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COMBINED PROCESS FOR METAL REMOVAL AND
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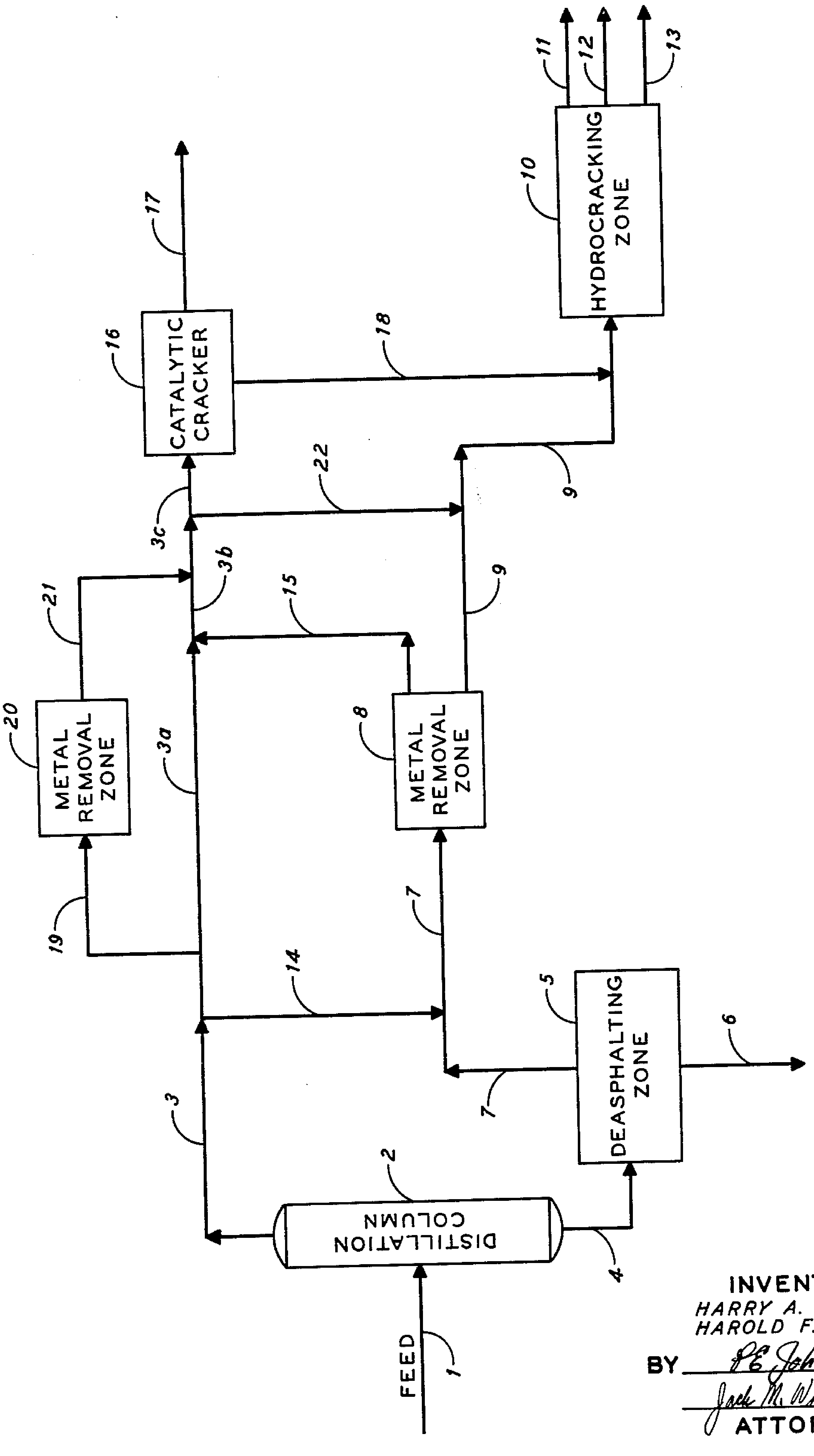

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# COMBINED PROCESS FOR METAL REMOVAL AND HYDROCRACKING OF HIGH BOILING OILS

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This invention relates to processes for the conversion of high-boiling hydrocarbon oils to lower-boiling hydrocarbon products by catalytic hydrocracking. More particularly, the invention relates to hydrocracking processes wherein a high-boiling hydrocarbon oil feed is pretreated to remove metal contaminants including sodium. Still more particularly, the invention relates to a process wherein a residuum feed is treated to remove asphaltic materials and metal contaminants and then hydrocracked.

The idea of catalytically hydrocracking high-boiling hydrocarbon oils to obtain lower-boiling more valuable products is not new. Practical attainment of this objective, however, is another matter. High temperature-high pressure destructive hydrogenation, proposed years ago, was too expensive ever to be used commercially on a wide scale when any other choice was available to the refiner. Recently, new hydrocracking processes have been developed which convert hydrocarbon middle distillates and gas oils to gasoline; for example, the process of U.S. Patent No. 2,944,006 to J. W. Scott, Jr. This process is very economical because it achieves high yields of high grade products at moderate operating conditions of temperature and pressure. An acidic hydrocracking catalyst is used, and nitrogen compounds are removed from the feed. It is desired to extend this type of operation to the conversion of the heaviest and least valuable portions of the crude barrel, e.g. residuum. Serious problems of catalyst fouling or deactivation arise, however, when one attempts to hydrocrack very heavy or high-boiling hydrocarbon oils.

It is an object of this invention to provide an improved hydrocracking process for the conversion of high-boiling hydrocarbon oils. Another object is to provide a hydrocracking process for the production of lower boiling hydrocarbon products from petroleum residuum.

We have found that the aforementioned problems of catalyst fouling when hydrocracking heavy feeds are to a large extent caused by metal contaminants in the feed. This is rather surprising, for it had been thought that the presence of metals in the feed to a catalytic hydrocracking process would have no adverse effects. For example, nickel is one of the principal metal contaminants in many crude oils, but nickel is a desirable component of an active hydrocracking catalyst. The deposition of additional nickel on the catalyst would hardly be expected to be deleterious. This is in distinct contrast to the situation in catalytic cracking, where elevated temperature and low pressure are used and the bad effects of metal contaminants are entirely due to their catalytic activity at those conditions. At the high hydrogen partial pressure and lower temperature conditions of hydrocracking, the catalytic activity of heavy metal contaminants would be predicted to be advantageous. However, it has now been found that the critical metal contaminant in the feed to a hydrocracking process is sodium.

It appears that metals capable of reacting as bases adsorb on acidic sites of the hydrocracking catalysts, thereby diminishing their cracking activity. Alkali metals and alkaline-earth metals so react. Sodium is the principal metal found in many crude hydrocarbon stocks which acts in this manner. In addition, heavy metals commonly found in the highest boiling portions of crude hydrocarbon oils contribute to catalyst activity loss by depositing on the catalyst and physically obscuring active catalyst sites. Copper, nickel, iron, and vanadium are among the most common contaminants of this type. It is believed that the naturally occurring metal contaminants are present in the high-boiling oils primarily as organometallic compounds, such as porphyrins. Additional impurities may be introduced during processing. For example, secondary recovery processes such as water flooding may increase the sodium content of crude petroleum.

We have found that if sodium is substantially removed from high-boiling hydrocarbon oils, other basic-reacting metal contaminants will also be removed, and the oil can then be hydrocracked successfully. Sodium is the most difficult to remove. Hence, processes removing sodium will usually remove the heavy metal contaminants as well, but the converse is not necessarily true.

In accordance with the invention high-boiling hydrocarbon oil, containing metal contaminants including sodium, is converted to lower boiling hydrocarbon products by removing metal contaminants including sodium from the high-boiling oil, recovering high-boiling oil containing substantially less metals, and then hydrocracking the recovered oil. A preferred method of removing the metal contaminants is by catalytic hydrogenation. For best results it is desired that the sodium content of the recovered oil to be hydrocracked be less than 16 parts per million by weight (p.p.m.). Still more preferably the sodium content is reduced to less than 2 p.p.m., particularly when the recovered oil is to be hydrocracked using an acidic hydrocracking catalyst. Also, in this latter case, it is preferred that the recovered oil contain less than 0.5 p.p.m. of heavy metals other than iron.

In accordance with a preferred embodiment of the invention, lower-boiling hydrocarbon products are produced from hydrocarbon residuum, containing metal contaminants including sodium, by deasphalting the residuum to obtain a deasphalted oil containing substantially less metal contaminants, removing metal contaminants from the deasphalted oil and recovering deasphalted oil substantially free of metal contaminants, and then hydrocracking the recovered deasphalted oil to lower-boiling products.

In a still more preferable embodiment, the invention is used to produce lower boiling valuable hydrocarbon products from reduced crude petroleum. A reduced crude is distilled under vacuum to obtain a heavy vacuum gas oil and a residuum. The residuum is deasphalted to obtain a deasphalted oil. Metal contaminants are removed from the deasphalted oil, and preferably from the heavy vacuum gas oil as well, and the recovered substantially metal-free residuum and vacuum gas oil are then hydrocracked in admixture. This is a particularly good way to upgrade highly paraffinic crudes, such as those produced in the Minas oil fields of Sumatra, which are quite resistant to catalytic cracking.

The attached block flow diagram illustrates certain of the above and other embodiments of the invention. Reference to the diagram will be made from time to time herein to aid understanding of the following detailed description.

The feed to the process of this invention may be any high-boiling hydrocarbon oil containing metal contaminants, principally oils boiling above about 650° F. The original source of the oil may be any hydrocarbonaceous deposit of ancient origin, including, besides crude petroleum, such materials as gilsonite, shale oil, oil sands, and the like. Metal contaminants are found in increasing concentrations in the higher-boiling portions of these hydrocarbonaceous materials, probably as organometallic compounds having condensed ring structures. The most common metals, and the most troublesome, are sodium, vanadium, nickel, and copper. Iron is invariably present in relatively high concentration. However, it is so difficult to exclude iron contamination, for example, as a corrosion product, that catalysts sensitive to poisoning by iron are rarely used.

Light and medium boiling range gas oils distilled from crude petroleum rarely contain significant amounts of metal contaminants, and these stocks can already be successfully hydrocracked by known processes. Metal contamination may appear in the heavy gas oils; for example, vacuum gas oils from reduced crude. The depth of distillation of crude oil is often controlled with respect to the cut point at which metal contamination of the distillate appears, so that the metals are concentrated in the residuum. Metal contamination may then appear in the heavy gas oils produced by coking, resid stripping, vis-breaking, and other residuum conversion processes. Hence, the preferred feed stocks for the process of this invention are reduced crude, heavy gas oils, the residuum itself, and portions thereof.

Crude residuum contains in addition to metal contaminants various other nondistillable asphaltic materials, or pitch or tar. Included therein are various heterocyclic compounds of sulfur, nitrogen, oxygen, and metals, and other condensed ring structures. These materials interfere with processes for removing metals. Accordingly, a residuum feed is first deasphalted before removing the metals. Of course, the deasphalting step itself is also a metal removal step, because a large portion of the metal contaminants are present in structures removable by the processes contemplated.

A brief review of the process steps contemplated for use with reduced crude feeds will be useful at this point. Referring to the diagram, high-boiling hydrocarbon oil such as reduced crude petroleum is introduced into the process in line **1**. For example, constituents of the crude oil boiling below about 600° F. or 650° F. have been removed from the feed by atmospheric distillation. Metal contaminants are concentrated in the reduced crude feed. The feed passes to column **2** where it is distilled to obtain vacuum gas oils, taken overhead in line **3**, and a residuum in line **4**. The residuum passes to deasphalting zone **5**. Asphaltic materials, or pitches, resins, or tars, are rejected through line **6**, and deasphalted oil is recovered in line **7**. The deasphalted oil contains substantially less metal contaminants than the residuum. This oil passes through line **7** to zone **8**, where the remaining metal contaminants are removed as completely as is practicable. Substantially metal-free deasphalted oil is recovered, and the recovered oil passes via line **9** to hydrocracking zone **10**. There the high-boiling oil is hydrocracked catalytically to products boiling below the initial boiling point of the oil in line **9**. Usually, there is obtained a middle distillate product in line **13**, a gasoline product in line **12**, and a lighter product in line **11**. The latter is usually subfractionated (not shown).

The deasphalting step may be any solvent decarbonizing procedure whereby compounds such as asphaltenes, pitches, resins, or tars are caused to separate from the bulk of the oil on the basis of their molecular weight, configuration, or size. The preferred process is propane deasphalting, but other light paraffins having 2 to 5 carbon atoms to the molecule may be used instead of or with the propane. The deasphalted oil forms an extract phase with the light paraffin solvent, which separates from the tarry raffinate or asphalt. The deasphalted oil is then recovered from the solvent, which is reused. How completely the asphaltic materials are removed depends on the nature of the residuum, the relative proportions of solvent and residuum, the nature of the solvent, and the efficiency of the process itself. Since the separation is not based strictly on the boiling point of the materials removed, the deasphalted oil will still contain very high-boiling oils and some contaminating compounds of sulphur, nitrogen, oxygen, and metals of the type not removable by deasphalting. In accordance with the invention the remaining metal contaminants are substantially removed from the deasphalted oil in the next step.

The demetallization step may be any process capable of removing metal contaminants, including sodium, from high-boiling oil. The preferred method is catalytic hydrogenation. However, metal contaminants can also be removed by contacting the oil with a solid adsorbent such as alumina, silica-alumina, cracking catalysts, molecular sieves, and certain resins. Also, metal contaminants can be removed by oxidation, either with chemical reagents or with air or oxygen, in the presence of various promoters, or catalysts, such as chromium oxide, or oxygen transfer agents. The oxidized metal compounds are thereby rendered insoluble and may be separated from the oil by desalting, filtration, centrifugation, or other physical separation processes.

When the metal contaminants are removed by adsorption, the adsorbed metals may be removed from the adsorbent, to permit reuse, for example by oxidizing and then abrading the metals off, or by contacting the oxidized adsorbent with an ion exchange resin in an aqueous medum. The metals are thereby transferred to the ion exchange resin which can be regenerated chemically in a well-known manner.

As mentioned, however, it is preferred to remove the metal contaminants by catalytic hydrogenation. In that process the high-boiling oil containing metal contaminants is contacted at temperatures of 350–800° F. and pressures of 200–3000 p.s.i.g. with hydrogen in the presence of a sulfur-resistant hydrogenation catalyst. Usually, the catalyst will comprise one or more of the oxides, sulfides, or other compounds of metals of Group VI and/or Group VIII of the Periodic Table, alone or supported on a carrier. The carrier is typically a refractory oxide support, such as alumina, silica, or silica-alumina, but charcoal and other inert materials may also be used. Under the influence of hydrogen, the organometallic compounds are readily decomposed to the metals, which usually deposit on or between the catalyst particles.

If only metal removal is to be accomplished in the catalytic hydrogenation, an inexpensive catalyst of low activity may be used and discarded when deactivated by the fouling effect of the metal deposits. However, it is often advantageous to accomplish considerable removal of other contaminants such as nitrogen, sulfur, and oxygen, along with the demetallization, in which case a more active catalyst is preferred. Examples of good catalysts are cobalt-molybdate, nickel sulfide-tungsten sulfide, molybdenum sulfide, tungsten sulfide, and nickel sulfide-molybdenum sulfide. Such catalysts can be prepared by a variety of known procedures.

Rather than discarding the more expensive high-activity catalysts, they may be regenerated as required periodically by burning coke deposits from the catalyst and then blowing or washing the resulting metal fines, comprising the metal contaminants removed from the high-boiling oil, from the catalytic hydrogenation reactor. It may be mentioned that the catalytic hydrogenation process also converts a portion of the organo-metallic compounds to insoluble metal fines. A portion of these fines may entrain in the treated oil effluent of the catalytic hydrogenation process, rather than depositing on the catalyst. Accordingly, it is desirable to remove any such insoluble entrained fines by a physical separation process, such as settling, filtration, centrifugation, and the like, prior to hydrocracking the oil.

The demetallization may be accomplished by contacting the oil with the catalyst or adsorbent in a fixed bed contacting zone, or as a slurry or ebulliating bed of solid particles. Oil and hydrogen may be passed concurrently upwards or downwards through the catalyst, or countercurrent flow may be used. The simplest method is to pass the oil and hydrogen concurrently downward through a fixed bed of catalyst particles, and to recycle hydrogen separated from the oil effluent. The metal-free oil is then passed to the hydrocracking zone of the process of this invention.

In the hydrocracking zone the oil is contacted at 400–900° F., 500–5000 p.s.i.g., at a liquid hourly space velocity of 0.2–10 LHSV, in the presence of 2,000–15,000 s.c.f. of hydrogen per barrel of oil, with an active hydrocracking catalyst. This contacting may also be done in any of the abovementioned ways—i.e. slurry, moving bed, or fixed bed; concurrent or countercurrent; and in a single or multiple stages.

The catalyst may be either an acidic hydrocracking catalyst or a nonacidic hydrocracking catalyst. In either event, it will comprise a composition having hydrogenation-dehydrogenation activity as well as cracking activity, in the form of the oxides, sulfides, or other compounds of one or more metals of Groups V, VI, VII, and VIII incorporated with or supported on a carrier which has cracking activity. The catalysts are classified as being either acidic or nonacidic, according to the types of reactions which they selectively promote. Thus, acidic hydrocracking catalysts tend to dealkylate branched-chain aromatics and to crack naphthenes and paraffins to isoparaffins. A high yield of isobutane is a characteristic of an acidic hydrocracking catalyst. Nonacidic hydrocracking catalysts tend to dealkylate both branched-chain aromatics and naphthenes, to hydrogenate more, and to produce considerably less isoparaffins. Acidic hydrocracking is preferred to produce gasoline, while nonacidic hydrocracking is preferred to produce middle distillates. There are possible gradations of acidity in between these two extremes.

The catalysts disclosed as preferred for metal removal by catalytic hydrogenation make acceptable nonacidic hydrocracking catalysts. For hydrocracking, however, higher temperatures and lower space velocities are used, e.g. about 800° F. and 0.2 LHSV.

Preferred acidic hydrocracking catalysts comprise cobalt or nickel sulfide on an active cracking catalyst support. Acidic hydrocracking is preferred in this invention because lower temperatures of 550–750° F. and higher space velocities of 0.3–5 LHSV may be used, and the cracking is more selective so that less normally gaseous hydrocarbon fragments are produced. Acidic hydrocracking is also preferred when the feed is highly paraffinic, because saturated hydrocarbons are quite resistant to nonacidic hydrocracking.

Acidic hydrocracking catalysts are sensitive to nitrogen contaminants in the feed in that the nitrogen compounds convert to ammonia which titrates or neutralizes the acidic sites on the catalyst. Accordingly, the nitrogen content is preferably below about 10 p.p.m., though it may be as high as 200 p.p.m. The deactivating effect of basic metal contaminants is believed to be analogous, in that the acidic sites are also titrated by the metals. For example, after 2000 p.p.m. of lithium was deposited on a catalyst comprising 5% nickel (sulfided) on a silica-alumina cracking catalyst support, the hydrocracking activity of the catalyst was just half of the lithium-free catalyst. Sodium is a more common metal contaminant. Hence, the sodium content of the substantially metal-free oil is preferably not more than about 16 p.p.m. by weight. Superior results are obtained when using an acidic hydrocracking catalyst if the sodium content of the oil is reduced to below 2 p.p.m.

The metal removal step may precede or follow a step wherein nitrogen compounds are removed from the oil feed to the hydrocracker. The nitrogen removal may be by acid washing, absorption, or other means including catalytic hydrogenation.

As mentioned, the feed to the process of this invention may be any high-boiling oil containing metal contaminants. Referring again to the diagram, the vacuum gas oil obtained in line 3 may also contain metal contaminants, depending on the depth of distillation in column 2. The gas oils also are desirably converted to lower boiling products. Conventionally, this may be done by passing the gas oil through lines 3, 3*a*, 3*b*, and 3*c* to catalytic cracker 16. Metals then deposit on the cracking catalyst causing, in the case of metals usch as nickel and vanadium, undesired dehydrogenation reactions increasing the coke and gas make. This is an effect quite distinct from metal poisoning of the hydrocracking catalyst, for in the hydrocracking zone the high hydrogen partial pressure and lower temperature effectively suppress the dehydrogenation equilibria.

To counteract the effect of metal deposits on the cracking catalyst, a slip stream of catalyst may be continuously withdrawn and either discarded or else treated to deactivate or remove the metal contaminants and then returned to the cracker. In one method the metals are deactivated by treating the catalyst slip stream with hydrogen at elevated temperature. In another method the catalyst slip stream is contacted in aqueous suspension with a cation exchange resin to transfer the metals from the catalyst to the resin, which may be regenerated chemically. These methods are not readily applicable to the hydrocracking catalyst because it is difficult to control the treatments to differentiate between the metal contaminants and the active metal components of the catalyst.

Cracked products such as gasoline are recovered in line 17. In addition, there is always a refractory unconverted portion withdrawn as a slurry oil or light or heavy cycle oil in line 18. In accordance with one embodiment of this invention, this cracked cycle oil is admixed with the metal-free deasphalted oil in line 9 and also hydrocracked in zone 10. It is known to hydrocrack cracked cycle oils alone or in admixture with similar stocks, but heretofore it had not been thought feasible to hydrocrack them in admixture with non-distillable oils. Removal of the metal contaminants from the residuum makes this possible.

If the refinery does not already have a catalytic cracker, this invention makes it more profitable to hydrocrack the heavy gas oils than to catalytically crack them. Often this is true even if there is an existing catalytic cracker. Thus, the vacuum gas oil in line 3 may be hydrocracked in admixture with the deasphalted residuum by passing the gas oil through lines 3, 3*a*, 3*b*, and 22 to line 9. With a suitable feed in line 1, column 2 may be operated to exclude metals from the gas oil so that metal removal need be applied only to the residuum, by deasphalting in zone 5 and demetaling in zone 8.

Usually some organometallic compounds will distill with the gas oil, particularly if it is a heavy vacuum gas oil boiling above about 900° F. (corrected to atmospheric pressure). Metals should then be removed from the gas oil. One procedure is to demetal separately by passing the gas oil through line 3, line 19, metal removal zone 20, line 21, line 3*b*, and line 22 to line 9. Superior results are obtained, however, by treating in admixture—by passing the gas oil through line 3 and line 14 to line 7. Metal contaminants are removed from the admixture in zone 8, and the resulting metal-free admixture is recovered and passed through line 9 to hydrocracker 10. When metals are removed by catalytic hydrogenation, treating the oils in admixture as above has the advantage that the viscosity of the deasphalted oil is lowered, and there also appears to be a synergistic effect in facilitating removal of the contaminants.

Metal removal from the gas oil and deasphalted oil in admixture may also be used to advantage even if it is not desired to hydrocrack the gas oil. The metal-free admixture produced in zone 8 may be separated into a lower boiling portion, comprising predominantly metal-free gas oil, recovered in line 15, and a higher boiling portion, comprising predominantly metal-free deasphalted oil, recovered in line 9. The higher boiling portion passes via line 9 to hydrocracking zone 10. The lower boiling portion passes via line **15** to line 3*b*, thence through line 3*c* to catalytic cracker **16**. The cracked cycle oil in line **18** may then be hydrocracked.

In all of the above embodiments minor portions of various streams may be withdrawn from further treating without departing from the spirit and scope of the invention, particularly where an intermediate stream is salable. Thus, a portion of stream **18** may be withdrawn and used as bunker fuel or as a cutter for the tars in line **6**. When two-stage hydrocracking is used in zone **10**, a portion of the intermediate product may be recovered as high purity diesel fuel.

The present invention is particularly valuable in increasing the yield of low-boiling hydrocarbon products from highly paraffinic crudes such as Minas. The waxy nature of this crude makes it quite difficult to process by conventional refining techniques, such as catalytic cracking, even though it contains less sulfur and nitrogen contaminants than many North American crudes. Minas crude has a gravity of about 35.3° API, a viscosity at 130° F. of about 56 SSU, a sulfur content of about 0.07 weight percent, and a pour point of +95° F. Over 50 volume percent boils above 750° F. The following example illustrates one manner in which this invention can be used to convert the heaviest portions of Minas crude to valuable lower-boiling products.

*Example 1.*—From 25,000 barrels per day (b.p.d.) of Minas crude here is obtained by atmospheric distillation 9,400 b.p.d. of distillates boiling below about 650° F. and 15,600 b.p.d. of reduced crude. The reduced crude is then distilled under vacuum to obtain 1,625 b.p.d. of a light vacuum gas oil boiling below 750° F., 8,975 b.p.d. of a heavy vacuum gas oil, and 5,000 b.p.d. of residum boiling above 1,050° F. The residuum has a gravity of about 18.5° API, a viscosity of about 648 SSU at 130° F., and contains 0.16% sulfur. Twenty-one metal contaminants have been identified in the residuum, and others are probably also present. The most important metal contaminants are the following:

| | p.p.m. |
|---|---|
| Sodium | over 42 |
| Vanadium | about 1 |
| Iron | 13–14 |
| Nickel | about 40 |
| Copper | about 7 |

The residuum is propane deasphalted to obtain 3,000 b.p.d. of propane-deasphalted-oil and 2,000 b.p.d. of pitch. The propane-deasphalted-oil contains only about 14 p.p.m., sodium about 0.1 p.p.m. vanadium, about 1.3 p.p.m. nickel, and about 0.1 p.p.m. copper. The propane-deasphalted-oil is blended with the heavy vacuum gas oil, giving 11,975 b.p.d. of admixture. Metal contaminants are substantially completely removed from the admixture by catalytic hydrogenation, and the resulting metal-free admixture is then hydrocracked with an acidic hydrocracking catalyst comprising about 6% nickel (sulfided) on an active acidic silica-alumina cracking catalyst support. Operating at conditions of 500–800° F. and 1500–2500 p.s.i.g., there is obtained from the hydrocracking zone 6,910 b.p.d. of a kerosene or stove oil boiling from 320° F. to 650° F.; 4,050 b.p.d. of a gasoline product suitable for catalytic-reforming, boiling from 180° F. to 320° F.; and 3,230 b.p.d. of lighter products. Of the light products, the equivalent of only 300 b.p.d. are light gases, 1,040 b.p.d. are butanes, and 1,890 b.p.d. are a $C_5$–1800° F. cut. Total conversion is achieved in the hydrocracking zone by recycling to extinction any unconverted material boiling above 650° F. Product distribution may be varied by selecting a different initial boiling point for the material recycled or by recycling only part of the unconverted feed, or by using once-through operation.

The preferred method of removing the metals is by catalytic hydrogenation. The efficiency of the catalytic hydrogenation process is greatly improved when the feed is first deasphalted. The following example illustrates a preferred usage of catalytic hydrogenation to remove metal contaminants from a propane-deasphalted-residuum of Minas crude.

*Example 2.*—A 20% to crude residuum of Minas crude was propane deasphalted to obtain a 60% yield of deasphalted oil. The deasphalted oil was passed through a bed of sulfided 6% nickel-20% moylbdenum on alumina, catalyst together with 4500 s.c.f. of hydrogen per barrel at a liquid hourly space velocity of 0.4 volumes of oil per volume of catalyst per hour and at a hydrogen partial pressure of 1800 p.s.i.a. In successive runs three different temperatures were used, with results as shown in the following tabulation:

| | Deasphalted Oil Feed | Run | | |
|---|---|---|---|---|
| | | A | B | C |
| Temperature, ° F | ------------ | 700 | 725 | 750 |
| Gravity, ° API | 27.3 | 28.8 | 29.5 | 31.5 |
| Nitrogen content, p.p.m | 1,200 | 300 | 200 | 30 |
| Metal content: | | | | |
| Sodium | 14 | 4 | 2.5 | 0.8 |
| Vanadium | <0.1 | 0.01 | ------ | ------ |
| Nickel | 1.3 | 0.06 | 0.05 | 0.04 |
| Iron | 45 | 1.4 | 1.3 | 0.07 |
| Copper | 0.1 | ------ | ------ | ------ |

When an attempt was made to remove metals from the residuum by catalytic hydrogenation (without first deasphalting), metals removal was incomplete, and the catalyst deactivated quite rapidly. Thus, a cobalt-molybdenum-alumina sulfactive hydrogenation catalyst removed 75% of the nickel from Minas residuum when first put on stream at 600–650° F., 1,000 p.s.i.g., 0.5 LHSV, and with 3,000 s.c.f. of $H_2$ per barrel; but after only 10 hours it would remove only 20% of the nickel. Based on this and other data, it was predicted that the catalyst used in Example 2 would be substantially deactivated in about 100 hours or less at the conditions used in that example. Surprisingly, it was found that deactivation or fouling proceeded only slowly. Run C was continued for over 250 hours with no apparent deactivation of the catalyst. Also, it was surprisingly found that the rate at which nitrogen compounds were hydrogenated to ammonia was some 3 to 5 times the predicted rate based on the physical properties of the deasphalted oil. The improved operation is attributed to the removal of metals and other condensed ring structures in the deasphalting step. Thus, a particularly preferred and novel process embodiment of this invention, for the conversion of residua to lower boiling products, comprises propane deasphalting the residuum, removing metals from the deasphalted oil by catalytic hydrogenation, and then hydrocracking the oil, in that order.

The type of hydrocracking process used is selected on the basis of the types of products desired. However, the selection is to a considerable extent restricted by other factors such as the nitrogen content of the oil and the metal content of the oil. Thus, for example, the product produced in Run C of Example 2 had a sufficiently low sodium content and a sufficiently low nitrogen content such that this material could be subjected directly to hydrocracking with an acidic hydrocracking catalyst although a lower nitrogen content would be preferred. Both the sodium content and the nitrogen content of the material produced in Run A of Example 2 are higher than would be desired in the feed to an acidic hydrocracking catalyst. A two-stage hydrocracking process would preferably be selected wherein the nitrogen content as well as the sodium content would be further reduced in a denitrification first stage ahead of an acidic hydrocracking second stage. Any of the products of Example 2 could be hydrocracked using a non-acidic catalyst, but it would be preferred to use an oil having a sodium content at least as low as that of Run B.

We claim:

1. A process for the conversion of reduced crude petroleum to lower boiling valuable products, which comprises the steps:

(1) distilling, under vacuum, reduced crude petroleum containing heavy metal contaminants and sodium to obtain a heavy vacuum gas oil and a residuum containing metal contaminants including more than 16 p.p.m. of sodium;

(2) solvent treating residuum, obtained in step (1), in a deasphalting residual zone to obtain deasphalted oil of reduced metal content but containing more than 2 p.p.m. sodium;

(3) catalytically hydrogenating deasphalted residual oil, obtained in step (2), by contacting with hydrogen in a hydrogenation zone containing a sulfur-resistant hydrogenation catalyst at 350–800° F. and 200–3000 p.s.i.g., to remove metal contaminants including sodium and thereby obtain demetalized deasphalted residual oil containing less than 2 p.p.m. sodium and less than 0.5 p.p.m. of heavy metals other than iron; and

(4) catalytically hydrocracking demetalized deasphalted residual oil, obtained in step (3), by contacting in a catalytic hydrocracking zone with an active acidic hydrocracking catalyst at conditions of 550–750° F., 500–5000 p.s.i.g., and 0.2–10 LHSV, in the presence of 2,000–15,000 standard cubic feet of hydrogen per barrel of oil.

2. A process for the conversion of reduced crude petroleum containing metal contaminants including sodium and heavy metals to lower boiling valuable products which comprises:

(1) distilling reduced crude petroleum under vacuum to obtain a heavy vacuum gas oil containing organometallic compounds and a residuum containing most of the metal contaminants,

(2) solvents deasphalting said residuum to obtain a deasphalted residual oil containing less metal contaminants than said residuum and an asphaltic residuum in which metal contaminants are concentrated,

(3) removing metal contaminants from said deasphalted residual oil, and recovering deasphalted residual oil substantially free of metal contaminants,

(4) removing metal contaminants from said heavy vacuum gas oil, and recovering gas oil substantially free of metal contaminants, and

(5) hydrocracking the recovered oils to obtain lower boiling valuable hydrocarbon products by contacting with an active hydrocracking catalyst in the presence of 2000–15,000 standard cubic feet of hydrogen per barrel of oil at 400–900° F., 500–5000 p.s.i.g. and 0.2–10 LHSV.

3. The process of claim 2 wherein metal contaminants are removed from said deasphalted oil by a catalytic hydrogenation process which converts a portion of the organometallic compounds to insoluble metal fines, at least a portion of which fines is entrained in the deasphalted oil recovered from said process, and said insoluble entrained fines are removed by a physical separation process prior to hydrocracking said recovered oil.

4. The process of claim 2 wherein metal contaminants are removed from said heavy vacuum gas oil and from said deasphalted residual oil by catalytic hydrogenation to obtain recovered oils containing less than 2 p.p.m. sodium and less than 0.5 p.p.m. of heavy metals other than iron, and the recovered oils are hydrocracked using an acidic hydrocracking catalyst.

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