July 12, 1966 T. V. INWOOD ET AL 3,260,663

MULTI-STAGE HYDROCRACKING PROCESS

Filed July 15, 1963 4 Sheets-Sheet 1

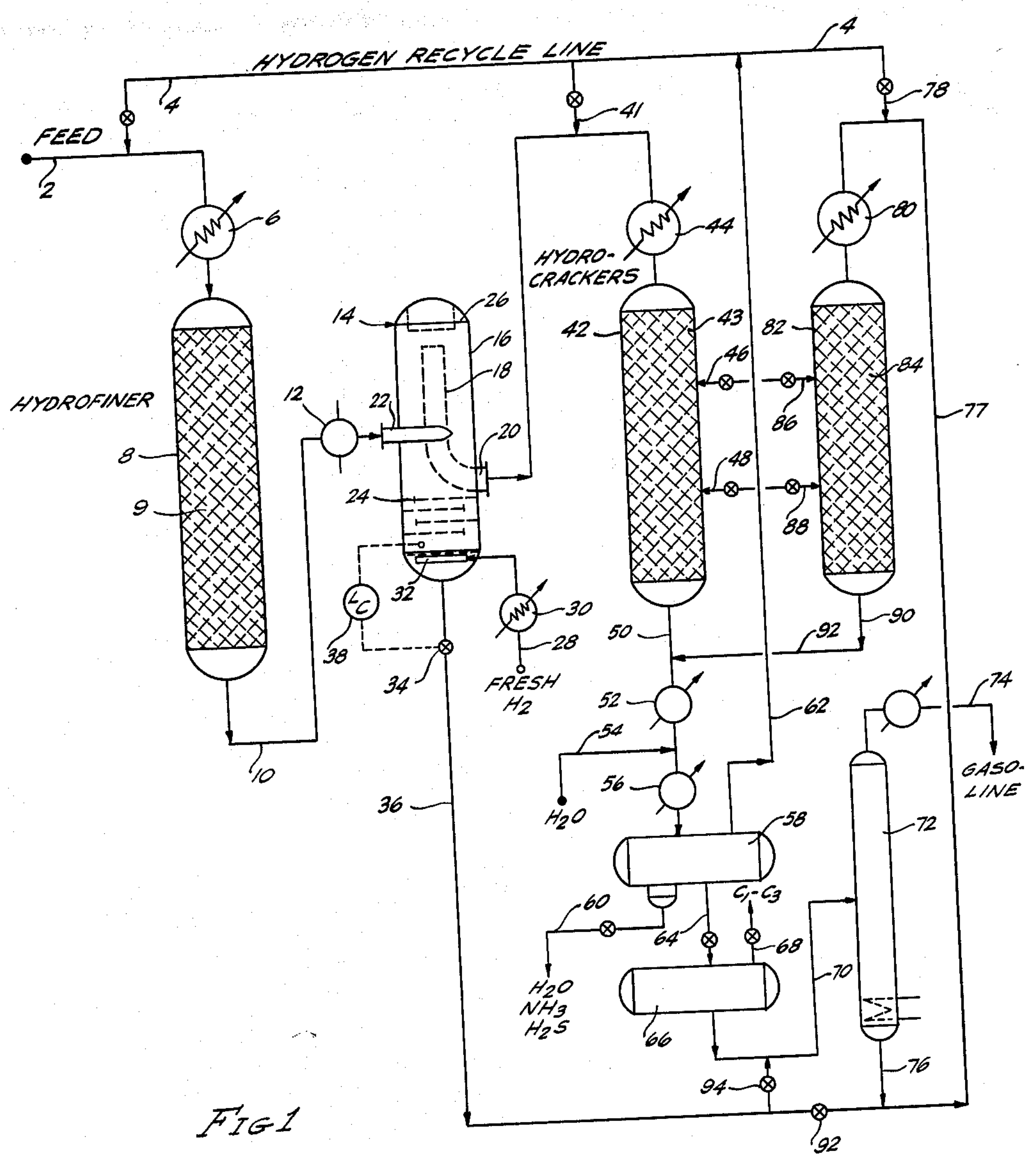

FIG 1

INVENTORS
TEXAS V. INWOOD
PAUL F. HELFREY
RAOUL P. VAELL
BY James S. Henderson
ATTORNEY

July 12, 1966 T. V. INWOOD ET AL 3,260,663

MULTI-STAGE HYDROCRACKING PROCESS

Filed July 15, 1963 4 Sheets-Sheet 2

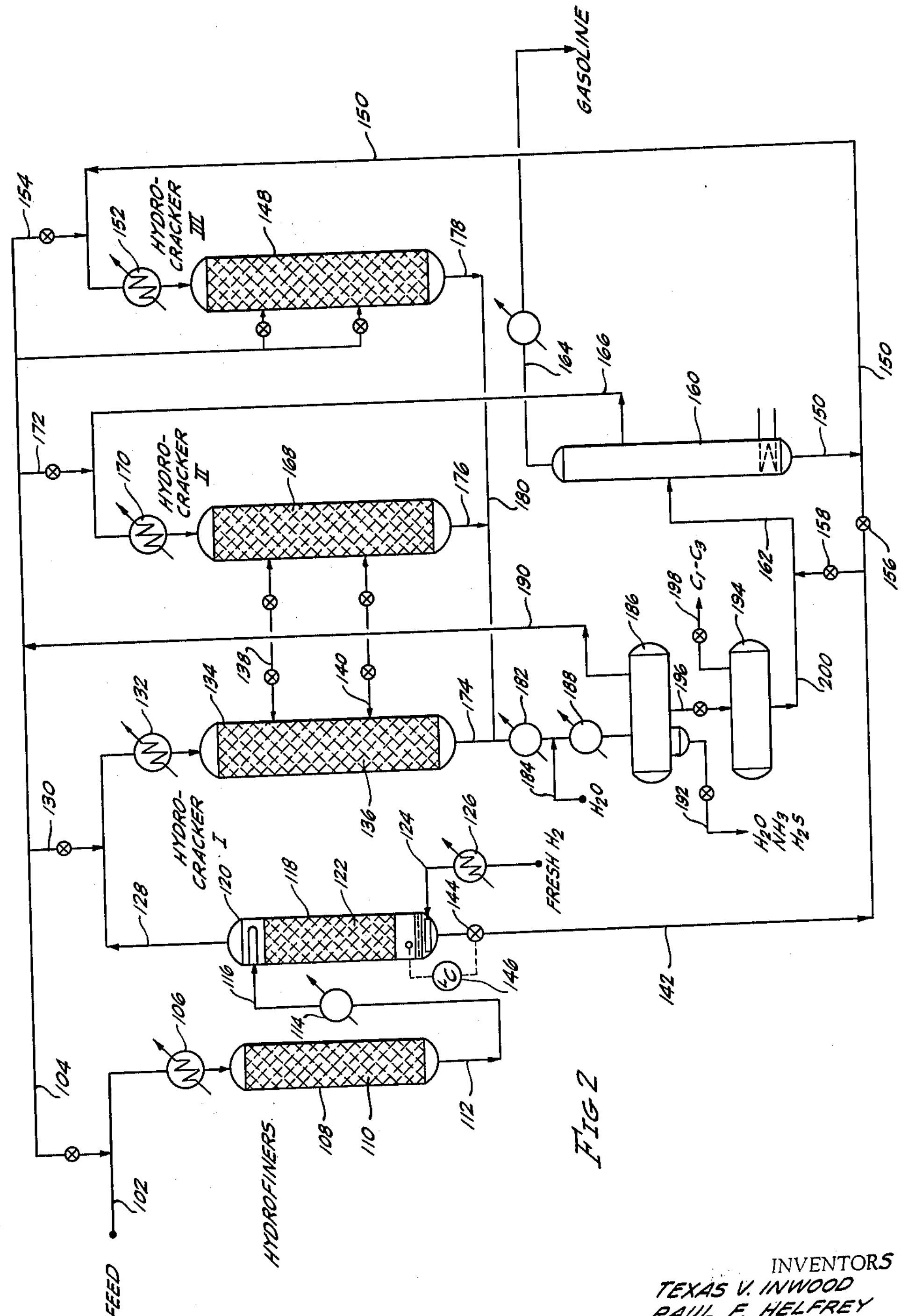

FIG 2

INVENTORS
TEXAS V. INWOOD
PAUL F. HELFREY
RAOUL P. VAELL

BY James S. Henderson

ATTORNEY

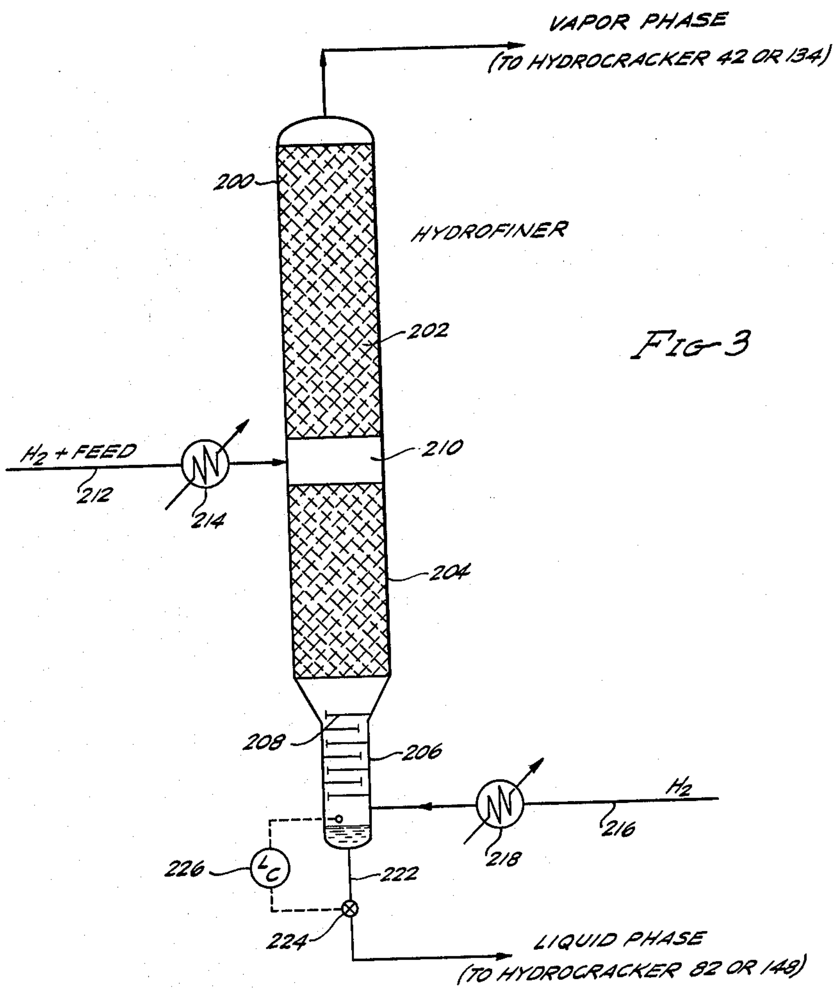

FIG-3

INVENTORS
TEXAS V. INWOOD
PAUL F. HELFREY
RAOUL P. VAELL
BY James S. Henderson
ATTORNEY

MULTI-STAGE HYDROCRACKING PROCESS

Filed July 15, 1963 4 Sheets-Sheet 4

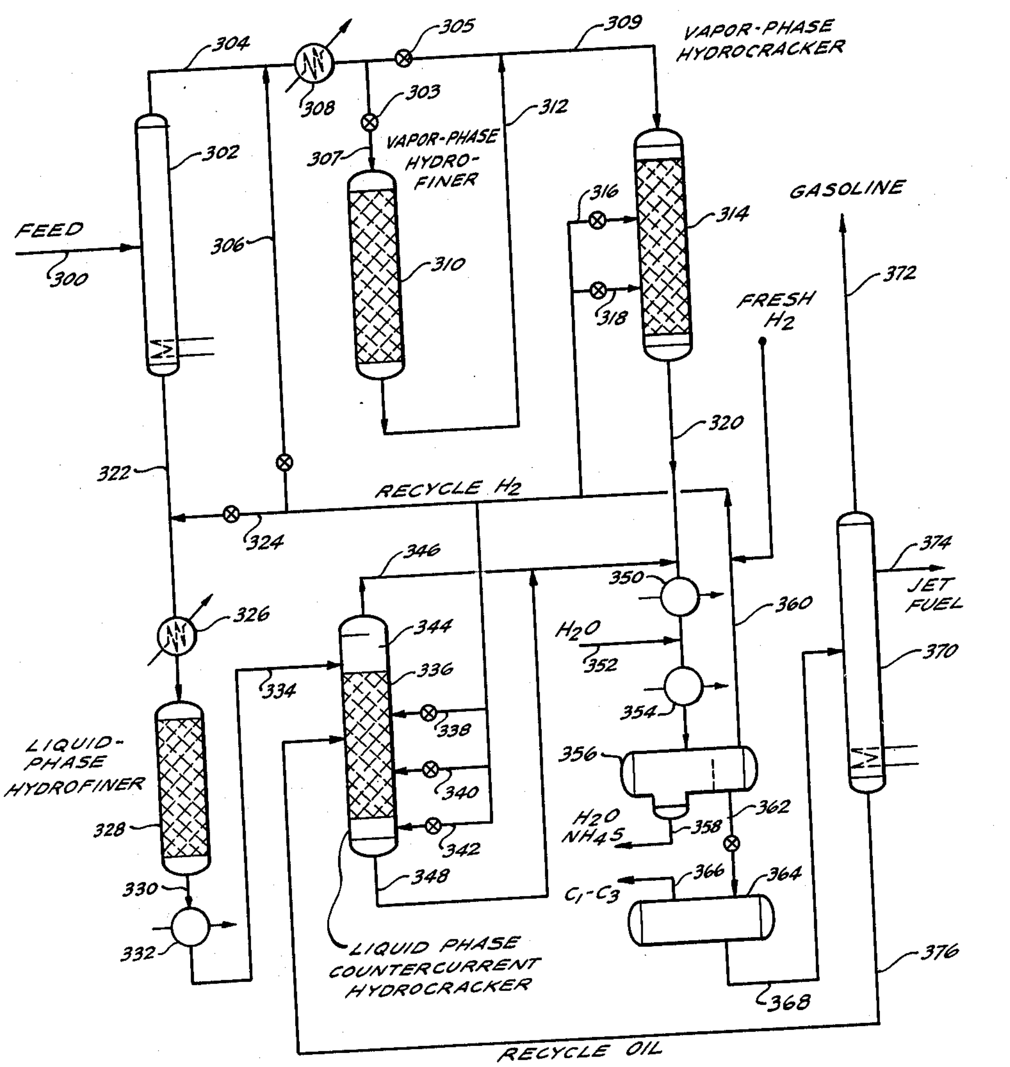

FIG-4

INVENTORS
TEXAS V. INWOOD
PAUL F. HELFREY
RAOUL P. VAELL
BY Lannas S. Henderson
ATTORNEY

United States Patent Office

3,260,663

Patented July 12, 1966

3,260,663

MULTI-STAGE HYDROCRACKING PROCESS

Texas V. Inwood, La Habra, Paul F. Helfrey, Whittier, and Raoul P. Vaell, Los Angeles, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Filed July 15, 1963, Ser. No. 295,029
21 Claims. (Cl. 208—59)

This application is a continuation-in-part of application Serial No. 151,999, filed November 13, 1961, and now abandoned.

This invention relates to the catalytic hydrocracking of hydrocarbons to produce lower boiling hydrocarbons, boiling for example in the gasoline or jet fuel range. In broad aspect, the invention relates to split-feed hydrocracking, wherein a full-range feedstock containing nitrogen and/or sulfur compounds is split into a light fraction relatively rich in nitrogen and/or sulfur compounds and a heavy fraction relatively lean in nitrogen and/or sulfur compounds, and each fraction is separately hydrocracked under optimum conditions, said optimum conditions including a relatively high hydrocracking temperature for the light fraction and a relatively low temperature for the heavy fraction. More specifically, the invention embraces certain novel procedures for integrating a hydrofining pretreatment with such split-feed hydrocracking, whereby at least the heavy feed fraction may be prehydrofined, and all the hydrofiner effluent, both vapor phase and liquid phase, may be sent directly to the hydrocrackers without substantial interstage cooling, depressuring, purification, reheating, repressuring, etc. A sub-combination of this "intergral" hydrofining-hydrocracking process involves simply separating a relatively heavy hydrocarbon fraction from the hydrofiner effluent, whereby the remaining light hydrocarbon fraction may be more efficiently hydrocracked in the presence of the inorganic decomposition products, ammonia and/or hydrogen sulfide, which were produced in the hydrofiner.

Briefly stated, in a more comprehensive aspect, the invention comprises the following steps: (1) the initial feedstock is subjected to catalytic hydrofining with added hydrogen in such manner that separate liquid phase and vapor phase hydrofiner effluents are produced, each comprising a substantial portion of the initial feed; (2) the liquid phase, after substantial hydrofining has taken place, is stripped with hydrogen at essentially hydrofining temperatures and pressures to remove ammonia, hydrogen sulfide and light hydrocarbons; (3) the stripped liquid phase is subjected to catalytic hydrocracking under relatively mild conditions; (4) the vapor phase effluent from the hydrofining, mixed if desired with stripping vapors from step (2), is then subjected to catalytic hydrocracking under relatively severe conditions; and (5) gasoline, or other desired low-boiling hydrocarbon fraction, synthesized in each hydrocracking zone is recovered.

According to a preferred embodiment of the invention, at least a portion of the stripping of hydrofiner liquid phase (step 2) is carried out integrally during the hydrofining by providing a countercurrent flow of hydrogen upwardly through the lower portion of the reactor to strip out the ammonia and light hydrocarbons from the downflowing liquid phase, the resulting stripping vapors being withdrawn from the hydrofiner at an upper point, along with the vapor phase hydrofiner effluent. This preferred mode of operating may be carried out either (1) by admitting feed-plus-hydrogen at the top of the hydrofiner, admitting an additional hydrogen stream at the bottom, and removing vapor phase effluent at a mid-point or (2) by admitting feed-plus-hydrogen at a mid-point to the hydrofiner, admitting an additional hydrogen stream at the bottom, and removing vapor phase effluent from the

top. In either case the liquid phase gravitates downwardly in the lower portion of the reactor, countercurrently to the hydrogen admitted at the bottom.

According to another preferred embodiment of the invention, the initial feedstock is first fractionated into a light fraction which is subjected to vapor-phase hydrocracking (after hydrofining if desired), and a heavy fraction which is separately hydrofined, mainly in the liquid phase, with concurrent flow of feed and hydrogen. The total effluent from the liquid phase hydrofiner is then separated, without substantial cooling or depressuring, into a hydrofined liquid phase and a hydrofined vapor phase. The hydrofined liquid phase is then subjected to hydrocracking in countercurrent flow with hydrogen to strip out dissolved ammonia, hydrogen sulfide and light hydrocarbons concurrently as hydrocracking proceeds. All vapor phase and liquid phase hydrocracker effluents, as well as the vapor phase hydrofiner effluent, are then combined and treated for product and recycle gas recovery, with unconverted oil being recycled to the countercurrent-flow, liquid-phase hydrocracker.

The feedstocks employed in catalytic hydrocracking processes ordinarily comprise mineral oil fractions boiling between about 400° and 1,000° F. Such feedstocks normally contain hydrocarbons boiling over the entire spectrum, between the initial boiling point and the end-boiling-point. It is well known in catalytic cracking that optimum cracking temperatures vary for hydrocarbons of different molecular weight. For example, where the desired product is gasoline (comprising mostly hydrocarbons in the C_6–C_{12} range), the optimum cracking temperature for converting a C_{13} hydrocarbon to gasoline will be higher than the optimum temperature for converting a C_{20} or C_{30} hydrocarbon to gasoline. Therefore, when the feedstock contains hydrocarbons spread over the entire C_{12} to C_{30} molecular weight range, it is necessary to select a hydrocracking temperature which is a compromise between the optimum for converting hydrocarbons on either end of the range. One of the objectives of this invention is to provide a simple and inexpensive pre-fractionating step which permits separation of the feed into a relatively low molecular weight portion, and a relatively high molecular weight portion, each of which may be separately hydrocracked under more nearly optimum conditions of temperature and pressure.

Another major difficulty in hydrocracking processes is encountered in connection with feedstocks containing organic nitrogen compounds. These nitrogen compounds are mostly basic in character, and tend to poison the acidic cracking centers of hydrocracking catalysts. To overcome this difficulty, the feedstock is often subjected to a preliminary catalytic hydrofining treatment in order to convert the nitrogen compounds to ammonia, and the product is then condensed and washed to remove the ammonia. The remaining nitrogen-free hydrocarbons are then subjected to hydrocracking. The principal objection to this pretreatment process is that the facilities required for condensing, washing, reheating and repressuring the hydrofiner effluent, are very expensive.

It is also known in catalytic hydrocracking that the poisoning effect of nitrogen compounds can be counteracted by operating at higher hydrocracking temperatures. However, this procedure is objectionable in the case of feedstocks containing substantial amounts of high-boiling components, boiling for example above about 650° F. High-temperature hydrocracking of feedstocks containing such high-boiling constituents leads to rapid deactivation of the catalyst due to coke formation. However, this objection would, at least in part, disappear if most of the high-boiling constituents could be removed from the portion of the hydrocracking feed which contains nitrogen compounds. It will thus appear that in the process of this invention, the separate treatment of the low-boiling portion of feed is cooperatively interrelated with the minimizing of catalyst deactivation due to nitrogen compounds. Due to the prehydrofining treatment, substantially all of the nitrogen compounds are converted to low-boiling nitrogen bases such as ammonia, which will then appear in the vapor phase portion of the hydrofiner effluent. This entire vapor phase portion may be contacted directly with the hydrocracking catalyst at suitably elevated temperatures which not only are optimum for cracking efficiency of the hydrocarbons, but also for avoiding the poisoning effect of nitrogen compounds.

It will be noted that all of the advantages discussed above are obtainable herein regardless of the particular procedure employed for producing separate liquid- and vapor-phase hydrofiner effluents. However, still further advantages accrue in the preferred modes of operation wherein separate liquid phase hydrofining is carried out substantially in the absence of the light, vapor phase feed fraction. This mode of operation provides greater flexibility, and if desired, a more extended treatment (lower space velocity) for the liquid phase portion than for the vapor phase portion. The latter is normally desirable in that the high molecular weight nitrogen compounds in the liquid phase are more refractory and require more extended treatment for their removal.

From the foregoing, it will appear that one objective of this invention is to provide optimum conditions of hydrocracking for different boiling range portions of the feedstock. An overall objective is to obtain all of the substantial benefits of prehydrofining without the normally accruing disadvantage of the expensive condensation, washing, reheating and repressuring facilities required for separate, or non-integral hydrofining. A more specific objective is to pretreat the feedstock in such a manner that all of the components therein, principally low-boiling hydrocarbons and low-boiling nitrogen compounds, which can be efficiently hydrocracked at high temperatures are conveniently segregated into a vapor phase fraction which can be so treated, while the heavier hydrocarbons are recovered essentially nitrogen-free and in condition for a separate low-temperature hydrocracking treatment. A still further objective is to provide hydrofining facilities which will effect maximum removal of nitrogen compounds without overtreatment of the lower boiling portions, thus minimizing the overall volume of hydrofining catalyst and reactor space required. Other objectives will be apparent from the more detailed description which follows.

The invention may perhaps be more readily understood with reference to the accompanying drawings. FIGURE 1 is a flowsheet illustrating the invention in one of its simpler aspects. FIGURE 2 is a flowsheet illustrating a modification of the invention employing three separate hydrocracking zones, the hydrofining operation being performed with integral separation of liquid phase and vapor phase. FIGURE 3 is a cross-sectional view of an alternative form of hydrofining unit, which can be employed in either of the modifications shown in FIGURES 1 and 2. FIGURE 4 is a flowsheet illustrating one modification of the invention utilizing feed-prefractionation, separate hydrofining of the heavy and light fractions, and countercurrent-flow hydrocracking. In the succeeding description, it will be understood that the drawings have been simplified by the omission of certain conventional elements such as valves, pumps, compressors, and the like. Where heaters or coolers are indicated, it will be understood that these are merely symbolic, and in actual practice many of these will be combined into banks of heat exchangers and fired heaters, according to standard engineering practice.

Referring more particularly to FIGURE 1, the initial feedstock is brought in via line **2**, mixed with recycle and makeup hydrogen from line **4**, preheated to incipient hydrofining temperature in heater **6**, and then passed directly into hydrofiner **8**, containing a bed of hydrofining catalyst **9**, where hydrofining proceeds under substantially conventional conditions. Suitable hydrofining catalysts include for example mixtures of the oxides and/or sulfides of cobalt and molybdenum, or of nickel and tungsten, preferably supported on a carrier such as alumina or alumina containing a small amount of coprecipitated silica gel. Other suitable catalysts include in general the oxides and/or sulfides of the Group VIB and/or Group VIII metals, preferably supported on substantially non-cracking adsorbent oxide carriers such as alumina, silica, titania, and the like. The hydrofining operation may be conducted either adiabatically or isothermally, and under the following general conditions:

HYDROFINING CONDITIONS

	Operative	Preferred
Temperature, ° F. (avg. bed)	600–850	650–825
Pressure, p.s.i.g.	500–3,000	800–2,000
LHSV, v./v./hr.	0.5–10	1–5
H_2/oil ratio, s.c.f./b.	500–15,000	1,000–10,000

The above conditions are suitably adjusted so as to reduce the organic nitrogen content of the feed to below about 25 parts per million, and preferably below about 10 parts per million.

The total hydrofined product from hydrofiner **8** is withdrawn via line **10** and transferred via heat exchanger **12** to a centrifugal separator-stripper **14**, which may be of the Webre cyclone type. It will be understood that exchanger **12** may be used either to cool the mixed-phase effluent from the hydrofiner, or to heat it, as may be necessary to obtain the desired phase separation in separator **14**. The illustrated separator-stripper **14** consists of an outer cylindrical shell **16** enclosing an axially positioned, open-ended vapor outlet conduit **18**, which extends upwardly to near the top of shell **16**, and terminates downwardly at vapor outlet port **20**, located peripherally below the center portion of shell **16**. The feed inlet conduit **22** enters shell **16** tangentially thereto, so that the liquid portion of entering feed spirals downwardly inside shell **16**, and collects on stripping trays **24**. The entering vapor phase portion of feed spirals upwardly around vapor outlet conduit **18** and enters the top thereof and thence flows downwardly and out through vapor outlet port **20**. In order to prevent entrainment of liquid in the gas phase, a depending cylindrical drip-ring **26** is provided in the top of the separator. In this manner, the liquid and gas phases are rapidly and effectively separated.

To effect stripping of ammonia, hydrogen sulfide and light hydrocarbons from the liquid phase on stripping trays **24**, fresh hydrogen required in the process is brought in through line **28**, preheated in heater **30**, and injected into the bottom of the separator by means of a distributing ring **32**, or the equivalent. This hydrogen flows upwardly, countercurrently to the descending liquid on trays **24**, and the stripping vapors are removed via outlet conduit **18**, along with the vapor phase portion of feed. Normally, about 300–10,000 s.c.f. of hydrogen per barrel of liquid phase is adequate. The hydrogen admitted via line **28** may also include recycle hydrogen if the fresh makeup hydrogen is insufficient to provide the desired stripping action.

It is normally found that satisfactory phase separation for purposes of this invention can be obtained in separator **14** at pressures within about 300 p.s.i.g. of the hydrofiner pressure, and normally within about 200° F. of the hydrofiner effluent temperatures. This presupposes a feedstock boiling in the gas-oil range, and containing at least about 20% of components boiling above 650° F. Preferably, the temperature is adjusted, if necessary, so that about 20–80% of the feed will be recovered from the stripper as liquid phase.

The liquid phase accumulating in the bottom of separator **14** is withdrawn via valve **34** and line **36**, more or less continuously in response to liquid level controller **38**. Due to the fractionation and stripping effected in separator **14**, this liquid portion normally will contain less than about 10% of hydrocarbons boiling below 450° F., and less than about 10 parts per million of nitrogen. Preferably the stripping should be controlled so as to reduce the nitrogen level to below about 5 parts per million. This liquid portion will be treated as hereinafter described.

The vapor phase from separator **14**, withdrawn via outlet conduit **20** and transfer line **40**, constitutes the feed to first hydrocracker **42**. This vapor phase comprises the unused hydrogen from the hydrofiner, the hydrogen used for stripping in the separator, and most of the feed hydrocarbons boiling below about 650° F. Preferably, the conditions in separator **14** are suitably adjusted so that the hydrocarbon content of the vapor phase effluent will comprise less than about 5 mole-percent of hydrocarbons boiling above 650° F. It will be apparent also that this vapor-phase effluent contains substantially all of the ammonia and hydrogen sulfide formed in the hydrofiner. The final mixture is thus well suited to hydrocracking operations conducted at relatively high temperatures. Normally, it is unnecessary to admit additional hydrogen, but if desired additional recycle hydrogen can be added via line **41**. From line **40**, the mixture is passed via preheater **44** (if needed) into the top of first hydrocracker **42**, which is filled with a suitable hydrocracking catalyst **43**, to be described hereinafter, and passes downwardly therethrough.

The process conditions in first hydrocracker **42** are suitably adjusted so as to provide about 20–60% conversion to gasoline per pass, while at the same time permitting relatively long runs between regenerations, i.e., from about 2 to 8 months. The range of operative conditions contemplated for hydrocracker **42** are as follows:

LIGHT FEED HYDROCRACKER CONDITIONS

	Operative	Preferred
Temperature, ° F. (avg. bed)	600–850	650–800
Pressure, p.s.i.g.	500–3,000	800–2,000
LHSV, v./v./hr.	0.5–10	0.7–5
H_2/oil ratio, s.c.f./b.	500–15,000	1,000–10,000

Those skilled in the art will readily understand that when ranges of operating conditions are specified as above, a large number of determinative factors are involved. Thus, highly active catalysts, or fresh catalysts at the beginning of a run, will be used in conjunction with lower temperatures than will less active, or partially deactivated, catalysts. The lower limit of pressure to be utilized in a given operation will normally depend upon the desired run length. Lower pressures generally result in a more rapid deactivation of the catalyst, and hence where extremely long run lengths are desired, pressures of above about 1,000 p.s.i.g. are mandatory. However, economically feasible run lengths are normally obtainable with most catalysts and feedstock within the 600–2,000 p.s.i.g. pressure range.

Since the hydrocracking reaction is exothermic, it is usually desirable to maintain a more nearly isothermal temperature profile in hydrocracker **42**, e.g., by the injection of cool quench hydrogen at one or more points, as illustrated via lines **46** and **48**.

The effluent from hydrocracker **42** is withdrawn via line **50**, partially cooled and condensed in cooler **52**, then mixed with wash water from line **54**, and transferred via final condenser **56** to high-pressure separator **58**. The purpose of the wash water is to remove water-soluble impurities such as ammonia, hydrogen sulfide and salts thereof, although in most cases it is unnecessary to remove all the hydrogen sulfide. Normally about 15 pounds of water per barrel of liquid hydrocarbon is sufficient for removing ammonia and salts. It is preferable to inject the wash water prior to the final cooling in condenser **56**, in order to avoid the condensation of solid salts in the transfer lines, as might occur if final cooling to, e.g., 200° F. were carried out before the injection of water.

A three-phase separation takes place in high pressure separator **58**. Spent wash water containing dissolved impurities is discharged via line **60**, and recycle hydrogen is withdrawn via line **62** and returned to hydrogen recycle line **4** for reuse in the hydrofining and hydrocracking reactors. Liquid hydrocarbons in separator **58** are withdrawn via line **64** and flashed into low-pressure separator **66**, from which dissolved light hydrocarbon gases are exhausted via line **68**. The liquid hydrocarbon fraction in separator **66** is transferred via line **70** to fractionating column **72**, from which the desired gasoline product is withdrawn as overhead via line **74**. The bottoms fraction from column **72** is withdrawn via line **76**, and in the preferred operation is blended with the stripped liquid phase hydrofiner effluent from line **36** by opening valve **92** and closing valve **94**. However, in some cases, it may be desirable to divert the liquid phase hydrofiner effluent to column **72** by opening valve **94** and closing valve **92**, so as to fractionate out any gasoline-boiling-range material. In either case however, the bulk of the liquid-phase hydrofiner effluent will be blended with unconverted oil from the hydrocrackers, and the blend will constitute feed to second hydrocracker **82**. The blended feed in line **77** is then mixed with recycle hydrogen from line **78**, and transferred via preheater **80** into the top of second hydrocracker **82**, where the mixture passes downwardly in contact with a bed of hydrocracking catalyst **84**.

It will be apparent that the feedstock treated in hydrocracker **82** differs considerably from the feed to the first hydrocracker, in that it is substantially free of nitrogen compounds and has a lower gravity. It may also be substantially free of sulfur compounds, and hence the second hydrocracker may be operated entirely sweet if desired by removing hydrogen sulfide from the recycle gas to that stage. Due to the substantial absence of nitrogen compounds, lower temperatures and higher conversion levels can be maintained in hydrocracker **82** than in hydrocracker **42**, assuming equal catalyst activities. The process conditions in hydrocracker **82** are preferably adjusted so as to provide about 30–80% conversion to gasoline per pass, said conversion also being about 1.1 to 4 times higher than in first-stage hydrocracker **42**. To achieve these objectives, the hydrocracking conditions should be suitably correlated within the following general ranges:

HEAVY FEED HYDROCRACKER CONDITIONS

	Operative	Preferred
Temperature, ° F. (avg. bed)	400–800	500–750
Pressure, p.s.i.g.	500–3,000	800–2,000
LHSV, v./v./hr.	0.5–10	0.7–5
H_2/oil ratio, s.c.f./b.	500–15,000	1,000–10,000

It will be noted that the above temperature ranges overlap the ranges previously specified for hydrocracker **42**. It is contemplated however, assuming approximately equal catalyst activities in the two zones, that the temperature in hydrocracker **42** will be maintained about 20°–120° F. higher than in hydrocracker **82**, depending mainly upon the nitrogen content of the feed. In cases where the respective catalyst activities are unequal, the temperature differential will be modified upwardly or downwardly from this range, so as to maintain the differential conversion levels previously specified. Assuming a feed nitrogen content of at least about 0.01% by weight, the optimum conversion per pass in hydrocracker **82** will generally be about 1.2 to 2 times higher than the conversion per pass in hydrocracker **42**.

To maintain the desired temperature profile in hydrocracker **82**, one or more quench points may be utilized wherein cool recycle hydrogen is admitted and mixed with the reactants, as illustrated via lines **86** and **88**.

The effluent from hydrocracker **82** is withdrawn via line **90**, and may if desired be treated separately for the recovery of gasoline and recycle oil. However, in the modification illustration, the effluent is transferred via line **92** to effluent line **50** from hydrocracker **42**, and the mixture is condensed, water-washed and fractionated as previously described. It will be apparent therefore that the bottoms product removed from column **72** will constitute the unconverted oil from both hydrocrackers, and the gasoline product removed via line **74** will comprise the gasoline synthesized in each reactor. The feed to hydrocracker **82** will also comprise, in addition to the unconverted oil from each hydrocracker, at least the bulk of the liquid phase which as withdrawn from separator **14** via line **36**.

Referring now to FIGURE 2, this modification illustrates a dual-hydrofining system providing for more extended hydrofining of the heavy portion of feed, and also illustrates the use of three separate hydrocracking zones for different portions of the feed, with the conditions in each zone being adjusted to the characteristics of the feed to the respective zone. This modification provides for maximum efficiency in each of the contacting zones.

The initial feedstock is brought in through line **102**, blended with recycle hydrogen from line **104**, and passed via preheater **106** to mixed-phase hydrofiner **108** containing a bed of granular hydrofining catalyst **110**. In hydrofiner **108**, the conditions of hydrofining are substantially the same as those previously described in connection with hydrofiner **8** of FIGURE 1, except that higher space velocities will normally be employed, e.g., from about 1.5 to 10. The effluent from mixed-phase hydrofiner is wthdrawn via line **112** and, if desired, passed through heat exchanger **114** for suitable temperature adjustment, and then transferred via line **116** into open space **120** in the top of separator-hydrofiner **118**, where phase separation takes place.

The liquid feed portion which separates in space **120** trickles downwardly through catalyst bed **122**, countercurrently to an ascending stream of preheated hydrogen admitted through line **124** and preheater **126**. This hydrogen stream may comprise the whole of the fresh make-up hydrogen required for the system, and may also, if desired, include some of the recycle hydrogen. The rising hydrogen stream in hydrofiner **118** keeps the liquid phase saturated with hydrogen, and a sufficient excess is present to provide turbulence and to strip out dissolved light hydrocarbons, ammonia, and the like. Other process conditions in hydrofiner **118** are generally similar to those in hydrofiner **108**.

The combined vapors accumulating in space **120** are continuously withdrawn via line **128**, blended if desired with recycle hydrogen from line **130**, and passed via heater **132** into the top of first hydrocracker **134** containing a bed of granular hydrocracking catalyst **136**. Hydrocracking proceeds in reactor **134** under conditions substantially the same as those previously described in connection with hydrocracker **42** of FIGURE 1, cool quench hydrogen being admitted at one or more points via lines **138** and **140**.

The liquid phase accumulating in the bottom of hydrofiner **118** is withdrawn via line **142** and valve **144** in response to liquid level controller **146**. If the initial feedstock and the process conditions in hydrofiner **118** are such that the liquid phase contains only a minor proportion of hydrocarbons boiling below about 650° F., it is preferably transferred, without depressuring, directly to third hydrocracker **148** via line **150** and preheater **152**. To operate in this manner, valve **156** is open and valve **158** closed. However, if the liquid phase in line **142** contains a substantial proportion, e.g., at least 20% of hydrocarbons boiling below about 650° F., it may be preferable to close valve **156** and open valve **158**, so that the liquid portion will flow into fractionator **160** via line **162**.

In fractionator **160**, the combined liquid products from the three hydrocracking zones, and if desired the liquid phase from hydrofiner **118**, are fractionated to recover the desired gasoline product, as well as selected feed fractions for hydrocrackers **168** and **148**. A side-out boiling predominantly in the 400°–650° F. range is withdrawn via line **166** and transferred to second catalytic hydrocracker **168** via preheater **170**, in admixture with recycle hydrogen admitted via line **172**. A bottoms fraction boiling mostly above 650° F. is withdrawn from column **160** via line **150** and transferred to third catalytic hydrocracker **148** via preheater **152**, in admixture with recycle hydrogen admitted via line **154**.

It will thus be apparent that first hydrocracker **134** serves to hydrocrack the entire vapor phase from hydrofiner **108**, which contains ammonia and hydrogen sulfide, and comprises hydrocarbons boiling mostly in the 400°–650° F. range; second hydrocracker **168** serves to hydrocrack unconverted recycle oil, and hydrofiner effluent if desired, boiling mostly in the 400°–650° F. range and being essentially free of nitrogen compounds; while third hydrocracker **148** serves to hydrocrack hydrofiner effluent and unconverted recycle oil boiling mostly above 650° F., this feed also being essentially free of nitrogen compounds. It will thus be apparent that different hydrocracking conditions will be optimum in each hydrocracker, assuming equal catalyst activity in each unit. Due to the presence of ammonia and nitrogen compounds in first hydrocracker **134**, temperatures about 20°–120° F. higher than in second hydrocracker **168** will normally be employed therein. And, due to the lower boiling range of the feed to second hydrocracker **168**, as compared to the feed to third hydrocracker **148**, temperatures about 20°–100° F. higher will be utilized in the former than in the latter. Assuming a feed boiling substantially in the 400°–650° F. range for hydrocrackers **134** and **168**, and a feed boiling predominantly above 650° F. for reactor **148**, suitable temperature conditions are illustrated in the following table, the other process conditions being substantially the same as those described in connection with reactors **42** and **82** of FIGURE 1.

TABLE 1

	Average Bed Temperature, ° F.	
	Operative	Preferred
Hydrocracker 134	650–850	700–825
Hydrocracker 168	500–800	550–750
Hydrocracker 148	400–750	450–700

The optimum temperatures within these ranges will depend to a large extent upon the type of catalysts employed in the respective hydrocracking zones. In general, the conditions of temperature and catalyst are suitably adjusted so as to provide a conversion to 400° F. end-point gasoline in hydrocracker **134** of about 20–50% by volume; 30–75% in hydrocracker **168**; and a conversion to 550° F.-minus material in reactor **148** of about 30–80% by volume.

It will be noted that a common product recovery system is also provided in FIGURE 2, but it is not intended to exclude modifications wherein separate product recovery systems are provided for each hydrocracking zone. Effluent from hydrocrackers **134**, **168** and **148** is withdrawn via lines **174**, **176** and **178** respectively, and blended in line **180**. The mixed effluent in line **180** is then partially condensed in cooler **182**, mixed with wash water from line **184**, and transferred to high-pressure separator **186** via final condenser **188**. Hydrogen-rich recycle gas is withdrawn from separator **186** via line **190**, spent wash water is discharged via line **192**, and condensed liquid hydrocarbons are flashed into low-pressure separator **194** via line **196**. Flash gases comprising light hydrocarbons are withdrawn from separator **194** via line **198**, and the remaining liquid phase is transferred via line **200** and line **162** to distillation column **160** for fractionation as previously described, either alone or in admixture wth the liqud phase from hydrofiner **118** and line **142**.

The sidecut fraction in line **166** from column **160**, constituting the feed to second hydrocracker **168**, may in many cases comprise an excellent jet fuel, and if desired a portion thereof may be diverted for use as jet fuel.

Many variations are contemplated of the processing schemes described above. One such variation, as illustrated specifically in FIGURE 3, embraces an alternative type of hydrofining unit **200**, comprising an upper hydrofining catalyst bed **202**, a lower hydrofining catalyst bed **204**, and if desired, a dependent stripping column **206** containing stripping trays **208**. Preheated feed-plus-hydrogen is introduced into interspace **210** via line **212** and preheater **214**, the vapor phase portion of feed passing upwardly through bed **202**, and the liquid phase gravitating downwardly through lower bed **204** and trays **208**, counter-currently to a preheated hydrogen stream admitted via line **216** and preheater **218**. Stripping vapors from column **206** and lower bed **204** mingle with the vapor phase feed in upper bed **202**, and the entire vapor phase is taken overhead via line **220** and sent to hydrocracker **42** or **134**, as previously described. Stripped liquid phase effluent is withdrawn via line **222** and valve **224**, in response to liquid level controller **226**, and sent to hydrocracker **82** or **148**, as previously described. This modification is advantageous in providing for a more efficient hydrofining of the vapor phase in the absence of liquid phase.

According to another modification of the invention shown in FIGURE 2, hydrofiner **118** may be omitted, and the total hydrofiner **108** effluent in line **112** fed into the open space at the top of hydrocracker **148**, where phase-separation is allowed to take place. The resulting liquid phase is then allowed to gravitate downwardly through hydrocracker **148**, countercurrently to a rising stream of hydrogen which mingles at the top with the vapor-phase hydrofiner effluent. The total vapor phase from the top of hydrocracker **148** is then taken off and transferred to hydrocracker **134** for treatment as previously described. Thus, by modifying hydrocracker **148** to operate with countercurrent flow, the entire hydrofining unit **118** can be omitted at the expense of a slight decrease in overall hydrofining efficiency, and hydrocracking catalyst efficiency in hydrocracker **148**.

Reference is now made to FIGURE 4, which illustrates a modified version of the FIGURE 1 process, providing for maximum hydrofining catalyst efficiency and for longer run lengths in the vapor phase hydrocracker. In the succeeding description, the hydrofining and hydrocracking conditions may be presumed to be the same as those described in connection with FIGURE 1, unless some change is indicated. The principal operational modifications over FIGURE 1, lie in the use of a feed prefractionator for making a sharper cut between the vapor phase feed and the liquid phase feed, the provision of separate hydrofiners for liquid and vapor phase, and the provision of a countercurrent liquid phase hydrocracking reactor.

Initial feedstock is brought in through line **300** and fractionated in column **302** to obtain a relatively sharp separation of feed into a light fraction and a heavy fraction, the cut point normally lying somewhere in the range between about 500° and 700° F., preferably about 600–650° F. It is preferred to operate column **302** so that the light feed fraction contains less than about 1% by volume of hydrocarbons having a true boiling point above about 700° F., and the heavy feed fraction contains less than about 5% by volume of hydrocarbons having a true boiling point below the selected cut point. By substantially eliminating heavy hydrocarbons from the light feed, the succeeding vapor phase hydrocracker can be operated with maximum efficiency for long periods of time, e.g., 12–24 months. By substantially reducing the amount of light hydrocarbons in the liquid phase, the effective activity of dissolved hydrogen in the succeeding liquid phase hydrofiner is increased, thus improving hydrofining efficiency.

The light feed fraction from column **302** is taken overhead via line **304**, mixed with recycle and fresh hydrogen from line **306** and then either subjected directly to hydrocracking, or to hydrofining followed by hydrocracking. The choice between these two alternatives depends upon several factors. If the initial feed contains less than about 200 p.p.m. of nitrogen, then hydrofining of the light fraction will often be unnecessary, since the permissible higher hydrocracking temperatures for the light fraction can effectively overcome the slight poisoning effect of small amounts of nitrogen. If the end-point of the selected light fraction is below about 500° F., even higher hydrocracking temperatures can be used, thus increasing even further the nitrogen tolerance. In any case, the choice depends upon the balancing of economic factors in the particular unit concerned, mainly the cost of more frequent hydrocracking catalyst regenerations versus the cost of the hydrofining unit.

If hydrofining is not to be utilized, valve **303** is closed and valve **305** opened, whereby the mixture in line **304** passes through preheater **308** where it is heated to hydrocracking temperatures, and transferred via line **309** directly to vapor-phase hydrocracker **314**. If hydrofining is desired, valve **303** is opened and valve **305** closed, whereby the mixture in line **304** passes through preheater **308**, line **307** and vapor-phase hydrofiner **310**. Effluent from hydrofiner **310** is then withdrawn via line **312** and passed via line **309** through vapor-phase hydrocracker **314**, to which additional cool quench hydrogen may be admitted interstage via lines **316** and **318**.

Due to the substantially complete elimination of heavy hydrocarbons from the feed to hydrocracking **314**, the run lengths obtainable therein are extended, e.g., about 2 to 6 months, over the runs obtainable in hydrofiner **42** of FIGURE 1. Effluent from hydrocracker **314** is withdrawn via line **320** and treated for purification and product recovery in admixture with liquid-phase hydrocracker effluent, as will be subsequently described.

Heavy liquid feed from column **302** is withdrawn via line **322**, blended with recycle and fresh hydrogen from line **324**, preheated to hydrofining temperature in heater **326**, and passed through liquid-phase hydrofiner **328**. Due to the more complete elimination of light feed hydrocarbons from hydrofiner **328**, space velocities 5–20% higher than those required in hydrofining zone **204** of FIGURE 3 may be utilized. Effluent from hydrofiner **328** is withdrawn via line **330**, partially cooled in heat exchanger **332** and transferred via line **334** to the top of countercurrent liquid-phase hydrocracker **336**, into which hydrogen may be injected via lines **338**, **340** and **342**. The rising hydrogen stream mingles with the downflowing oil, vaporizing a portion thereof, and stripping out H_2S, NH_3 and like impurities generated in hydrofiner **328**, and the entire vapor-phase effluent from hydrocracker **336**, plus the vapor phase from hydrofiner **328**, is withdrawn via separation zone **344** and line **346**. Unconverted oil is withdrawn as bottoms via line **348**. In cases where total conversion of the initial feed to gasoline is desired, this bottoms fraction may be recycled directly back to the top of hydrocracker **336** along with the feed in line **334**. However, in cases where mid-boiling-range products such as jet fuels are also to be recovered, the liquid-phase product in line **348** is transferred to vapor-phase effluent line **346**, and the entire effluent from hydrocracker **336** then mingles with vapor-phase hydrocracker effluent in line **320**.

The mixed effluent in line **320** is then partially cooled in condenser **350**, mixed with wash water injected via line **352**, and further cooled in condenser **354**. The condensed mixture is then transferred to high-pressure separator

356, wherein a three-phase separation takes place. Spent wash water containing dissolved ammonia and ammonium sulfide is withdrawn via line 358, recycle hydrogen substantially free of ammonia via line 360, and high-pressure condensate via line 362. The liquid condensate in line 362 is then flashed into low-pressure separator 364, from which light flash gases are withdrawn via line 366. Low-pressure condensate in separator 364 is then transferred via line 368 to fractionating column 370, from which the gasoline product is withdrawn overhead via line 372, a desired jet fuel product as a side-cut via line 374, and remaining bottoms fraction via line 376, which is recycled, preferably to a mid-point in hydrocracker 336. In cases where the entire bottoms from hydrocracker 336 is recycled directly back to the liquid-phase hydrocracker, the bottoms fraction from column 370 will comprise mainly the unconverted hydrocarbons from vapor-phase hydrocracker 314.

By operating hydrofiner 328 in the absence of light hydrocarbons, and because hydrocracker 336 is operated counter-currently, important hydrofining economies are realized. Firstly, as noted, the effective activity of dissolved hydrogen in the liquid phase in hydrofiner 328 is inherently greater due to the absence of light hydrocarbons. This promotes hydrofining efficiency. Secondly, due to the provision of countercurrent flow in hydrocracker 336, the hydrofining in hydrofiner 328 need not be as complete as would otherwise be required. Whereas, in a concurrent hydrocracker, it is normally necessary to reduce the organic nitrogen level to below about 10 parts per million, in the modification illustrated the organic nitrogen level of the hydrofiner effluent may be for example about 25–50 parts per million. In this case, the removal of nitrogen is completed in the upper portion of catalyst in hydrocracker 336. Thus, by the initial sharp fractionation of feed in column 302, and the provision of countercurrent flow in hydrocracker 336, the overall hydrofining capacity, in terms of total hydrofining catalyst required, may be reduced by about 25–50% over that required in the modification of FIGURE 1.

The feedstocks which may be treated herein include in general any mineral oil fraction having an initial boiling point above the conventional gasoline range, i.e., above about 400° F., and having an end-boiling-point of up to about 1,000° F. This includes straight-run gas-oils, coker distillate gas oils, deasphalted crude oils, cycle oils derived from catalytic or thermal cracking operations and the like. These fractions may be derived from petroleum crude oils, shale oils, tar sand oils, coal hydrogenation products and the like. Specifically, it is preferred to employ feedstocks boiling between about 400° and 900° F., having an API gravity of 15° to 35°, containing at least about 20% by volume of acid-soluble components (aromatics+olefins), and at least about 20% by volume of hydrocarbons boiling above 650° F. Such oils may also contain from about 0.1% to 5% of sulfur and from about 0.001% to 2% by weight of nitrogen.

The hydrocracking catalysts to be employed in the hydrocracking units described above may consist of any desired combination of a refractory cracking base with a suitable hydrogenating component. Suitable cracking bases include for example mixtures of two or more refractory oxides such as silica-alumina, silica-magnesia, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, silica-zirconia-titania, acid treated clays and the like. Acidic metal phosphates such as aluminum phosphate may also be used. The preferred cracking bases comprise composites of silica and alumina containing about 50%–90% silica; coprecipitated composites of silica, titania and zirconia containing between 5% and 75% of each component; partially dehydrated, zeolitic, crystalline molecular sieves, e.g., of the "X" or "Y" crystal types, having relatively uniform pore diameter of about 8 to 14 Angstroms, and comprising silica, alumina and one or more exchangeable zeolitic cations. Any of these cracking bases may be further promoted by the addition of small amounts, e.g., 1 to 10% by weight, of halogen or halides such as fluorine, boron trifluoride or silicon tetrafluoride.

The foregoing cracking bases are compounded, as by impregnation, with from about 0.5% to 25% (based on free metal) of a Group VIB or Group VIII metal promoter, e.g., an oxide or sulfide of chromium, tungsten, cobalt, nickel, or the corresponding free metals, or any combination thereof. Alternatively, even smaller proportions, between about 0.05% and 2% of the metals platinum, palladium, rhodium or iridium may be employed. The oxides and sulfides of other transitional metals may also be used, but to less advantage than the foregoing.

A particularly suitable class of hydrocracking catalysts is composed of about 75–95% by weight of a coprecipitated base containing 5–75% SiO_2, 5–75% ZrO_2 and 5–75% TiO_2, and incorporated therein from about 5–25%, based on free metal, of a Group VIII metal or metal sulfide, e.g., nickel or nickel sulfide.

In the case of the zeolitic molecular sieve type catalysts, it is preferable to add the hydrogenating metal by ion-exchange. This can be accomplished by digesting the molecular sieve base in its ammonium or alkali metal forms, with an appropriate solution of a compound of the hydrogenating metal wherein the metal appears in the cation, as described in Belgian Patent No. 598,686.

The molecular sieve type cracking bases, when compounded with a Group VIII noble metal hydrogenating component, are particularly useful for hydrocracking at relatively low temperatures of 400–700° F., and relatively low pressures of 500–2,000 p.s.i.g. It is preferred to employ molecular sieves having a relatively high SiO_2/Al_2O_3 ratio, e.g., between about 2.5 and 10. The most active forms are those wherein the exchangeable zeolitic cations are hydrogen and/or a divalent metal such as magnesium, calcium or zinc. In particular, the "Y" molecular sieves, wherein the SiO_2/Al_2O_3 ratio is about 5/1–6/1, are preferred, either in their hydrogen form, or a divalent metal form, preferably magnesium. Normally, such molecular sieves are prepared first in the sodium or potassium form, and the monovalent metal is ion-exchanged out with a divalent metal, or where the hydrogen form is desired, with an ammonium salt followed by heating to decompose the zeolitic ammonium ion and leave a hydrogen ion. It is not necessary to exchange out all of the monovalent metal; the final compositions may contain up to about 6% by weight of NaO, or equivalent amounts of other monovalent metals. Catalysts of this nature are more particularly described in Belgian Patents Nos. 598,582, 598,682, 598,683 and 598,686.

As in the case of the X molecular sieves, the Y sieves also contain pores of relatively uniform diameter in the individual crystals. In the case of X sieves, the pore diameters may range between about 6 and 14 A., and this is likewise the case in the Y sieves, although the latter usually are found to have crystal pores of about 9 to 10 A. in diameter.

The following examples are cited to illustrate more concretely, exemplary process conditions and results, but are not intended to be limiting.

Example I

This example illustrates the results obtainable in a typical operation of the process described in FIGURE 1, using as feed a 400–860° F. boiling range coker gas-oil containing 2% of sulfur and 0.3% of nitrogen by weight, and having an API gravity of 22°, and with stripped liquid phase from stripper 16 being sent directly to hydrocracker 82. The hydrofining catalyst is composed of about 4% cobalt sulfide plus 16% of molybdenum sulfide impregnated on a silica-stabilized (5% SiO_2) activated alumina support. The hydrocracking catalyst in both zones is a magnesium "Y" molecular sieve containing about 3% by weight of zeolitic magnesium, and loaded with 0.5% by weight of palladium (Linde hydrocracking catalyst MB 5382). The operating conditions are as follows:

TABLE 2

Operating Conditions	Hydro-finer 8	Separator 14	Hydro-cracker 42	Hydro-cracker 82
LHSV	1.0	----------	1.5	1.5
Pressure, p.s.i.g	1,550	1,540	1,530	1,540
Temperature, ° F.:				
Start of run	700	725	700	450
End of run	750	725	850	700
H_2/oil ratio, s.c.f./b	5,000	[a] 2,000	10,000	8,000
Conversion to 400° F. end-point gasoline, vol.-percent per pass	5	----------	40	65
5-95% feed boiling range, ° F.	420-800	----------	420-650	420-800

[a] Based on liquid phase and added stripping hydrogen only; approximately 50% of feed in liquid phase.

On the basis of an operation utilizing 10,000 barrels per day of initial feed, with total recycle of unconverted oil to hydrocracker 82, and using a recycle gas containing about 1% by volume of H_2S, the approximate yields are as follows:

TABLE 3

Conversion to gasoline and lighter	vol. percent	100
C_1–C_3 dry gas	s.c.f./b. feed	80
Liquid products:		
Butanes	b./d.	1,100
C_5–C_6	b./d.	2,400
C_7–400° F.	b./d.	8,900
Total liquid products	b./d.	12,400
Chemical H_2 consumption	s.c.f./b. feed	2,800

TABLE 3

Product Quality	C_5-C_6	C_7-400° F.
Gravity, ° API	82	49
Research octane +3 ml. TEL	99	80
Basic nitrogen, p.p.m.	----------	<0.2

Example II

This example illustrates the results obtainable by the operation described in Example I, but using as the catalyst in each hydrocracking reactor a coprecipitated composite of a 20% silica, 50% zirconia, 30% titania hydrocracking base, on which is deposited 20% by weight of nickel in the form of nickel sulfide. The operating conditions are as follows:

TABLE 4

Operating Conditions	Hydro-finer 8	Separator 14	Hydro-cracker 42	Hydro-cracker 82
LHSV	1.0	----------	1.5	1.5
Pressure, p.s.i.g	1,550	1,540	1,530	2,000
Temperature, ° F.:				
Start of run	700	725	740	700
End of run	750	725	850	850
H_2/oil ratio, s.c.f./b	5,000	[a] 2,000	10,000	8,000
Conversion to 400° F. end-point gasoline, vol.-percent per pass	5	----------	35	55
5-95% feed boiling range, ° F.	420-800	----------	420-650	420-800

[a] Based on liquid phase and added stripping hydrogen only; approximately 50% of feed in liquid phase.

On the basis of an operation utilizing 10,000 barrels per day of initial feed, the approximate yields are as follows:

TABLE 5

Conversion to gasoline and lighter	vol. percent	100
C_1–C_3 dry gas	s.c.f./b. feed	100
Liquid products:		
Butanes	b./d.	1,300
C_5–C_6	b./d.	2,400
C_7–400° F.	b./d.	8,600
Total liquid products	b./d.	12,300
Chemical H_2 consumption	s.c.f./b. feed	3,000

Product Quality	C_5-C_6	C_7-400° F.
Gravity, °API	82	49
Research octane+3 ml. TEL	99	83
Basic nitrogen, p.p.m.	----------	<0.2

Example III

This example illustrates the results obtainable in the process modification shown in FIGURE 2, using the same feed, hydrofining catalyst and "Y" molecular sieve hydrocracking catalyst as in Example I. Operating conditions are as follows:

TABLE 6

Operating Conditions	Hydro-finer 108	Hydro-finer 118	Hydro-cracker 134	Hydro-cracker 168	Hydro-cracker 148
LHSV	1.0	[a] 1.5	1.5	1.5	1.5
Pressure, p.s.i.g	1,150	1,140	1,140	1,150	1,130
Temperature, ° F.:					
Start of run	700	700	700	550	450
End of run	750	750	850	700	670
H_2/oil, s.c.f./b	5,000	--------	11,000	8,000	8,000
sep'n zone	--------	7,000	--------	--------	--------
stripping zone	--------	[a] 3,000	--------	--------	--------
Conversion to 400° F. end-point gasoline, vol.-percent per pass	3	2	40	65	[b] 65-70
5-95% feed boiling range, ° F.	420-800	--------	420-650	420-650	650-800

[a] Based on liquid phase only; 40-60% of feed in liquid phase.
[b] Conversion to 550° F. minus material.

On the basis of an operation utilizing 10,000 barrels per day of initial feed, the approximate yields are as follows:

TABLE 7

Conversion to gasoline and lighter	vol. percent	100
C_1–C_3 dry gas	s.c.f./b. feed	60
Liquid products:		
Butanes	b./d.	1,100
C_5–C_6	b./d.	2,400
C_7–400° F.	b./d.	8,900
Total liquid products	b./d.	12,400
Chemical H_2 consumption	s.c.f./b. feed	2,800

Product Quality	C_5-C_6	C_7-400° F.
Gravity, °API	82	48
Research Octane+3 ml. TEL	99	83
Basic nitrogen, p.p.m.	----------	<0.2

Results analogous to those indicated in the foregoing examples are obtained when other hydrocracking catalysts and conditions, other feedstocks and other hydrofining conditions within the broad purview of the above disclosure are employed. It is hence not intended to limit the invention to the details of the examples or the drawings, but only broadly as defined in the following claims:

We claim:

1. A process for hydrocracking a mineral oil feedstock boiling over a substantial temperature range and containing a non-hydrocarbon impurity selected from the class

consisting of organic nitrogen compounds and organic sulfur compounds, which comprises:

(1) subjecting said feedstock plus added hydrogen to catalytic hydrofining under conditions of pressure, temperature and fluid distribution such that a substantial liquid phase is present in at least a portion of the hydrofining zone, and a substantial vapor phase is present in at least a portion of the hydrofining zone;

(2) stripping said liquid phase with hydrogen after substantial hydrofining has taken place and at substantially hydrofining pressure to produce a stripped liquid-phase hydrofiner effluent relatively lean in said impurities and a vapor-phase stripping effluent containing relatively light hydrocarbons and relatively rich in volatile decomposition products of said impurity;

(3) subjecting vapor-phase hydrofiner effluent from step (1), without intervening purification or depressuring to below the desired hydrocracking pressure, to catalytic hydrocracking in a first hydrocracking zone in the absence of said stripped liquid phase at a relatively high temperature;

(4) subjecting said stripped liquid-phase hydrofiner effluent, without further purification, to catalytic hydrocracking in a second hydrocracking zone at a relatively low temperature; and

(5) recovering desired low-boiling hydrocarbons from each of said hydrocracking zones.

2. A process as defined in claim **1** wherein said feedstock is first fractionated into a relatively high-boiling fraction and a relatively low-boiling fraction, the high-boiling fraction being subjected to liquid phase hydrofining in said step (1), and wherein said low-boiling fraction is subjected to a separate vapor-phase catalytic hydrofining, and total effluent therefrom, including volatile decomposition products of said impurity, is blended with said vapor-phase stripping effluent for high-temperature hydrocracking in said first hydrocracking zone.

3. A process as defined in claim **1** wherein said feedstock is first fractionated into a relatively high-boiling fraction and a relatively low-boiling fraction, the high-boiling fraction being subjected to liquid-phase hydrofining in said step (1), and wherein said low-boiling fraction is blended directly with said vapor-phase stripping effluent for high-temperature hydrocracking in said first hydrocracking zone.

4. A process as defined in claim **1** wherein said feedstock, without prior fractionation, is subjected to said hydrofining step (1), and wherein total effluent therefrom is then separated into liquid-phase hydrofiner effluent for stripping in step (2), and a vapor-phase effluent for high-temperature hydrocracking in said first hydrocracking zone.

5. A process as defined in claim **1** wherein at least a portion of said hydrogen stripping of liquid phase in step (2) is carried out integrally with hydrofining step (1) by maintaining countercurrent flow of hydrogen and liquid feed therein.

6. A process for converting an impure hydrocarbon feedstock boiling above the gasoline range to lower boiling hydrocarbons, which comprises:

(1) subjecting said feedstock to hydrofining with added hydrogen over a sulfactive hydrofining catalyst under hydrofining conditions such that a substantial portion of the feed is in the liquid phase and a substantial portion is in the vapor phase;

(2) subjecting said liquid phase, after substantial hydrofining has taken place, to stripping with hydrogen at essentially hydrofining temperatures and pressures to produce a vapor-phase stripping effluent rich in volatile impurities and comprising most of the feed hydrocarbons boiling below about 650° F., and a stripped liquid phase rich in heavier hydrocarbons and lean in volatile impurities;

(3) subjecting vapor-phase effluent from said hydrofining, in admixture with vapor-phase stripping effluent from step (2), to catalytic hydrocracking in a first hydrocracking zone in the absence of said stripped liquid phase under relatively severe conditions including a temperature between about 600° and 850° F.;

(4) subjecting said stripped liquid phase to catalytic hydrocracking in a second hydrocracking zone under relatively mild conditions including a temperature between about 400° and 800° F.; and

(5) recovering low-boiling hydrocarbons synthesized in each of said hydrocracking zones.

7. A process as defined in claim **6** wherein each of said hydrofining, stripping, and hydrocracking steps are performed at substantially the same pressures, decreasing progressively no more than that occasioned by the dynamic pressure drop through the system.

8. A process as defined in claim **6** wherein at least a portion of said hydrogen stripping of liquid phase is carried out during a liquid phase hydrofining operation wherein said liquid phase is passed downwardly through a bed of hydrofining catalyst, and hydrogen is passed countercurrently upwardly therethrough forming said vapor-phase stripping effluent.

9. A process as defined in claim **6** wherein the hydrocracking catalyst employed in at least one of said hydrocracking zones is a dehydrated, zeolitic molecular sieve of the Y crystal type containing zeolitic cations from the group consisting of hydrogen and divalent metals, and promoted with a Group VIII noble metal hydrogenating component.

10. A process as defined in claim **6** wherein said hydrocarbon feedstock is a gas oil containing at least about 0.01% nitrogen and a substantial proportion of hydrocarbons boiling above about 650° F., and wherein said lower boiling hydrocarbons produced therefrom comprise gasoline.

11. A process as defined in claim **10** wherein the hydrocracking conditions in said first and second hydrocracking zones are adjusted and correlated so as to provide a conversion per pass to gasoline in said second hydrocracking zone which is (a) between about 30% and 80% by volume, and (b) between about 1.2 and 2 times the conversion per pass to gasoline in said first hydrocracking zone.

12. A process for converting an impure hydrocarbon feedstock boiling above the gasoline range to lower boiling hydrocarbons, which comprises:

(1) subjecting said feedstock to hydrofining with added hydrogen over a sulfactive hydrofining catalyst under hydrofining conditions such that a substantial portion of the feed is in the liquid phase and a substantial portion is in the vapor phase;

(2) subjecting said liquid phase, after substantial hydrofining has taken place, to stripping with hydrogen at essentially hydrofining temperatures and pressures to produce a vapor-phase stripping effluent rich in volatile impurities and comprising most of the feed hydrocarbons boiling below about 650° F., and a stripped liquid phase rich in heavier hydrocarbons but lean in volatile impurities;

(3) subjecting vapor-phase effluent from said hydrofining in admixture with vapor-phase stripping effluent from step (2) to catalytic hydrocracking in a first hydrocracking zone in the absence of said stripped liquid phase under relatively severe conditions, including a temperature between about 650° and 850° F. and a pressure between about 500 and 3,000 p.s.i.g.;

(4) subjecting at least the high-boiling portion of said stripped liquid phase to catalytic hydrocracking in a third hydrocracking zone under relatively mild conditions including a temperature between

about 400° and 750° F. and a pressure between about 500 and 3,000 p.s.i.g.;

(5) subjecting the effluents from said first and third hydrocracking zones to condensation and fractionation to recover (a) the desired low-boiling hydrocarbon product, (b) a high-boiling recycle oil, and (c) an intermediate boiling-range side-cut;

(6) recycling said high-boiling recycle oil to said third hydrocracking zone;

(7) subjecting said intermediate boiling-range side-cut to catalytic hydrocracking in a second hydrocracking zone at intermediate severity conditions including a temperature between about 500° and 800° F. and a pressure between about 500 and 3,000 p.s.i.g.; and

(8) treating the effluent from said third hydrocracking zone as defined in step (5) above.

13. A process as defined in claim **12** wherein said feedstock contains at least about 10 parts per million of nitrogen in the form of organic compounds.

14. A process as defined in claim **13** wherein said hydrogen-stripping step is controlled so as to reduce the nitrogen content of the stripped liquid phase to below about 5 parts per million.

15. A process as defined in claim **12** wherein at least a portion of said hydrogen stripping of liquid phase is carried out during a liquid phase hydrofining operation wherein said liquid phase is passed downwardly through a bed of hydrofining catalyst, and hydrogen is passed countercurrently upwardly therethrough, forming said vapor-phase stripping effluent.

16. A process as defined in claim **12** wherein the hydrocracking catalyst employed in at least one of said hydrocracking zones is a dehydrated, zeolitic molecular sieve of the Y crystal type containing zeolitic cations from the group consisting of hydrogen and divalent metals, and promoted with a Group VIII noble metal hydrogenating component.

17. A process as defined in claim **12** wherein said hydrocarbon feedstock is a gas oil containing at least about 0.01% nitrogen and a substantial proportion of hydrocarbons boiling above about 650° F., and wherein said lower boiling hydrocarbons produced therefrom comprise gasoline.

18. A process for hydrocracking a mineral oil feedstock boiling above the gasoline range and containing a nonhydrocarbon impurity selected from the class consisting of organic nitrogen compounds and organic sulfur compounds, which comprises:

(1) subjecting said feedstock to fractional distillation to produce a light fraction boiling below about 700° F. and a heavy fraction boiling above about 500° F.;

(2) subjecting said light fraction in the absence of said heavy fraction to vapor-phase catalytic hydrofining with added hydrogen at an elevated pressure;

(3) subjecting said heavy fraction to a separate liquid-phase catalytic hydrofining with added hydrogen at an elevated pressure;

(4) subjecting total effluent from said vapor-phase hydrofining without intervening purification, to vapor-phase catalytic hydrocracking under conditions of pressure and temperature adjusted to give a substantial conversion per pass to gasoline;

(5) separating total effluent from said liquid-phase hydrofining, without substantial cooling or depressuring, into a vapor-phase fraction and a liquid-phase fraction;

(6) subjecting said liquid-phase fraction, without intervening purification, to liquid-phase catalytic hydrocracking at an elevated temperature and pressure in countercurrent flow with hydrogen, and recovering therefrom a vapor-phase hydrocracker effluent and a liquid-phase hydrocracker effluent;

(7) combining said vapor-phase hydrocracker effluent, said vapor-phase fraction from step (5), and the total effluent from said vapor-phase hydrocracking, and cooling and condensing the resulting mixture to recover recycle gas and liquid condensate;

(8) fractionating said liquid condensate to recover gasoline and a high-boiling recycle oil; and

(9) recycling said recycle oil to said countercurrent liquid-phase hydrocracking step (6).

19. A process as defined in claim **18** wherein said liquid-phase hydrocracker effluent is fractionated in admixture with said liquid condensate in step (8).

20. A process for hydrocracking a mineral oil feedstock containing relatively high-boiling hydrocarbons, relatively low-boiling hydrocarbons and nitrogen compounds, which comprises:

(A) segregating said feedstock into two fractions (a) and (b), fraction (a) being relatively rich in low-boiling hydrocarbons and nitrogen compounds and relatively lean in high-boiling hydrocarbons, and fraction (b) being relatively lean in low-boiling hydrocarbons and nitrogen compounds and relatively rich in high-boiling hydrocarbons;

(B) subjecting fraction (a) to catalytic hydrocracking at a relatively high temperature in the absence of fraction (b); and

(C) subjecting fraction (b) to catalytic hydrocracking at a relatively low temperature in the absence of fraction (a).

21. In an integral hydrofining-hydrocracking process wherein a mineral oil feedstock boiling over a substantial temperature range, and containing a non-hydrocarbon impurity selected from the class consisting of organic nitrogen compounds and organic sulfur compounds, is first subjected to catalytic hydrofining with added hydrogen to effect substantial decomposition of said non-hydrocarbon impurity with resultant formation of an inorganic impurity from the class consisting of ammonia and hydrogen sulfide, and wherein effluent from said hydrofining, still containing said inorganic impurity, is then subjected to catalytic hydrocracking at temperatures sufficiently high to effect a substantial hydrocracking of hydrocarbons, the improvement which comprises: separating from said hydrofiner effluent prior to said hydrocracking, a relatively heavy fraction of the hydrocarbon component thereof, so that the resulting feed to said hydrocracking step, still containing said inorganic impurity, is relatively lean in heavy hydrocarbons, whereby reduced hydrocracking catalyst deactivation rates are obtained.

References Cited by the Examiner

UNITED STATES PATENTS

2,627,495	2/1953	Lanning	208—80
2,839,450	6/1958	Oettinger	208—110
2,911,356	11/1959	Hanson	208—110
2,952,626	9/1960	Kelly et al.	208—59
3,132,087	5/1964	Kelly et al.	208—59
3,159,564	12/1964	Kelley et al.	208—59

PAUL M. COUGHLAN, *Primary Examiner.*

ALPHONSO D. SULLIVAN, DELBERT E. GANTZ, *Examiners.*

A. RIMENS, *Assistant Examiner.*