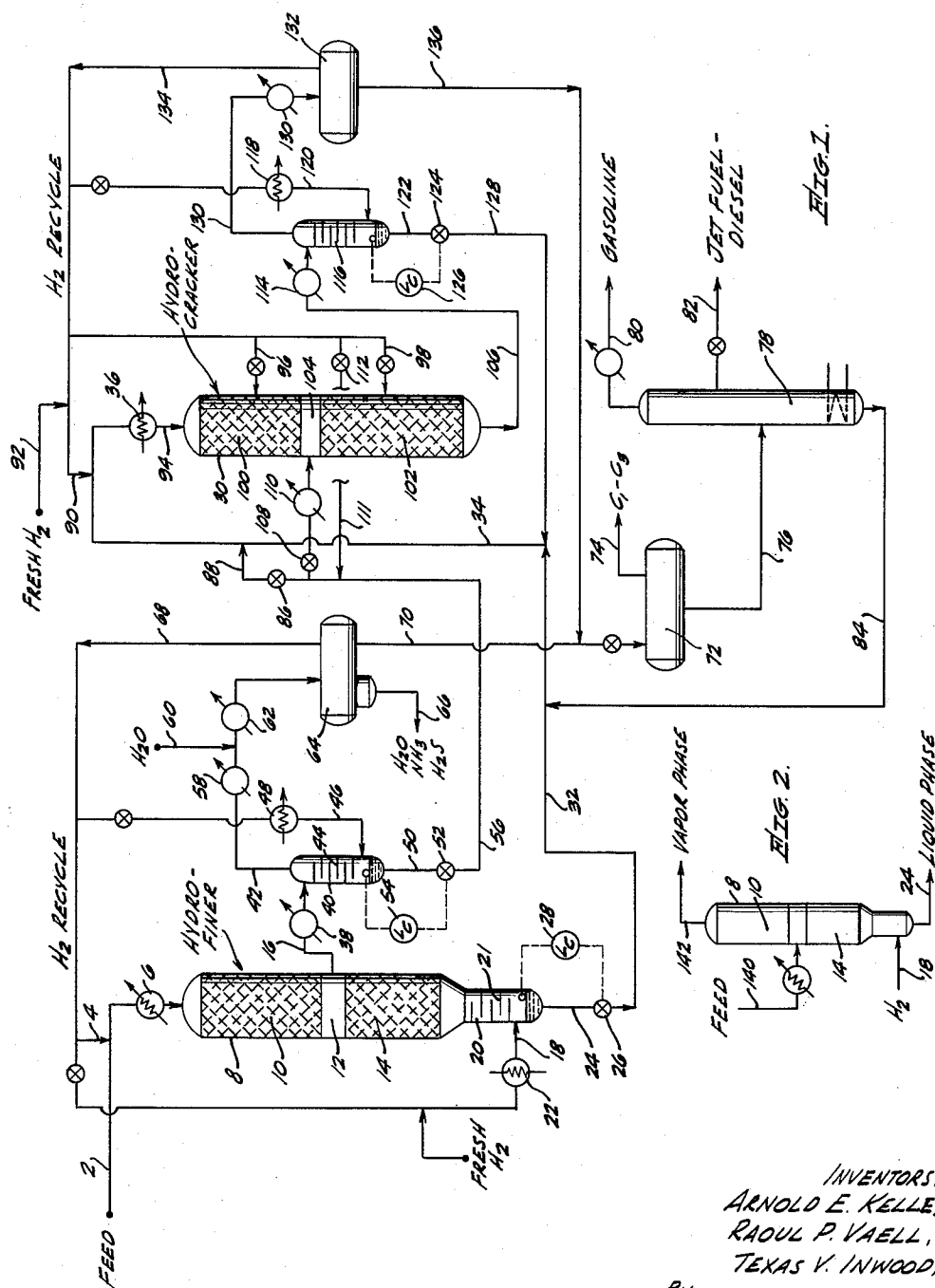


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1

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INTEGRAL HYDROFINING-HYDRO-
CRACKING PROCESS

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This invention relates to the catalytic hydrogenation and/or hydrocracking of hydrocarbons to produce e.g., hydrogenated aromatics, or lower boiling hydrocarbons, boiling for example in the gasoline or jet fuel range. In one aspect, the invention embraces an "integral" hydrofining-hydrocracking process, the hydrofining treatment being integrated in such a manner that the bulk of the hydrofiner effluent boiling above the gasoline range can be sent directly, and essentially nitrogen-free, to the hydrocracking zone with a minimum of intervening cooling, depressuring, washing, reheating and repressuring. The invention is particularly concerned with the treatment of high end-point feedstocks which are contaminated with organic nitrogen and/or sulfur compounds.

Briefly stated, the invention comprises the following essential steps: (1) the initial feedstock is subjected to catalytic hydrofining with added hydrogen under conditions such that both a liquid phase and a vapor phase 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 vapor phase effluent from the hydrofiner, together with the stripping vapors from step (2), are then cooled sufficiently to condense out a substantial portion of the remaining hydrocarbons; (4) the resulting condensate is stripped with hydrogen at essentially hydrofining pressures to remove ammonia, hydrogen sulfide, and dissolved light hydrocarbons; (5) the stripped liquid phase from step (2) and the stripped condensate from step (4) are then subjected to catalytic hydrogenation or hydrocracking substantially in the absence of catalyst poisons such as ammonia or hydrogen sulfide; and (6) the gasoline, or other desired hydrocarbon fraction synthesized in the hydrogenation zone, is recovered by condensation and fractionation.

According to a preferred embodiment of the invention, at least a portion of the stripping of 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 hydrofiner to strip out 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 operation 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. The invention also embraces several other modifications which will become apparent as the description proceeds.

A 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

2

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 of 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 minimized 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.

In the catalytic hydrogenation of aromatic hydrocarbons, many catalysts, and especially the more active ones such as platinum and other noble metals, are sensitive to poisoning by sulfur compounds. Noble metal hydrocracking catalysts may also be sulfur-sensitive in some cases. It is therefore desirable in many cases to remove sulfur compounds, as well as nitrogen, from hydrogenation or hydrocracking feedstocks. This may be achieved quite efficiently by catalytic hydrofining, but subject to the same disadvantages previously noted, involving expensive interstage treatments to remove hydrogen sulfide.

It is therefore, the overall objective of this invention to provide a convenient and economical method for removing nitrogen and/or sulfur compounds from hydrogenation or hydrocracking feedstocks. A more specific 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 still further objective is to provide hydrofining facilities which will effect a maximum removal of nitrogen and sulfur compounds without over-treatment 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 drawing, which is a flowsheet illustrating several modifications. In the succeeding description, it will be understood that the drawing has 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 hydrogen from line 4, preheated to incipient hydrofining temperature in heater 6, and then passed directly into the top of hydrofiner 8, which contains an upper bed of hydrofining catalyst 10 where mixed-phase hydrofining proceeds under substantially conventional, concurrent downflow conditions. The mixed-phase effluent from upper hydrofining catalyst bed 10 emerges into an inter-space 12, where the initial phase separation takes place. Product vapors, comprising vapor phase effluent from bed 8 and vapor-phase stripping effluent from lower catalyst bed 14, are withdrawn via line 16 and treated as hereinafter described. The liquid phase portion of effluent from bed 8 gravitates downwardly through lower cat-

alyst bed 14, countercurrently to a stream of hydrogen admitted at the bottom of the reactor via line 18.

In the modification illustrated, a small optional stripping column 20, containing a series of stripping trays 21, is provided below catalyst bed 14, through which the liquid portion of feed percolates countercurrently to the hydrogen stream and collects in the bottom, forming a liquid seal. The purpose of the stripping column is to assure that ammonia generated in the lower portion of catalyst bed 14 will also be removed. For efficient stripping, the hydrogen admitted via line 18 should preferably be preheated to approximately the temperature prevailing in the reactor, as by means of heater 22. The ratio of hydrogen to oil in catalyst bed 14 and stripping column 20 preferably ranges between about 500 and 15,000 s.c.f. per barrel of oil, at reactor pressures between about 400 and 2,000 p.s.i.g. and temperatures between about 400° and 800° F.

The stripped heavy oil accumulating in the bottom of stripping column 20 is taken off via line 24 and valve 26, in response to liquid level controller 28, and is transferred directly to hydrocracker 30, via lines 32 and 34 and heat exchanger 36, as will be subsequently described.

Suitable hydrofining catalysts for use in hydrofiner 8 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	600-850	650-825
Pressure, p.s.i.g.	400-3,000	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 nitrogen content of the feed to below about 25 parts per million, and preferably below about 10 parts per million.

The vapor phase which is taken off from hydrofiner 8 via line 16 comprises hydrogen saturated with hydrocarbons of all boiling range, and also containing ammonia and hydrogen sulfide. The light hydrocarbons, boiling in and below the gasoline range, comprise mostly hydrocarbon fragments derived from the decomposition of sulfur and nitrogen compounds in hydrofiner 8, since very little true hydrocracking occurs therein. It is desired to recover at minimum expense, and in an ammonia-free condition, the bulk of the hydrocarbons boiling above the gasoline range for treatment in hydrocracker 30. For this purpose, the total vapor phase in line 16 is transferred via cooler 38 to a small separator-stripping column 40. At reactor pressures, it is normally found that the bulk of these heavier hydrocarbons can be condensed out of the vapor phase by cooling the same to about 400°-600° F. It is undesirable to cool the vapor any more than is required to produce a substantial desired amount of liquid condensate; generally it is unnecessary to go below about 300° F. It will be understood that stripping column 40 is operated at substantially the same pressure prevailing in the hydrofiner, or within about 100 p.s.i.g. thereof.

The cooled mixed-phase material entering the top of separator-stripper 40 separates in the upper portion thereof, the vapor phase going overhead via line 42, and the liquid portion gravitating downwardly over stripping trays 44, countercurrently to a rising stream of preheated

hydrogen admitted near the bottom thereof via line 46, thereby stripping light hydrocarbons and ammonia therefrom. Hydrogen rates similar to those prescribed for stripper 20 may be employed, and the stripping hydrogen is preheated in heater 48 to about the same temperature as the entering mixed-phase effluent from cooler 38.

The liquid phase accumulating in the bottom of stripper 44 will of course contain some high-boiling hydrocarbons, but will consist primarily of light gas oil boiling in the 400° to 600° F. range. This liquid phase is withdrawn via line 50 and valve 52 in response to liquid level controller 54, and is then transferred via line 56 to hydrocracker 30, where it is subjected to hydrocracking under one of two alternate modifications hereinafter described.

The vapor phase overhead from stripper 44 comprises mostly gasoline-boiling-range hydrocarbons, but will still contain a considerable proportion of light gas oil hydrocarbons. It is also heavily contaminated with ammonia and/or hydrogen sulfide. To effect recovery and purification of the various components, the total vapor phase in line 42 is partially cooled and condensed in cooler 58, then mixed with wash water from line 60, and transferred via final condenser 62 to high pressure separator 64. The purpose of the wash water is to remove water-soluble impurities, including ammonia and hydrogen sulfide and salts thereof. Normally about 15 pounds of water per barrel of liquid hydrocarbon is sufficient for this purpose. It is preferable to inject the wash water prior to the final cooling in condenser 62, in order to avoid 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 64. Spent wash water containing dissolved impurities is withdrawn via line 66, and purified recycle hydrogen is withdrawn via line 68 for reuse in the hydrofiner and stripping columns associated therewith, as previously described. Liquid hydrocarbons in separator 64 are withdrawn via line 70 and flashed into low pressure separator 72, from which light hydrocarbon gases are exhausted via line 74. The liquid hydrocarbon fraction in separator 72 is transferred via line 76 to fractionating column 78, from which the desired gasoline product is taken overhead via line 80.

As will become apparent from the succeeding description, the hydrocarbon fraction admitted to separator 72 via line 70 also includes the hydrocarbon product from hydrocracker 30. Hence, fractionating column 78 serves to recover both the minor proportion of gasoline synthesized in the hydrofiner, and the major portion synthesized in hydrocracker 30. If desired, a side-cut jet fuel or diesel fraction may be recovered from the column via line 82. The bottoms fraction from column 78, comprising unconverted gas oil hydrocarbons from hydrocracker 30, and remaining gas oil hydrocarbons from hydrofiner 8, is taken off via line 84 and blended with the liquid phase hydrofiner effluent in line 32, and the mixture is then transferred via line 34 and exchanger 36 to hydrocracker 30. Alternatively, where stripper 116 is utilized as described below, it may be preferable to mix the bottoms fraction in line 84 with the stripped condensate in line 56, and divert the mixture via preheater 110 into the mid-section of hydrocracker 30, as will be described below in connection with alternate B. It should be noted further that the bottoms fraction from column 78 need not necessarily be recycled to the hydrocracker; if 100% conversion of the feedstock is not desired, all or a portion of the bottoms fraction in line 84 may be diverted from the process for other uses, e.g., as feed to a catalytic cracking unit.

The operation of hydrocracker 30 will now be described in reference to the two principal alternate modifications referred to above.

Alternate A.—In this modification, the entire feed to the hydrocracker enters the top and flows downwardly there-

through in a conventional manner. This is the simplest modification, and may be preferred in cases where the light gas oil feed derived from stripper 40 constitutes a very minor portion of the fresh feed to the hydrocracker. To operate in this manner, valves 108 and 112 are closed, and the stripped condensate in line 56 is transferred via open valve 86 and line 88 to line 34, which contains the main feed stream derived from stripper 20 and recycle oil line 84. The mixture is blended with recycle and fresh hydrogen derived from lines 90 and 92, and the temperature is suitably adjusted in exchanger 36, which may either be a heater or a cooler, depending upon the temperature of the feed mixture in line 34, as well as upon the desired hydrocracking temperature, which in turn will depend upon the relative activity of the hydrocracking catalyst. Normally however, since the hydrogen mixed with the feed is relatively cool, some preheating will be required. In any case, the mixture of hydrogen and oil, at suitable inlet hydrocracking temperatures is admitted via line 94 into the top of hydrocracking reactor 30 and passes downwardly therethrough under suitable hydrocracking conditions hereinafter prescribed.

Hydrocracker 30 may be operated under either adiabatic or isothermal conditions, and in the latter case, the reaction being exothermic, it may be desirable to admit cool quench hydrogen at one or more points in the reactor as illustrated via lines 96 and 98. It will be noted that the catalyst in hydrocracker 30 is divided into an upper bed 100 and a lower bed 102, separated by an interspace 104. This has no particular significance in reference to alternate A, and hence in this case a single unitary catalyst bed may be utilized. Effluent from the hydrocracker is taken off via line 106 and treated for product recovery as hereinafter described.

Alternate B.—Since the liquid phase hydrofiner effluent from stripper 20 has a considerably higher average molecular weight than the stripped condensate from stripper 40, it may be advantageous in some cases to take advantage of the different optimum cracking temperatures for these two fractions by introducing them separately into the reactor in zones where optimum temperatures prevail for the respective fraction. This is particularly feasible in cases where the initial feed to the hydrofiner contains substantial proportions, e.g., more than about 20% by volume, of hydrocarbons boiling in the 400°–600° F. range, in which case the stripped condensate in line 56 will comprise a substantial proportion of the total feed to the hydrocracker. Selective treatment of the two feed fractions is effected in this alternate by maintaining upper hydrocracking bed 100 at a relatively lower average temperature than lower hydrocracking bed 102, and feeding the heavy fraction of feed into the top of the reactor while feeding the lighter fraction into the top of the lower hydrocracking catalyst bed. The differential temperatures required in this mode of operation can in most cases be maintained by allowing hydrocracking to proceed in reactor 30 under more nearly adiabatic conditions, with a minimum of quenching via lines 96 and 98. It is contemplated that upper hydrocracking bed 100 may be maintained at an average bed temperature about 20°–100° F. lower than the average bed temperature in lower hydrocracking bed 102. Preferably, upper bed 100 is maintained at an average temperature between about 500° and 750° F., and lower bed at 102 at 550°–800° F.

To effect selective treatment of the feed fractions in this manner, valve 86 is closed and valve 108 is opened, thereby diverting stripped condensate in line 56 through preheater 110 into interspace 104, where it mingles with the downflowing effluent from upper bed 100. It is also desirable in this case to mix the light feed with hydrogen via line 111 and open valve 112. By operating in the manner prescribed, upper hydrocracking bed 100 serves primarily to crack the heavy gas oil feed to light gas oil, while lower bed 102 serves primarily to convert light gas oil components to gasoline. Maximum catalyst effi-

ciency, and efficiency of conversion to gasoline is obtained.

In either of the above alternate modes of operation, the hydrocracker effluent in line 106 is next passed through a partial condenser 114 and thence into an optional separator-stripper 116, which functions similarly to stripping column 40. The purpose of separator-stripper 116 is to provide for economical recovery of a substantial proportion of unconverted oil from the hydrocracker before it is cooled to final condensation temperatures, thus minimizing the utilities and facilities required for reheating the recycle oil. Normally, the temperature of the hydrocracker effluent is reduced in cooler 114 to about 400°–700° F., and about 500–10,000 s.c.f. of hydrogen per barrel of liquid condensate is admitted near the bottom of the stripper via preheater 118 and line 120, to effect countercurrent stripping of light hydrocarbons from the condensate. The condensate accumulating in the bottom of stripper 116 comprises the heaviest components of the unconverted oil, and is more or less continuously removed via line 122 and valve 124, in response to liquid level controller 126, and recycled to the hydrocracker via lines 128 and 34.

The vapor phase from separator-stripper 116 is taken overhead via line 130, and comprises the uncondensed vapor phase effluent from the hydrocracker as well as the stripping vapors from stripper 116. This combined vapor phase is then transferred via final condenser 130 into high pressure separator 132, from which hydrogen-rich recycle gas is taken off via line 134 and reused in the process as previously described. The condensed hydrocarbons in separator 132 are withdrawn via line 136 and blended with the liquid hydrocarbons in line 70, and the resulting mixture is flashed into low pressure separator 72 and fractionated in column 78 as previously described.

As indicated above, the use of stripper-separator 116 is optional, and in many cases, especially in small installations, may not be economically justifiable. In these cases, it is preferable simply to omit the stripper, and send the hydrocracking effluent in line 106 directly through final condenser 130 and high pressure separator 132. Where the stripper is employed however, it will be apparent that the recycle bottoms fraction recovered from column 78 will have a relatively lower average molecular weight than the recycle condensate from stripper 116. Its boiling range may approximate that of the condensate from stripper 40; hence the feasibility of combining these fractions for selective treatment in lower hydrocracking bed 102 as noted above.

Many variations are contemplated from the processing scheme described above and in the drawing. For example, as shown in FIGURE 2, it is entirely feasible to operate hydrofiner 8 with the total feed plus hydrogen entering interspace 12 via line 140, the vapor phase passing upwardly through bed 10 and the liquid phase gravitating downwardly through lower bed 14, countercurrently to the rising hydrogen stream admitted via line 18. The total vapor phase effluent is then taken off at the top of the hydrofiner via line 142 and sent to separator-stripper 40 via cooler 38. Liquid phase product is taken off as before, via line 24. This modification is advantageous in providing for a more efficient hydrofining of the vapor phase in the absence of liquid phase.

The process conditions in hydrocracker 30 are suitably adjusted so as to provide about 30–80% conversion to gasoline, or other desired product, per pass. It is preferred at the same time to adjust the operating conditions, preferably temperature, so as to permit relatively long runs between regenerations, i.e., from about 2–8 months. For these purposes, it will be understood that pressures in the high ranges will be used in connection with temperatures in the high range, while the lower operative pressures will normally be used in conjunction with the

lower temperatures. The range of operative conditions contemplated for hydrocracker 30 are as follows:

HYDROCRACKING CONDITIONS

	Operative	Preferred
Temperature, ° F	400-850	500-750
Pressure, p.s.i.g.	400-3,000	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. Also, the lower temperature ranges will normally be used in conjunction with feedstocks having high end-points, i.e., above about 750° F. 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 feedstocks within the 600-2,000 p.s.i.g. pressure range.

The hydrocracking 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°, and containing at least about 20% by volume of acid-soluble components (aromatics+olefins). Such oils may also contain from about 0.1% to 5% of sulfur and from about 0.01% to 2% by weight of nitrogen.

Hydrogenation feedstocks may comprise any of the foregoing hydrocracking feeds, and in addition many other aromatic concentrates as e.g., naphthalene or methyl naphthalene fractions.

It should be noted further that the process of this invention is especially amenable to the treatment of feedstocks boiling predominantly in the 550°-900° F. range. Where the feedstock is composed mainly of hydrocarbons boiling in the 400°-600° F. range, the alternate two-stage hydrocracking process disclosed in co-pending application Serial No. 137,366, filed September 11, 1961, may be more desirable, assuming that the size of the operation justifies the capital investment in a two-stage process. The process of this invention is primarily directed to the treatment of feedstocks which (1) contain a substantial proportion of heavy materials boiling above about 650° F., and (2) contain less than about 30% by volume of light components in the 400°-600° F. range.

The hydrocracking catalyst to be employed in the hydrocracking unit 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-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; co-precipitated composites of silica, titania and zirconia con-

taining 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 diameters of about 8 to 14 Angstroms, and comprising silica, alumina and one or more exchangeable zeolitic cations.

Any of the foregoing cracking bases may be further promoted by the addition of small amounts, e.g., 1 to 10% by weight, of 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% SiO₂, 5%-75% ZrO₂, and 5%-75% TiO₂, 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.

The molecular sieve type cracking bases, when compounded with a hydrogenating metal, are particularly useful for hydrocracking at relatively low temperatures of 400-700° F., and relatively low pressures of 400-1,500 p.s.i.g. It is preferred to employ molecular sieves having a relatively high SiO₂/Al₂O₃ ratio, e.g., between about 2.5 and 6.0. The most active forms are those wherein the exchangeable zeolitic cations are hydrogen and/or a polyvalent (preferably divalent) metal such as magnesium, calcium or zinc. In particular, the "Y" molecular sieves, wherein the SiO₂/Al₂O₃ ratio is about 5, are preferred, either in their hydrogen form, or a divalent metal form, preferably magnesium.

The Y molecular sieves can be prepared by heating an aqueous sodium aluminosilicate mixture at temperatures between about 25° and 125° C. (preferably 80-125° C.) until crystals are formed, and separating the crystals from the mother liquor. When a colloidal silica sol is employed as the source of silica, the aqueous sodium aluminosilicate mixture may have a composition as follows, expressed in terms of mole-ratios:

Na ₂ O/SiO ₂	0.2-0.8
SiO ₂ /Al ₂ O ₃	10-30
H ₂ O/Na ₂ O	25-60

When sodium silicate is used as the silica source, the optimum molar proportions are as follows:

Na ₂ O/SiO ₂	0.6-2.0
SiO ₂ /Al ₂ O ₃	10-30
H ₂ O/Na ₂ O	30-90

The "decationized," or hydrogen form of the Y zeolite may be prepared by ion-exchanging the alkali metal cations with ammonium ions, or other easily decomposable cations such as methyl substituted quaternary ammonium ions, and then heating to e.g., 300°-400° C., to drive off the ammonia. It is preferred that the degree of decationization, or hydrogen exchange, be at least about 40% of the maximum theoretically possible. The final composition should contain less than about 5% by weight of Na₂O.

The polyvalent metal (e.g., Mg, Ca, Sr, Ba, Zn, Mn, Ni, Cr, etc.) forms of the Y zeolite are prepared by conventional cation exchange methods, as e.g., by treating the sodium zeolite with an aqueous solution of magnesium chloride, calcium chloride, etc. It is preferred to replace at least about 40% of the monovalent metal cations with their equivalent of polyvalent cations; the activity of the catalyst generally increases as the degree of displacement of monovalent metals increases.

Mixed, hydrogen-polyvalent metal forms of the Y zeolite are also contemplated. Generally such mixed forms are prepared by subjecting a polyvalent metal-exchanged zeolite to further ion exchange with ammonium cations which are later driven off during a thermal activation treatment. Here again, it is preferred that at least about 40% of the monovalent metal cations be replaced with any desired combination of hydrogen ions and polyvalent metal cations.

The hydrogenating promoter may be incorporated into the molecular sieve type cracking bases by any method which gives a suitably intimate admixture. Among acceptable methods are (1) cation exchange using an aqueous solution of a suitable metal salt wherein the metal itself forms the cation; (2) cation exchange using an aqueous solution of a suitable metal compound in which the metal is in the form of a complex cation with coordination complexing agents such as ammonia, followed by thermal decomposition of the cationic complex; (3) conventional impregnation with an aqueous solution of a suitable metal salt, followed by drying and thermal decomposition of the metal compound. The ion-exchange methods (1) and (2) are much to be preferred in that a more uniform and complete subdivision of the metal on the zeolite is obtained.

Method (1) above is generally employed to introduce metals of the iron group, while method (2) is generally best adapted for the noble metals of Group VIII. When method (1) is employed to introduce an iron group metal, it is desirable to carry out subsequent thermal activation treatments in a nonoxidizing or reducing atmosphere in order to avoid oxidizing the metal and displacing it from the zeolite lattice. But in the case of the Group VIII noble metals such precautions are generally unnecessary, and thermal decomposition of the cationic complex can be carried out in air if desired.

The ion-exchange of hydrogenating metal onto the zeolite may be carried out by the usual methods described above in connection with the ion-exchange of polyvalent metals generally. In fact, the two steps may be combined if desired by using an aqueous solution of a mixture of salts, or a single salt in cases where the desired polyvalent metal is also the desired hydrogenating metal. Generally, however, it is preferable to carry out first the ion-exchange step for forming the hydrogen and/or polyvalent metal zeolite, and then perform the ion-exchange step providing the hydrogenating metal.

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 12 Å., and this is likewise the case in the Y sieves, although the latter usually are found to have crystal pores of about 8 to 10 Å. in diameter.

Non-cracking hydrogenation catalysts for use herein may comprise any of the previously noted transitional metal hydrogenating components, preferably supported on a neutral, adsorbent carrier having an extended surface area of e.g., 50-300 square meters per gram. Suitable carriers include for example, activated alumina, silica gel, activated charcoal, clays and the like. Hydrogenating catalysts comprising a noble metal such as platinum, palladium or rhodium are especially preferred since they are highly active and most susceptible to poisoning by sulfur compounds. Hydrogenating conditions are in general similar to the hydrocracking conditions above described, except that temperatures in the lower range of about 400°-600° F. are generally preferred.

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

Example

This example illustrates the results obtainable in a typical operation of the process described in the drawing, with the liquid phase from the hydrofiner being treated

serially in two superimposed beds of hydrocracking catalyst, and the liquid condensate from stripper 40 being treated only in the second of the two beds. The feed is a 400°-850° F. boiling range coker gas-oil containing 2% of sulfur and 0.3% of nitrogen by weight, and having an API gravity of 22°. The hydrofining catalyst is composed of about 4% cobalt sulfide plus 16% of molybdenum sulfide impregnated on a silica-stabilized (5% SiO₂) activated alumina support. The hydrocracking catalyst 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 1

Operating Conditions	Hydrofiner 8		Stripper 40	Hydrocracker 30	
	Upper bed 10	Lower bed 14		Upper bed 100	Lower bed 102
LHSV	1.5	2.0		2.0	2.0
Pressure, p.s.i.g.	1,550	1,550	1,540	1,530	1,530
Temperature, ° F., ^a Start					
of run	700	700	500	450	520
End of run	750	750	500	670	700
H ₂ /oil s.c.f./b.	5,000	3,000	3,000	8,000	8,000
Conversion to 400° F. end-point gasoline, vol. percent per pass				Both beds	
				65	

^a Average bed temperatures.

On the basis of an operation utilizing 10,000 barrels per day of initial feed, and with total recycle of unconverted oil to the hydrocracker, the approximate yields are as follows.

TABLE 2

Conversion to gasoline and lighter	100 vol. percent.
C ₁ -C ₃ dry gas	100 s.c.f./b. feed.
Liquid products:	
Butanes	950 b./d.
C ₅ -C ₆	2,400 b./d.
C ₇ -400° F.	9,050 b./d.
Total liquid products	12,400 b./d.
Chemical H ₂ consumption	2,400 s.c.f./b. feed.

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

In the foregoing example, about 30% by volume of the total feed to the hydrofiner is recovered as condensate from separator-stripper 40. If this condensate is blended with the stripped liquid phase from the hydrofiner, and the mixture then subjected to hydrocracking at 1.0 space velocity, and an isothermal bed temperature adjusted to give 65% conversion per pass to gasoline, similar product distribution and yields are obtained, except for somewhat higher dry gas and butane makes. The run length is also somewhat decreased as a result of a more rapid rate of catalyst deactivation.

Results analogous to those indicated in the foregoing example 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 example or the drawing, but only broadly as defined in the following claims.

We claim:

1. In a hydrogenation process wherein a hydrocarbon feedstock, a substantial portion of which boils above about 550° F., and which contains an organic impurity from the class consisting of sulfur compounds and nitrogen compounds, is first subjected to hydrofining over a sulfactive hydrofining catalyst at elevated pressures and temperatures such that a substantial portion of feed in the hydrofiner is in the liquid phase and a substantial portion

is in the vapor phase, and wherein a selected, purified, heavy fraction of the resulting hydrofiner effluent is then subjected to a catalytic hydrogenating reaction at elevated temperatures and pressures over a hydrogenation catalyst which is sensitive to poisoning by said impurity, the improved method for recovering and purifying said selected heavy fraction from the hydrofiner effluent with a minimum of interstage cooling, depressuring, washing, reheating and repressuring, which comprises:

- (1) subjecting said liquid phase, after substantial hydrofining has taken place, to stripping with hydrogen at essentially hydrofining temperatures and pressures to strip out dissolved volatile decomposition products of said impurity;
- (2) cooling vapor phase effluent from said hydrofining in admixture with stripping vapors from step (1) to a temperature substantially below its initial temperature without substantial depressuring, to effect a partial condensation of liquid hydrocarbons therefrom;
- (3) stripping the liquid condensate from step (2) with hydrogen without substantial depressuring to remove dissolved volatile decomposition products of said impurity; and
- (4) combining stripped liquid phase effluent from step (1) with stripped condensate from step (3) to form said selected purified heavy fraction.

2. A process as defined in claim 1 wherein remaining vapor phase hydrofiner effluent from step (2) is further cooled and condensed and washed with water to remove decomposition products of said impurity, and wherein a high-boiling fraction of the resulting washed condensate is combined with said selected purified heavy fraction.

3. A process as defined in claim 1 wherein said volatile decomposition products comprise ammonia, and wherein said hydrogenating catalyst is a hydrocracking catalyst comprising a hydrogenating metal supported on a solid, adsorbent, acidic cracking base having an extended surface area.

4. A process as defined in claim 1 wherein said volatile decomposition products comprise hydrogen sulfide, and wherein said hydrogenating catalyst comprises a Group VIII noble metal supported on a solid, adsorbent base having an extended surface area.

5. A process as defined in claim 1 wherein said feedstock contains a substantial proportion of hydrocarbons boiling above about 650° F., and less than about 30% by volume of hydrocarbons boiling below about 600° F.

6. A process as defined in claim 1 wherein said stripping of liquid phase hydrofining product is carried out during hydrofining by passing said liquid phase downwardly countercurrently to a rising stream of hydrogen in at least a portion of said hydrofining catalyst.

7. A process as defined in claim 1 wherein said hydrofining and at least a portion of said stripping of liquid phase hydrofining product are effected simultaneously by (1) passing initial feedstock plus hydrogen downwardly through a first bed of hydrofining catalyst; (2) effecting a liquid phase-vapor phase separation of effluent from said first catalyst bed under hydrofining conditions of pressure and temperature; and (3) passing the liquid phase from said separation downwardly through a second bed of hydrofining catalyst countercurrently to a rising stream of hydrogen, thereby effecting simultaneous hydrofining and stripping of said liquid phase.

8. A process as defined in claim 1 wherein said hydrofining and at least a portion of said stripping of liquid phase hydrofining product are effected simultaneously by (1) subjecting said initial feedstock plus hydrogen to a preliminary liquid-vapor phase separation under substantially hydrofining conditions of temperature and pressure; (2) passing the resulting vapor phase through a first bed of hydrofining catalyst; and (3) passing the resulting liquid phase from said separation downwardly through a second bed of hydrofining catalyst counter-currently to a rising stream of hydrogen, thereby effecting simultaneous hydrofining and stripping of said liquid phase.

9. A process for hydrocracking a hydrocarbon feedstock initially contaminated with organic nitrogen compounds, and containing a substantial proportion of hydrocarbons boiling above about 550° F., 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 strip out dissolved ammonia; (3) cooling vapor phase effluent from said hydrofining in admixture with stripping vapors from step (2) to a temperature substantially below its initial temperature without substantial depressuring, to effect a partial condensation of liquid hydrocarbons therefrom; (4) stripping the liquid condensate from step (3) with hydrogen without substantial depressuring to remove dissolved ammonia; (5) subjecting said stripped liquid phase hydrofiner effluent plus added hydrogen to hydrocracking in a first bed of hydrocracking catalyst at an average bed temperature T_1 ; (6) blending effluent from said first hydrocracking catalyst bed with said stripped condensate; and (7) subjecting the resulting blend to hydrocracking in a second bed of hydrocracking catalyst at an average bed temperature T_2 which is substantially higher than T_1 .

10. A process as defined in claim 9 wherein T_1 is between about 500° and 750° F. and T_2 is between about 550° and 800° F.

11. In a hydrocracking process wherein a wide-boiling-range hydrocarbon feedstock is subjected to catalytic hydrocracking in a hydrocracking zone in which relatively high temperatures prevail in a downstream section and relatively low temperatures prevail in an upstream section, the improvement which comprises dividing said feedstock into a relatively low-boiling fraction and a relatively high-boiling fraction, passing said high-boiling fraction plus hydrogen serially through said low-temperature section then through said high-temperature section, and passing said low-boiling fraction only through said high-temperature section in admixture with effluent from said low-temperature section.

12. A process as defined in claim 11 wherein said hydrocracking catalyst comprises a Group VIII metal hydrogenating component deposited upon a zeolitic, aluminosilicate molecular sieve cracking base.

References Cited in the file of this patent

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