hydrocracking processes have been developed which are highly effective for converting distillates to high quality products, for example the process of U.S. Patent 2,944,006 to J. W. Scott, Jr. Such processes, however, require as feed a noncoking, low-nitrogen-content oil because they employ acidic hydrocracking catalysts whose activity is capable of being rapidly titrated away by nitrogen compounds, dependent on the concentration of nitrogen compounds in the reaction zone. Consequently, such processes have not successfully been used with residua feeds, which are notorious for having high nitrogen contents and tending to form coke. If the feed contains coke-forming constituents, the catalyst fouls too rapidly, such that a major advantage of the hydrocracking process, namely, the ability to operate continuously for a long time, is lost. If the feed contains an excessive amount of nitrogen compounds, the catalyst may be titrated and deactivated thereby, requiring use of a higher temperature. At higher temperatures, coke formation occurs more rapidly. If very high pressures are used to prevent coke formation, the hydrocracking process becomes too expensive.

When fed to a catalytic cracking process, either of the fluidized catalyst or bucket elevator type, residual oils crack readily but produce excessive amounts of coke, which can seriously reduce the throughput of the process because of limitations on the capacity for burning coke from the catalyst. Hetero-organic metal compounds in the residua permanently poison the catalyst activity, and nitrogen compounds cause poor selectivity for gasoline production. If nitrogen compounds in particular could be substantially eliminated from the residual oil, substantial improvements in selectivity and gasoline production could be achieved. Also, if the oil could be made noncoking in the sense of eliminating the inherent tendency of residual oils to form excessive amounts of coke, while retaining the property of being easily cracked, the oil would be the ideal type of feed for catalytic cracking.

Known conversion processes applied to residua produce oils which are either coke-forming, or high in nitrogen content, or both. Thus, the present invention is particularly concerned with the problem of producing noncoking, low nitrogen content, oil from residua, so that the oil can then be catalytically cracked and/or hydrocracked.

It has now been found that noncoking, low nitrogen content, crackable oil can be prepared from residua containing asphaltenes and nitrogen compounds by (1) separating asphaltic constituents from the residuum to obtain substantially nonasphaltic residuum containing nitrogen compounds, (2) thermally hydrocracking the nonasphaltic residuum to obtain a substantial conversion to distillates, and then (3) catalytically hydrocracking distillates so produced and the remaining nonasphaltic residuum from thermal hydrocracking. In this way even any remaining unconverted nonasphaltic residua from the catalytic hydrocracking can be made noncoking and of low nitrogen content. It is found that in many cases the nitrogen content of even the highest boiling products can be reduced to below 100 p.p.m. (total nitrogen by Kjeldahl), and often to below 20 p.p.m., even though the deasphalted residuum contains over 2000 p.p.m. nitrogen. Because nitrogen compounds tend to occur in highest concentration in the highest-boiling portions of crude oil, the deasphalted residuum will nearly always contain at least 1000 p.p.m. nitrogen, and it may contain percentage amounts if derived from a highly nitrogenous oil.

In accordance with an embodiment of the invention, a crude residuum containing asphaltenes and nitrogen compounds is solvent treated to extract asphaltic constituents, including asphaltenes, and thereby produce a substantially nonasphaltic oil. Nonasphaltic oil and hydrogen are passed through a thermal hydrocracking zone at elevated temperature and pressure for a time suffiicent to convert a substantial portion of the nonasphaltic oil to distillates. Resulting distillates and remaining residua are then passed with hydrogen through a catalytic hydrocracking zone containing a hydrocracking-denitrification catalyst at elevated temperature and pressure for a time sufficient to convert a substantial portion of the remaining residua to distillate oils. There is recovered from the effluent of the catalytic hydrocracking zone as noncoking, low nitrogen content, oil any remaining unconverted residua and at least the distillate oils produced which boil above about 700° F. In the process there are also produced lower boiling distillates which may be recovered directly as products rather than as oil intended to be further cracked. In particular, a low freezing point kerosene distillate can be recovered. In a preferred embodiment of the invention, at least the resulting distillate oils boiling above about 700° F. and up to about 900° F. are then passed together with hydrogen through a catalytic hydrocracking zone, containing an acidic hydrocracking catalyst whose activity would be rapidly titrated away by nitrogen compounds in the oil, and the oils are therein converted to higher quality distillates. Any remaining unconverted nonasphaltic residua, including the material boiling entirely above about 900° F., is a superior crackable oil feed for catalytic cracking.

Frequently the remaining unconverted residua of the process of this invention, if to be catalytically cracked, will make up only a portion of the total feed to the catalytic cracking process, the remainder being heavy gas oils of the type ordinarily employed as feed. A marked improvement in the gasoline yield from catalytic cracking is obtained if the noncoking, low nitrogen content, residua makes up a substantial portion of the feed, and such improvement can be obtained without making significantly more coke. Similarly, the distillate oils produced in accordance with the invention which are to be hydrocracked may make up only a portion of the total feed to the acidic catalyst catalytic hydrocracking process.

The attached drawing illustrates process flow paths and major equipment items as they may appear in an embodiment of the invention.

Referring to the drawing, crude petroleum or reduced crude in line **11** is distilled or stripped in still **12**, for

example a vacuum crude still, to remove the bulk of the distillate oils therefrom. There is thus obtained as bottoms an asphaltic residuum, containing asphaltenes and nitrogen compounds, in line **13**. The residuum is passed to extraction zone **14** wherein its is contacted with a solvent, such as a light paraffin introduced through **15**, to extract the nonasphaltic oil portion of the reiduum and produce a solution of nonasphaltic residuum in solvent in line **16**. The solvent is separated in solvent recovery zone **17** for reuse, thereby providing in line **18** the nonasphaltic deasphaltic oil. The asphaltic portion of the residuum, containing most of the asphaltenes, resins, and metal compounds, is not soluble in the solvent, and it is withdraw from extraction zone **14** through line **19**. This material may be disposed of in known ways, as in the production of asphalt, or it may be blended into heavy fuel oil, or it may be thermally cracked.

The deasphalted residua in line **18**, containing nitrogen compounds, is combined with hydrogen-rich gas in line **30** and passed through line **20** into furnace **21**, wherein the temperature is raised to the range 750–950° F., preferably 800–900° F., at elevated pressure of 500–5000 p.s.i.g., preferably 1000–4000 p.s.i.g. From furnace **21** the oil and hydrogen are passed through line **22** into thermal hydrocracking reaction zone **23**, which need be no more than an empty pressure vessel. It will be noted that furnace **21** and line **22** are in essence a part of the thermal hydrocracking zone. In the thermal hydrocracking zone a substantial portion, preferably at least 30%, of the nonasphaltic oil is converted to distillates boiling below 900° F., thereby providing in line **24** a mixture of hydrogen-rich gas, resulting distillates, and remaining residuum. In the embodiment shown the mixture is cooled in exchanger **25** and then passed to separation drum **26**. In drum **26** hydrogen-rich gas is separated from the liquid oil portion of the effluent and withdrawn via line **28**. A portion of this gas may be purged from the process through line **29** to limit the buildup of light by-product gases, which otherwise may reduce the hydrogen partial pressure too much. The bulk of the hydrogen-rich gas is recycled through line **30** for passage again through thermal hydrocracking zone. Makeup hydrogen is provided, in the embodiment shown, by line **40** taken from the subsequent catalytic hydrocracking stage.

At least the major liquid portion of the effluent of the thermal hydrocracking zone is withdrawn from drum **26** via line **27** and passed through furnace **31** to catalytic hydrocracking zone **32**. Hydrogen-rich gas is also introduced through line **42**. The catalytic reaction zone contains an active hydrocracking-denitrification catalyst, and is operated at conditions of elevated temperature in the range 650–900° F., preferably 700–850° F., and pressure in the range 1000–4000 p.i.s.g., with adequate residence time such that a substantial portion of the remaining residua, preferably at least 40%, is converted to distillates boiling below 900° F. The effluent of the reaction zone passes via line **33** through cooler **34**, and then via line **36** to separation drum **37**. A major function of the combination of treating steps just described is to effect the removal of the large amount of nitrogen compounds initially contained in the nonasphaltic residuum. Consequently, there will be a large amount of NH_3, produced by reaction of hydrogen with these nitrogen compounds, in the material in line **33**. To remove ammonia and thereby provide a low-nitrogen-content crackable oil, water may be introduced through line **35**, settled out in drum **37**, and withdrawn through line **38**. The bulk of ammonia (and H_2S which is also produced) can thus be removed in solution therein. Hydrogen-rich gas is separated from the liquid oil portion of the effluent and taken off through line **39**. As mentioned, a portion of this hydrogen may be passed via line **40** to provide makeup hydrogen for the thermal hydrocracking zone. Hydrogen makeup to the catalytic hydrocracking zone is provided by line **41**, thereby producing the hydrogen-rich gas which is introduced through line **42**.

From separation drum **37** the liquid oil portion is passed via line **43** to distillation zone **44**. This zone may comprise a plurality of columns, operated to separate normally gaseous materials and light hydrocarbons overhead as by line **45**, to recover one or more gasoline fractions as by line **46**, and to recover kerosene and/or diesel fuel fractions as by line **47**. Higher boiling distillate oils may be recovered through line **48**, and any remaining unconverted residua is recovered in line **49**. All or a portion of the residue withdrawn as through line **49** may be used as feed to a catalytic cracking process or as a source of lubricating oil. All or a portion of the heavy distillates of line **48** may be used as feed to a catalytic hydrocracking process wherein there is employed a so-called "acidic" hydrocracking catalyst, i.e., a hydrocracking catalyst whose activity is capable of being titrated away by nitrogen compounds at a rate depending on the concentration of nitrogen compounds in the reaction zone. The nitrogen content of the oil in line **48** is low enough, below 100 p.p.m., and the temperature and pressure conditions employed in subsequent hydrocracking are high enough, such that the catalyst is not deactivated by the nitrogen, yet the temperature is still low enough such that coking is avoided. As a result, the oil can be substantially hydrocracked to higher-quality, lower-boiling, distillates. As mentioned, with proper cooperative operation of extraction zone **14**, thermal hydrocracking zone **23**, and catalytic hydrocracking zone **32**, it is possible to produce unconverted residua in line **49** which also has such a low nitrogen content that it can be hydrocracked with the acidic catalyst. In that case, all or portions of lines **48** and **49** may be blended as noncoking, low-nitrogen-content, oil for hydrocracking. Thus, in one embodiment, all liquid products not recovered as light distillate fuels in distillation zone **44** may be taken as bottoms in line **49**, line **48** being unused.

The starting material in the process of this invention is crude residua containing asphaltic constituents and nitrogen compounds, for example, the bottoms from atmospheric or vacuum distillation of crude petroleum or similar hydrocarbonaceous material. Such residua nearly always contain at least 5% asphaltenes, and usually contain over 10% and up to 20% asphaltenes. In accordance with the invention it is found that in order to produce noncoking, low nitrogen content, crackable oil from such a starting material, it is first necessary to remove substantially the asphaltic constituents. This may be accomplished, as in the embodiment shown in the drawing, by dissolving the nonasphaltic constituents away from the asphaltenes by countercurrent contacting in a known manner with a liquefied hydrocarbon solvent such as propane, a mixture of propane and butane, or other paraffins, including isoparaffins having up to 8 carbon atoms to the molecule. Alternately, the asphaltenes may be extracted by treating the residuum with a solvent which dissolves them, for example, an aromatic distillate. The objectives in the solvent treating are to remove asphaltenes and also to reduce the concentration of heteroorganic compounds of nitrogen, sulfur, oxygen, and metals contained in the residuum. Preferred solvents are propane and mixtures of propane and butane, because the nonasphaltic oil produced therewith is noticeably less aromatic than the original residuum. Typical and preferred treating conditions include solvent to residuum ratioes between 3:1 and 10:1, temperatures of 120–225° F., and sufficient pressure to maintain the propane-butane liquid, i.e., 400–600 p.s.i.

The qualtity of the nonasphaltic residual oil obtained will vary depending on the solvent or solvents used, ratio of solvent to oil, temperature, and efficiency of contacting. Satisfactory and nearly equivalent results can be achieved, however, using substantially different treating systems and conditions. Thus, any treatment may be

found suitable wherein at least 25% of the residuum is rejected so as to include therein the highest molecular weight and the most aromatic and highly condensed unsaturated ring compounds, and most of the metal compounds, such that the recovered oil contains not over about 50 p.p.m. metals, not over about 5% asphaltenes, and has a Ramsbottom carbon value not over about 10 weight percent. More preferred qualities are metal contents below 30 p.p.m., Ramsbottom carbon below 6%, and asphaltenes below 3% as determined by ASTM D-893. In this analytical method, a very waxy feed may give an incorrect high result, for which correction should be made. The lower the asphaltene content the better, but there should be obtained a yield of at least 35% of deasphalted oil from the residuum. Thus, maximum yield in the extraction step is to be balanced against the decreased conversion permitted in the thermal and catalytic hydrocracking steps, else the catalyst will be rapidly fouled by coke.

The deasphalted oil is thermally hydrocracked by passing it and hydrogen through a contacting zone devoid of any effective amount of catalytic agent at elevated temperature and pressure, as previously described. The oil and hydrogen may be passed upflow or downflow through the contacting zone at a space velocity of 0.1–6 volumes of nonasphaltic oil per volume of contacting chamber per hour. The contacting zone may contain an inert packing such as Alundum, and/or distributing devices, to insure adequate contacting between the oil and hydrogen, but it is found particularly suitable to pass the oil and hydrogen upflow through an empty chamber. More efficient contacting is obtained in this manner. The conversion in the thermal hydrocracking zone is desirably high, at least 30%, and more preferably at least 40%, of the nonasphaltic residua being converted to distillates boiling below 900° F. Conversion is defined herein as volume of product boiling below 900° F. less volume of feed boiling below 900° F., divided by volume of feed boiling above 900° F. The properties of the nonasphaltic oil may, however, limit the conversion obtainable without encountering excessive coke formation in the thermal hydrocracking zone or the subsequent catalytic hydrocracking zone. Thus, too high a content of aromatics, or incomplete removal of asphaltenes or metals, frequently make it inadvisable to attempt to convert more than 60% of the nonasphaltic residuum in the thermal hydrocracking zone. Hydrogen consumption accompanying the thermal hydrocracking is generally less than about 500 standard cubic feet per barrel, but it is advisable to provide at least 1000 standard cubic feet of hydrogen per barrel and more preferably at least 2000 standard cubic feet of hydrogen per barrel in order to insure that the hydrogen partial pressure accounts for the major portion of the pressure in the zone.

The entire effluent of the thermal hydrocracking zone may be passed directly to the catalytic hydrocracking zone if conversion in the thermal hydrocracking zone is not so high as to result in the production of substantial amounts of normally gaseous by-products. This is a preferred arrangement in that cooling and reheating of the thermal hydrocracking zone effluent is thereby avoided. It is frequently found, however, that by-products produced in the thermal hydrocracking have a deleterious effect on the hydrocracking-denitrification catalyst, and consequently it is preferable to cool the effluent of the thermal hydrocracking zone at least sufficient to separate hydrogen-rich gas, for recycle, from the normally liquid portion of the effluent. Some of the light normally liquid distillates produced in the thermal hydrocracking may be recoverable directly as products, but it is usually found that the distillates have too high a nitrogen content and are somewhat unstable and olefinic. Consequently, it is preferred to pass all of the distillates and remaining residuum from the thermal hydrocracking zone to the catalytic hydrocracking zone, wherein they are surprisingly found to be much more readily purified and upgraded. At least the distillates boiling above about 400° F., or containing more than about 100 p.p.m. nitrogen, are passed to the catalytic hydrocracking zone together with the remaining nonasphaltic residuum, in the contemplated best operation.

In the catalytic hydrocracking zone there is employed a catalyst which has hydrocracking-denitrification activity at the conditions used therein. The catalyst is to promote purification by converting nitrogen compounds to NH_3, to crack high molecular weight molecules to smaller ones, and to hydrogenate disjointed molecules produced thereby and by the thermal hydrocracking. It must necessarily remain active in the presence of nitrogen compounds. Suitable catalysts comprise the combinations of sulfides of the iron group metals with the group VI metals which are active for hydrogenation and dehydrogenation. Preferred catalysts comprise the combination of the sulfides of nickel and at least one of the active Group VI metals, tungsten and molybdenum, intimately associated with or incorporated in a solid inorganic porous oxide support. Preferred supports are alumina and the group of siliceous cracking components consisting of silica-alumina, silica-magnesia, and silica-alumina-magnesia, wherein each of the oxides are present to the extent of at least 10%. Such catalysts can be prepared by a variety of methods, but probably the simplest procedure is to impregnate a preformed alumina or silica-magnesia catalyst of high surface area with compounds of nickel and molybdenum or tungsten, and then to calcine to convert the metal compounds to the oxides. These catalysts have high activity in the presence of nitrogen compounds when the metal oxides are converted to sulfides, which is readily accomplished at the startup of the process by passing a mixture of hydrogen and a vaporized sulfur compound providing H_2S into contact with the catalyst.

Selection of the catalyst to use in a particular installation is somewhat dependent on the character of the feed and the service for which it is intended. It is found that nickel-molybdenum-alumina catalysts perform very well with oils derived from aromatic crudes, such as California crudes, but do not appear to have sufficient cracking activity to convert oils derived from highly paraffinic crude, such as Minas, in which case, however, the nickel-tungsten-silica-magnesia catalysts are found to be very effective.

Conditions in the catalytic hydrocracking reaction zone are sufficiently severe in the ranges 600–900° F., preferably 700–850° F., and pressures of 1000–5000 p.s.i.g., preferably 1500–4000 p.s.i.g., and space velocities of 0.2–4 LHSV (volume of oil per volume of catalyst per hour) to convert a substantial portion of the remaining residua from thermal hydrocracking (boiling above 900° F.) to distillates boiling below 900° F. At least 40% conversion is accomplished, and more preferably at least 50% of the remaining residua is hydrocracked to distillate oil. Thus, by the combination of thermal hydrocracking and catalytic hydrocracking at least 50%, and generally more than 60%, of the nonasphaltic residua is converted to distillate oil boiling below 900° F. It is found that the remaining residua from thermal hydrocracking is much more readily hydrocracked and more readily denitrified than residua which has not been subjected to thermal hydrocracking. As a result, it is found that at the preferred conditions even the remaining unconverted residua in the effluent of the catalytic hydrocracking reaction zone is purified such that it has low nitrogen content making it an excellent feed for catalytic cracking. Also, it is found that whereas the thermal hyrocracking does not convert the materials identified by Conradson carbon or Ramsbottom carbon, rather instead concentrating such materials in the unconverted residua, the subsequent catalytic hydrocracking zone in combination therewith effectively converts the Ramsbottom carbon material and produces noncoking oil.

Hydrogen-rich gas is separated from the effluent of the catalytic hyrocracking zone, and the liquid hydrocarbon portion of the effluent is treated to recover some of the light distillates which need no further upgrading. The hydrogen-rich gas may be recycled with added makeup hydrogen. In one embodiment the hydrogen-rich gas may be recycled to the inlet to the thermal hydrocracking zone, when the entire effluent of the thermal hydrocracking zone is passed directly to the catalytic hydrocracking zone. The purity of the recycle hydrogen, however, then is found to decline rapidly at high conversions in the thermal hydrocracking zone, such that there is a deleterious effect on the hydrocracking catalyst unless a fairly large amount of gas is purged from the system. This in effect calls for a greater amount of makeup hydrogen. To minimize this amount of purging and makeup, it is found more advantageous to add makeup hydrogen to the catalytic zone, purging to the thermal zone, and then to take a gas purge from the thermal hydrocracking zone, wherein the hyrogen purity is not as critical. This embodiment thus requires a separation of hydrogen-rich gas from the effluent of the thermal hydrocracking zone.

Conditions in the combination of thermal hydrocracking and catalytic hydrocracking are adjusted so as to maintain the product nitrogen content, at least of the resulting distillates boiling below 900° F., below about 100 p.p.m. In the preferred embodiment where the high boiling products of the combination process are further hydrocracked in a catayltic hyrocracking process employing an acidic hydrocracking catalyst whose activity can be rapidly titrated away by nitrogen compounds, though nitrogen contents up to 100 p.p.m. are acceptable, it is preferred that the nitrogen content of the oil to be hydrocracked not exceed about 20 p.p.m. nitrogen. It is then possible to convert the oil entirely to lower-boiling higher-quality distillates at lower temperatures of below about 750° F., e.g. 500–700° F., at pressures of 1500–4000 p.s.i.g. and space velocities of 0.2–10 LHSV. The catalyst in this subsequent hydrocracking stage is particularly distinguished from the hydrocracking-denitrification catalyst by its sensitivity to nitrogen compounds. In composition, the catalyst usually differs by the absence of a Group VI metal component. Typical and preferred catalysts for use in the acidic catalytic hydrocracking zone are composed of iron group and/or noble metals on active siliceous cracking cataysts supports, a particularly preferred example being nickel sulfide on silica-alumina.

Because of its low nitrogen content the remaining unconverted residua boiling above 900° F. is a superior feed for catalytic cracking. In the catalytic cracking process the oil is contacted with a siliceous cracking catalyst such as silica-alumina in a known way, at elevated temperatures of 850–1150° F. and low pressures approaching atmospheric. Deposition of some coke on the catalyst inherently occurs, and is desired, at these conditions, as the catalyst is usually continuously circulated between the reaction zone and a regeneration zone where the coke is burned off to supply heat for the endothermic cracking reactions. The oil produced in the process of this invention, however, cracks to produce less coke and gas, and more gasoline as compared to oils of similar boiling range, whereby the catalytic cracking process can be kept in heat balance without the inordinate increase in catalyst circulation rate or decrease in feed throughput required when high nitrogen content residua are cracked. Generally, the residual oil produced in the process of this invention will contain less than 1000 p.p.m. nitrogen, frequently less than 100 p.p.m., and even less than 20 p.p.m. under best operation.

The following examples illustrate the practice of the invention and show the importance of the particular steps used therein and their sequence. The first two examples are illustrative of the manner in which noncoking, low nitrogen content, crackable oil can be prepared from vacuum-reduced crude petroleum residuum by means of the process of the invention.

Example 1

Vacuum reduced crude petroleum, being the highest boiling 23% of a California crude oil, was treated in a propane deasphalting process to dissolve the nonasphaltic constituents of the reduced crude. After separating the propane solvent there was recovered from the extract a nonasphaltic deasphalted oil in a yield of approximately 45% based on the residuum feed, having the properties set forth in the table hereafter. The deasphalted oil and hydrogen passed downflow through a reactor containing 10–14 mesh inert Alundum particles. The entire effluent of this reactor was cooled to condense the normally liquid hydrocarbons therein and to separate hydrogen-rich gas, which was recycled. Hydrogen consumption was 145 s.c.f. per barrel, which was supplied by makeup hydrogen. Light hydrocarbons having 5 or less carbon atoms to the molecule were separated from the liquid oils, and the liquid oils composed of material having 6 carbon atoms to the molecule or more were then mixed with hydrogen, heated, and passed downflow through a reactor containing a nickel sulfide-tungsten sulfide on silica-magnesia catalyst. The catalyst contained about 18% Ni and about 10% W, and was prepared by impregnating a commercial slica-magnesia cracking catalyst containing about 30% magnesia with nickel nitrate and ammonium tungstate, calcining, and sulfiding. The entire effluent of this reaction zone was then cooled to separate recycle hydrogen from the normally-liquid products. Conditions used, distillate yields, and properties of streams and fractions at various points in the process are summarized in the following Table I.

TABLE I

Conditions of Step		(1) Deasphalting [1]	(2) Thermal Hydrocracking	(3) Catalytic Hydrocracking
Temperature, ° F		~200	826	772.
Pressure, p.s.i.g.		~500	1,925	2,170.
Space Velocity, LHSV		(4–10 vols. C_3/vol. Residuum).	0.26	0.5.
	Residuum Feed			
S.c.f. H_2/Bbl			6,000 (recycle)	5,000 (once-through).
900° F.+Product Fraction, Volumes	220	95 (+5% 800–900° F.)	53.7	27.9.
Gravity, ° API	8.3	18.3	18.4	30.5.
Sulfur, wt. percent	1.5	1.0		
Nitrogen, p.p.m.[2]	1.0 wt. percent	4,800	5,925	14.
Nickel, p.p.m.	104	9		
Vanadium, p.p.m.	84	3		
Viscosity SSU at 210° F	10,200	321	275.7	
Asphaltenes	16.4	1.4		
Ramsbottom Carbon	12.3	2.7	3.96	1.
Resulting Distillates: Volume; Boiling Range; and Nitrogen Content.[2]			1.1 (wt.); C_1–C_4	
			1.2; C_5–180° F	
			6.8; 180–400° F; 269 p.p.m. N	6.4 (wt.); C_1–300° F.
			7.5; percent 400–500° F; 3,100 p.p.m. N.	29; 300–550° F.
			24.2; 700–900° F; 5,160 p.p.m. N.	34.6; 550–900° F; 7.5 p.p.m. N.

[1] Ranges given because deasphalted oil used was a blend of products from several parallel treatments at different conditions.
[2] After removal of ammonia.

It will be noted that even the unconverted bottoms from the final catalytic hydrocracking stage boiling entirely above 900° F. had a low nitrogen content of only 14 p.p.m. In contrast thereto, even the light distillates produced in the thermal hydrocracking stage have very high nitrogen contents. Also, the Ramsbottom carbon value for the unconverted bottoms from thermal hydrocracking and the nitrogen content thereof indicate that these compounds are concentrated in the bottoms instead of being converted in thermal hydrocracking. Nevertheless, by the combination with the catalytic hydrocracking stage the coke-forming and nitrogen-containing compounds are eliminated.

The following example presents results similarly obtained by thermal hydrocracking and catalytic hydrocracking, at somewhat different conditions, the deasphalted oil obtained similarly as in Example 1.

The following example, wherein thermal hydrocracking is omitted, further illustrates the cooperative effects between the thermal hydrocracking and catalytic hydrocracking zones in improving conversion, improving nitrogen removal, and improving the properties of the kerosene-boiling-range distillate product.

Example 3

The deasphalted oil obtained as in Examples 1 and 2 was passed directly to the catalytic hydrocracking zone operated as in Example 2, the thermal hydrocracking step being omitted. Conditions and results and properties of distillates produced are summarized in the following table, wherein corresponding data from Example 2 are reproduced for comparison.

TABLE III

	(Example 3)	(Example 2)	
Feed to Catalytic Hydrocracking	Deasphalted Resid	Thermal Hydrocracked Deasphalted Resid.	
Temperature ° F	770	772.	
Pressure p.s.i.g	2,170	2,212.	
Space Velocity LHSV	0.5	0.48.	
Percent Conversion of 900° F+	50	59.	
Overall % Conversion to 900° F−	50	81.	
Nitrogen Content of 400–700° F Fraction	10 p.p.m		
Nitrogen Content of 700° F+ Bottoms	195–320 p.p.m		
Nitrogen Content of 900° F+ Bottoms		12 p.p.m.	
Kerosene Distillate Produced, Yield	13.1%	24.5%, or 30.2%	
Boiling Range ° F	320–550	300–510	300–550.
Gravity ° API	34.9	39.4	38.3.
ASTM Smoke Point, p p.m	14	23	22.
IP Freeze Point, ° F	−59	−60	−44.
Aromatics, vol. percent		12.2	11.6.
Sulfur, p.p.m		9	

The nitrogen content of the material boiling above 700° F. produced by catalytic hydrocracking the deasphalted residuum without thermal hydrocracking is too high for it to be used as the feed to a catalytic hydrocracking process employing a catalyst which is sensitive to nitrogen contaminants. It is further to be noted that the kerosene distillate produced by the combination of deasphalting-thermal hydrocracking-catalytic hydrocracking is obtained both in higher yield and in higher quality as compared to the kerosene distillate obtained without the thermal hydrocracking step.

TABLE II

Conditions of Step	Thermal Hydrocracking	Catalytic Hydrocracking
Temperature, ° F	850	772.
Pressure, p.s.i.g	1,990	2,212.
Space Velocity, LHSV	0.52	0.48.
S.c.f. H_2/Bbl	5200, (recycle)	5,000 (once through).
900° F.+ Product Fraction: Volumes	47.2	19.4.
Gravity ° API	17.4	30.5.
Nitrogen, p.p.m	6,930	12.
Viscosity, SSU at 210° F	260.2	
Ramsbottom Carbon	4.6	
Resulting Distillates:		
Volumes per 100 vols	1.66 (wt.); C_1–C_4	
Deasphalted Resid; boiling range; and nitrogen content.		7.5 (wt.) C_1–300° F.
	12.9; C_5–412° F	
	8.2; 412–550° F; 1,233 p.p.m. N	30.2; 300–550° F.
	13.0; 550–700° F; 3,740 p.p.m. N	
	21.1; 700–900° F; 6,970 p.p.m. N	42.4; 550–900° F.; 6.3 p.p.m. N.

As shown, the noncoking, low-nitrogen-content, crackable oil was produced with a higher conversion in the thermal hydrocracking stage and with a higher conversion in the catalytic hydrocracking stage, whereby 59% of the remaining residuum from thermal hydrocracking was catalytically hydrocracked. It is particularly to be noted that, over-all, 80% of the nonasphaltic deasphalted residuim was converted to low-nitrogen-content distillates boiling below 900° F., and that the higher conversion was achieved in the catalytic hydrocracking stage at substantially the same conditions as used therein in Example 1. Thus, it appears that by virtue of the higher conversion in the thermal hydrocracking stage, the remaining material converted more readily in the catalytic stage. A distillate suitable for use as jet fuel can be recovered directly from the effluent of the catalytic hydrocracking zone.

The following example illustrates the unsatisfactory results obtained in terms of product quality when it is attempted to convert the deasphalted residuum entirely by thermal hydrocracking, omitting the subsequent catalytic hydrocracking step.

Example 4

In runs at two different pressures, deasphalted residual oil obtained as in the preceding examples was passed

downflow through the thermal hydrocracking zone with hydrogen at the conditions indicated in the following table, wherein there are also shown the product distribution and properties.

TABLE IV

Thermal Hydrocracking	Run 1	Run 2
Temperature, ° F	850	850
Pressure, p.s.i.g	1,989	1,000
Space Velocity, LHSV	0.24	0.28
S.c.f. H_2/bbl. (recycle)	6,030	5,300
H_2 Consumed, s.c.f./bbl	321	262
Products, Vol. Percent; p.p.m. N:		
Wt. Percent C_1–C_4, (weight)	1.62	1.67
Vol. Percent C_5–180° F	4.5	3.5
180–400° F. p.p.m. N	11.9; 454	17.8; 298
400–550 p.p.m. N	16.3; 1,855	17.8; 1,590
550–700 p.p.m. N	18.5; 4,160	19.8; 3,745
700–900 p.p.m. N	29.1; 7,450	30.6; 6,610
900° F.+ p.p.m. N	24.5	15.9, 11,000
900° F.+ Fractions:		
Gravity, ° API	14.0	8.1
Viscosity, SSU at 210° F	282	558.7
Ramsbottom Carbon, wt. percent		12
400–550° F. Distillates:		
Gravity, ° API	35.6	35.8
Aromatics, percent	19	24
Olefins, percent	35	31
Paraffins+Naphthenes, percent	46	45

Thus, even though 85% of the deasphalted residuum can be converted to distillates boiling below 900° F. by thermal hydrocracking alone, none of the products produced are of low enough nitrogen content to be suitable feeds to the catalytic hydrocracking process employing an acidic catalyst poisoned by nitrogen compounds. Also, the heavy oils are not improved feeds for catalytic cracking. The unconverted residual material is of much lower quality in terms of gravity, nitrogen content, and Ramsbottom carbon content, even as compared to the deasphalted oil itself. Also, the purity of the recycle hydrogen declined substantially as a result of light gaseous by-products produced, being only 65% hydrogen at the highest conversion and 77% hydrogen at the 75% conversion; whereas the recycle gas was 86% and the 93% hydrogen at the lower conversions of Examples 2 and 1.

The following example illustrates the unsatisfactory results obtained when the deasphalting step is omitted.

Example 5

Residuum stripper bottoms, i.e., vacuum reduced crude petroleum, was passed downflow through the thermal hydrocracking zone as in the preceding Examples 1 and 2 at 2000 p.s.i.g., 825° F., 0.3 LHSV, with 4000 s.c.f. H_2/bbl. After separation of the excess hydrogen, the normally liquid material in the effluent of the thermal hydrocracking zone was distilled, the product breakdown and properties being given in the table hereinafter. When it is attempted to catalytically hydrocrack the whole liquid product of thermal hydrocracking, the hydrocracking-denitrification catalyst is rapidly fouled by coke.

TABLE V

	Feed	Products of Thermal Hydrocracking						
Yield, vol. percent	100	3.0	7.6	11.2	15.7	18.7	15.6	31.9.
Boiling Range	90% above 935° F.	Start, 180° F.	180–400	400–550	550–700	700–900	900–1,000	1,000+.
Gravity, ° API	5.1	77.4	51.9	34.4	24.3	13.9	9.2	−1.9.
Aniline Point ° F			124	126	135	130		
Olefins, percent		20	9	8	2			
Aromatics, percent		4	13	31	49			
Sulfur, wt. percent	2.0							
Nitrogen, wt. percent	1.5				0.81	1.4	1.5	2.4.
Nickel p.p.m	136					.15	45	490.
Vanadium p.p.m	151					.02	9	310.
Asphaltenes vol. percent								
Ramsbottom Carbon	14.3					.22	4.1	~35.
Viscosity SSU at 210° F	~50,000					65.4	453	~106,000 at 275° F.
Benzene Insolubles, wt. %	.02–.03	Whole liquid product, 0.14						

Hydrogen consumption in the above example was 575 standard cubic feet per barrel, considerably higher than when the asphaltenes are first removed by propane deasphalting. Particularly to be noted are the high nitrogen contents in the distillates as well as the remaining residua, and that benzene insolubles were produced. The benzene insolubles are considered "coke," and they also cause further coke formation when this material is catalytically hydrocracked. When the feed is first propane deasphalted, the benzene insolubles do not form during thermal hydrocracking. Thus, it is seen that all three steps of (1) removing asphaltic constituents, (2) thermally hydrocracking, and (3) catalytically hydrocracking are essential in the process of this invention for the purpose of producing noncoking, low-nitrogen-content, crackable oil from residua.

It will be recognized that the process embodiment illustrated in the drawing and described herein is presented for the purpose of facilitating understanding of the sequence and nature of the major processing steps in the process. The flow scheme shown will be found to provide advantages of simplicity and ease of construction and operation. However, the precise means used for carrying out each step are capable of many variations and modifications, as by using different reactor configurations, series or parallel stages in each or any contacting zone, upflow or downflow of oil and hydrogen, concurrent or countercurrent. Recycle of all or a portion of the remaining unconverted residua from the catalytic hydrocracking-denitrification zone to that zone or to the thermal hydrocracking zone may be advantageous in some cases, as where only gasoline and light kerosene are to be produced by subsequent acidic catalyst hydrocracking. Generally, however, once-through operation is to be preferred as the unconverted residua can instead be used as feed to a catalytic cracking process to great advantage. Hence, the drawing should not be considered as limiting the process except in those respects indicated as essential in the claims appended hereto.

What is claimed is:

1. The process for preparing noncoking, low-nitrogen-content, crackable oil from crude residua containing asphaltenes and nitrogen compounds, which comprises: solvent treating crude residua to remove asphaltenes and thereby obtain substantially nonasphaltic residua containing nitrogen compounds, thermally hydrocracking said nonasphaltic residua to convert a substantial portion, less than all, thereof to distillates in a noncatalytic contacting zone, catalytically hydrocracking at least the unconverted portion of residua remaining after thermal hydrocracking to convert a substantial portion of said remaining residua to distillate oils in a reaction zone containing a hydrocracking-denitrification catalyst, whereby the resulting distillate oils and unconverted residua are substantially denitrified, separating hydrogen-rich gas and removing NH_3 from the effluent of said reaction zone, and recovering as noncoking, low-nitrogen-content, crackable oil, unconverted residua remaining after said catalytic hydrocracking and at least the resulting distillate oils boiling above about 700° F.

2. The process of claim **1** wherein by the combination

of said thermal hydrocracking and said catalytic hydrocracking more than 50% of said nonasphaltic residua is converted to distillate oils boiling below 900° F.

3. The process of claim 1 wherein at least 30% of said nonasphaltic residua is converted to distillates boiling below 900° F. by thermal hydrocracking, prior to catalytic hydrocracking.

4. The process of claim 3 wherein at least 40% of the remaining residua after thermal hydrocracking is converted to distillate oils boiling below 900° F. by said catalytic hydrocracking.

5. The process of claim 1 wherein said nonasphaltic residua has a nitrogen content of at least 1000 p.p.m. and at least the resulting distillate boiling above 700° F. and up to about 900° F., recovered as crackable oil, has a nitrogen content of less than 100 p.p.m.

6. The process of claim 5 wherein at least said resulting distillate recovered as crackable oil has a nitrogen content of less than 20 p.p.m.

7. The process of claim 1 wherein the temperature in the thermal hydrocracking zone is between 800° and 900° F. and the temperature in the catalytic hydrocracking zone is between 700° and 850° F.

8. The process of claim 1 wherein there is separately recovered from the effluent of the catalytic hydrocracking zone a low freezing point kerosene distillate.

9. The process of claim 1 wherein said hydrocracking-denitrification catalyst is composed essentially of sulfides of nickel and at least one of the active Group VI metals tungsten and molybdenum incorporated in a porous oxide support selected from the group of siliceous cracking components consisting of silica-alumina, silica-magnesia, and silica-alumina-magnesia.

10. The process which comprises preparing a noncoking, low-nitrogen-content distillate oil boiling above 700° F., by the process of claim 1, and then catalytically hydrocracking said distillate oil in a hydrocracking process employing an acidic hydrocracking catalyst whose activity can be titrated away by nitrogen compounds at a rate dependent on the concentration of nitrogen compounds in the crackable oil.

11. The process which comprises preparing a noncoking, low-nitrogen-content residual oil boiling above 900° F. by the process of claim 1, and then catalytically cracking said residual oil.

12. The process which comprises preparing noncoking, low-nitrogen-content crackable oil by the process of claim 1, separating said oil into a distillate portion boiling above 700° F. and up to about 900° F. and a residual portion boiling above about 900° F., catalytically hydrocracking said distillate portion using an acidic hydrocracking catalyst, and catalytically cracking said residual portion.

13. The process which comprises preparing a noncoking, low-nitrogen-content, residual oil boiling above 900° F. and having no definable end boiling point, by the process of claim 1, and then catalytically hydrocracking the recovered residual oil in a hydrocracking process employing an acidic hydrocracking catalyst whose activity can be rapidly titrated away by nitrogen compounds.

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