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MULTI-ZONE HYDROCRACKING PROCESS

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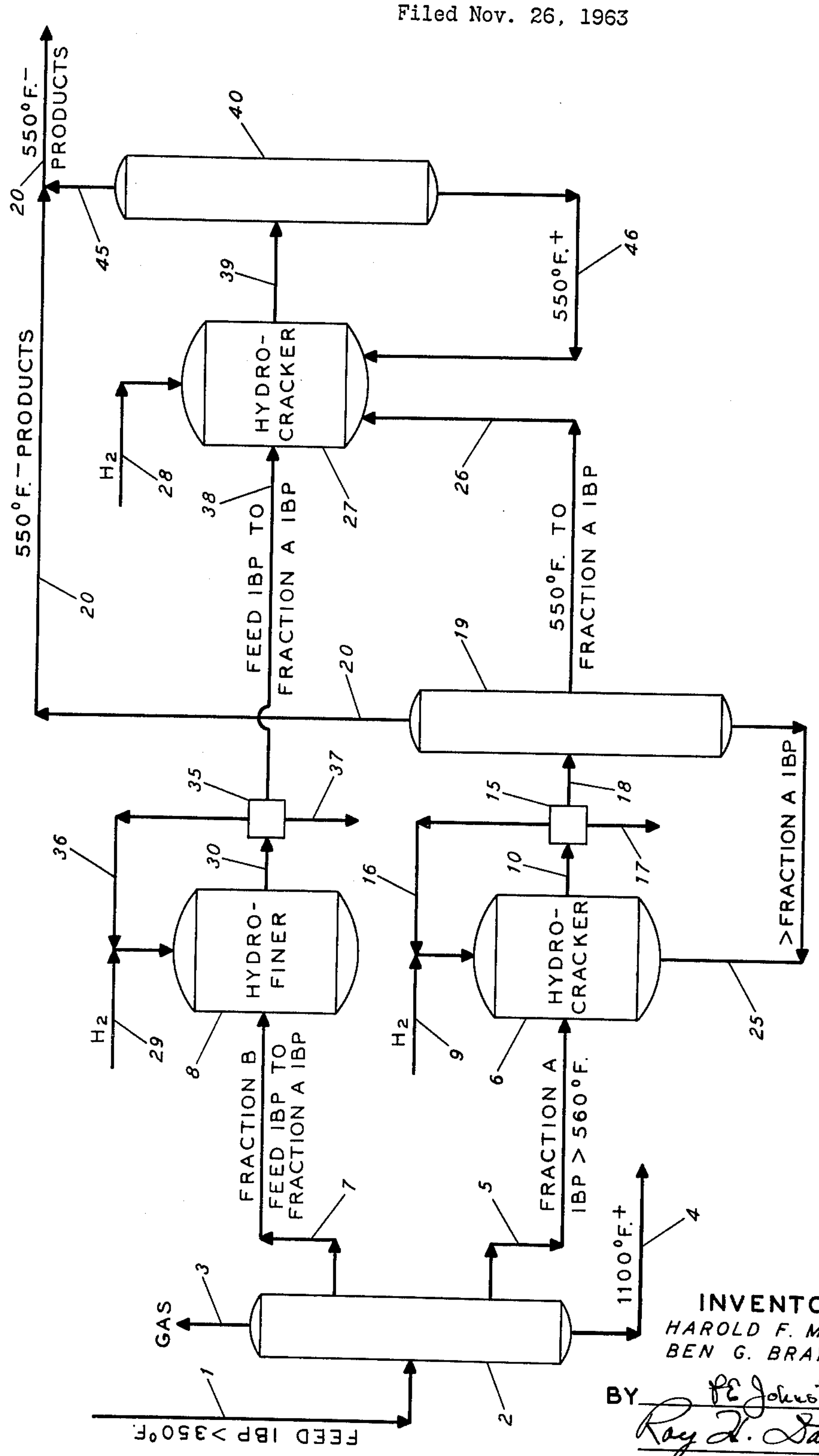

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MULTI-ZONE HYDROCRACKING PROCESS

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This invention relates to a hydrocarbon conversion process, more particularly to a hydrocarbon conversion process for converting petroleum distillate and residuum feeds into various valuable products, and still more particularly to a catalytic conversion process capable of producing middle distillates and gasoline from said feeds.

It is well known that nitrogen in a hydrocarbon feed is deleterious to certain hydrocracking catalystis, particularly highly acidic hydrocracking catalysts, and that in order to provide a practical process for producing gasoline over a highly acidic hydrocracking catalyst from a feed containing substantial amounts of nitrogen, it is generally necessary to first hydrofine the feed to remove substantially all of the nitrogen. Such highly acidic catalysts do not result in the production of substantial quantities of middle distillates, so that where gasoline production and also substantial middle distillate production is desired a hydrocracking catalyst having no more than weak acidity is desirable. While it is possible to meet the aforesaid problems by operating a two-stage process wherein a hydrofining-hydrocracking catalyst having no more than weak acidity is used in the first stage and a more acidic hydrocracking catalyst is used in the second stage, such a process still has undesirable aspects. Operation of the first stage at hydrofining conditions severe enough to reduce the nitrogen content of the feed to an acceptably low level frequently results in greater than desired amounts of hydrocracking, catalyst fouling and hydrogen consumption in that stage. On the other hand, operation of the first stage at less severe conditions which do not result in an excessive amount of hydrocracking frequently leaves a greater concentration of nitrogen in the effluent from the first stage than can be tolerated for sustained periods by the acidic catalysts in the second stage.

In view of the foregoing, it is an object of the present invention to provide a multi-stage process for converting nitrogen-containing feeds to gasoline and middle distillates wherein said feeds are hydrocracked and partially hydrofined with hydofining-hydrocracking catalysts having no more than weak acidity to produce middle distillate products and higher boiling materials and wherein selected portions of said higher boiling materials are hydrocracked in a subsequent stage in the presence of a more acidic catalyst, and wherein it is not necessary to remove substantially all of the nitrogen from said feeds with said catalysts having no more than weak acidity in order to produce a feed for said subsequent stage having an adequately low nitrogen content.

The invention will best be understood, and further objects and advantages thereof will be apparent, from the following description when read in conjunction with the accompanying drawing which is a diagrammatic illustration of process units and flow paths suitable for carrying out the process of the present invention.

In accordance with one embodiment of the present invention there is provided a process for producing gasoline and middle distillates from a hydrocarbon feed stock selected from the group consisting of nitrogen-containing petroleum distillates and petroleum residua boiling above 350° F., which comprises selecting two feed fractions each having different boiling ranges, the higher boiling of said fractions boiling above 560° F., hydrocracking said higher boiling fraction in the presence of from 1000 to 10,000 s.c.f. of hydrogen per barrel thereof in a

first conversion zone at a temperature of from 500° to 950° F., a pressure above 500 p.s.i.g., an LHSV of from 0.1 to 4.0, and a per-pass conversion of more than about 40 volume percent of said higher boiling fraction to products boiling below the initial boiling point thereof, with a hydrofining-hydrocracking catalyst having no more than weak acidity comprising at least one hydrogenating component selected from the Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals in intimate association with a silica-containing support, recovering at least one product boiling below 550° F. from said first conversion zone hydrofining the lower boiling of said fractions with a hydrofining catalyst in a second conversion zone to reduce the nitrogen content thereof under conditions that accomplish in said second zone a concurrent hydrocracking conversion of less than 30 volume percent of the feed thereto to products boiling below the boiling range of said feed, passing to a third conversion zone from said first zone a fraction boiling above 550° F. and below the initial boiling point of the feed to said first zone, removing ammonia from the hydrofined fraction from said second conversion zone and passing the resulting hydrofined fraction to said third conversion zone, and hydrocracking in said third conversion zone said fractions passed thereto to produce additional products boiling below 550° F.

In accordance with a more specific embodiment of the present invention there is provided a process for producing gasoline and middle distillates from a hydrocarbon feed stock selected from the group consisting of nitrogen-containing petroleum distillates and petroleum residua boiling above 350° F., containing materials boiling above 560° F., and also containing materials boiling below 560° F., which comprises separating said feed into two feed fractions each having different boiling ranges, the higher boiling of said fractions boiling above 560° F., hydrocracking said higher boiling fraction in the presence of 1000 to 10,000 s.c.f. of hydrogen per barrel thereof in a first conversion zone at a temperature of from 500° to 950° F., a pressure above 500 p.s.i.g., an LHSV of from 0.1 to 4.0, and a per-pass conversion of more than about 40 volume percent of said higher boiling fraction to products boiling below the initial boiling point thereof with a hydrofining-hydrocracking catalyst having no more than weak acidity comprising at least one hydrogenating component selected from the Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals in intimate association with a support substantially less acidic than a conventional silica-alumina hydrocracking support, recovering at least one product boiling below 550° F. from said first conversion zone, hydrofining the lower boiling of said fractions by contacting said fraction in a second conversion zone with a hydrofining catalyst comprising a hydrogenating component selected from the Group VI metals and compounds of Group VI metals and a hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals in intimate association with a support substantially comprising alumina at 500° to 800° F., 500 to 4,000 p.s.i.g., an LHSV of 0.2 to 10, and a per-pass conversion of less than 30 volume percent of said lower boiling fraction to products boiling below the initial boiling point thereof, in the presence of 500 to 10,000 s.c.f. of hydrogen per barrel of sad lower boiling fraction, passing to a third conversion zone from said first zone a fraction boiling above 550° F. and below the initial boiling point of the feed to said first zone, removing ammonia from the hydrofined fraction from said second conversion zone and passing the resulting hydrofined fraction to said third conversion zone and hydrocracking in said third conversion zone said fractions passed thereto to produce additional products boiling below 550° F.

Suitable feeds for use in the process of the present invention include nitrogen-containing petroleum distillates and nitrogen-containing petroleum residua and mixtures thereof, from which a higher boiling fraction, boiling above 560° F., and a lower boiling fraction can be selected. Heavy gas oils and catalytic cycle oils are excellent feeds to the process, as well as conventional FCC feeds and portions thereof. Residual feeds may include Minas and other paraffinic-type residua.

The aforesaid hydrofining catalyst comprises at least one hydrogenating component selected from the Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals. Preferred combinations of hydrogenating components include nickel sulfide and tungsten sulfide, nickel sulfide and molybdenum sulfide, and palladium sulfide and molybdenum sulfide.

The aforesaid hydrofining catalyst comprises a support, preferably one that is not more than moderately acidic, as compared with highly acidic supports such as silica-alumina. Said support preferably is alumina.

The aforesaid hydrofining-hydrocracking catalyst having no more than weak acidity comprises at least one hydrogenating component selected from the Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from the Group VIII metals and compounds of the Group VIII metals. Preferred combinations of hydrogenating components include nickel sulfide and tungsten sulfide, nickel sulfide and molybdenum sulfide, and palladium sulfide and molybdenum sulfide.

The aforesaid hydrofining-hydrocracking catalyst having no more than weak acidity comprises a support, preferably one that is moderately acidic, but not more than moderately acidic, as compared with highly acidic supports such as silica-alumina. Said support preferably is selected from the group consisting of silica-magnesia supports, silica-alumina supports containing less than 70 weight percent of silica, and silica-alumina-magnesia supports having a silica content less than 80 weight percent.

The aforesaid hydrofining-hydrocracking catalyst having no more than weak acidity is relatively nitrogen-insensitive compared with conventional acidic hydrocracking catalysts such as nickel sulfide on silica-alumina. Accordingly, the nitrogen content of the nitrogen-containing feed used in the process of the present invention may be relatively high and excellent hydrocracking results still may be obtained in the conversion zones containing said catalysts at reasonable temperatures without the necessity for rapidly raising the temperature to maintain conversion as is necessary when hydrocracking a high nitrogen content feed of a conventional acidic hydrocracking catalyst, such as nickel sulfide on silica-alumina. The nitrogen content of the feed in the present process may range from 10 parts per million to 7000 parts per million or more. The process is especially attractive for processing heavy feeds containing at least 500 parts per million nitrogen.

Although high nitrogen content feeds can be tolerated by said hydrofining-hydrocracking catalysts having no more than weak acidity, it will be noted that said catalysts also are excellent hydrodenitrification catalysts and are efficient in concurrently hydrofining as well as in hydrocracking the feed. Nevertheless, the process of the present invention may be rendered even more efficient if very high nitrogen content feeds are first hydrofined by conventional methods to at least somewhat reduce their nitrogen content before hydrocracking them in the presence of said catalysts having no more than weak acidity in accordance with the present invention.

The conversion zone in the process of the present invention containing said hydrofining-hydrocracking catalyst having no more than weak acidity is operated at combinations of conditions selected from within the following ranges that will produce the desired degree of hydrocracking; a temperature of about 500° to 950° F., preferably 650° to 850° F.; a hydrogen partial pressure of 500 to 3500 p.s.i.a., preferably 1000 to 2500 p.s.i.a.; an LHSV of from about 0.1 to 4.0, preferably 0.4 to 2.0; and a per-pass conversion above about 40 percent. The hydrogen flow to said conversion zone may be from 1000 to 10,000 s.c.f. per barrel of feed, and preferably 2500 to 8000 s.c.f. per barrel of feed. The higher hydrogen partial pressures, particularly with unrefined feeds, give lower catalyst fouling rates, and therefore, for longer catalyst lives, it is preferable to operate above 2000 p.s.i.g. total pressure and above 1000 p.s.i.g. hydrogen partial pressure.

The catalyst in the conversion zone subsequent to the hydrofining conversion zone and the hydrofining-hydrocracking conversion zone may be any conventional active acidic hydrocracking catalyst, for example nickel sulfide on silica-alumina, platinum on silica-alumina, cobalt sulfide on silica-alumina, various conventional fluorided acidic hydrocracking catalysts, etc.

Said subsequent conversion zone may be operated under conventional hydrocracking conditions, for example a total pressure of from 500 to 3000 p.s.i.g., a hydrogen partial pressure of at least 350 p.s.i.g., a temperature of from 550° to 850° F., an LHSV of from about 0.1 to 4.0, and a per-pass conversion above about 40 percent. Generally, at least 300 s.c.f. of hydrogen per barrel of feed will be supplied to said subsequent conversion zone, wherein normally from about 1000 to 2000 s.c.f. of hydrogen are consumed in the hydrocracking reaction per barrel of feed converted to synthetic products.

It is well known that nitrogen has an extremely deleterious effect upon the hydrocracking performance of acidic hydrocracking catalysts such as those used in said subsequent zone in the present process. It is well known that as the nitrogen content of the feed to a hydrocracking zone containing an acidic hydrocracking catalyst increases, the reaction temperature must be raised if desired conversion levels are to be maintained. It is also well known that if the temperature must be raised beyond a certain point, for example 850° F., side reactions and nonhydrocracking reactions occur to an intolerable extent. Accordingly, it is well known that the nitrogen content of the feed to a hydrocracking zone containing an acidic hydrocracking catalyst should be kept below about 50 parts per million, preferably below about 10 parts per million, and still more preferably below about 2 parts per million. Therefore, in a multi-stage process of the type with which the present invention is concerned, namely one in which a hydrofining-hydrocracking catalyst of not more than weak acidity, for example of moderate acidity, is used in a first stage and a highly acidic hydrocracking catalyst is used in a subsequent stage, the first stage heretofore has been operated at severe enough hydrofining conditions to reduce the nitrogen content of the total hydrofined feed to a level low enough for passing to the subsequent stage. Frequently, such severe conditions in the first stage have resulted in an undesirably high level of hydrocracking in that stage. Heretofore, the operator of such a process faced a dilemma; if the first stage were operated at sufficiently mild hydrocracking conditions, insufficient hydrofining would be accomplished to reduce the nitrogen content of the feed to the subsequent stage to a tolerably low level.

Heretofore, it has been thought that the nitrogen concentration in the effluent from the first stage of the aforesaid type of process has been distributed relatively uniformly through said effluent, and that if said effluent were fractionated, nitrogen would appear in the various fractions in approximately the same concentration. Very unexpectedly, it has now been discovered that this is not so, but rather that the nitrogen concentration in the synthetic portion of the effluent, namely that portion boiling below the initial boiling point of the feed, is very substantially lower than the nitrogen concentration in that portion of the effluent boiling within the feed boiling range. This surprising discovery has far-reaching consequences in the operation of a multi-stage process of the aforesaid type. In accordance with the present invention, it is now possible to operate a first stage, containing a hydrofining-hydrocracking catalyst having no more than weak acidity, at adequately mild hydrocracking conditions and permit the effluent from said stage to contain a much higher total nitrogen content than was heretofore possible. This is accomplished by processing in the subsequent stage containing a highly acidic caatlyst only those materials in the effluent from said first stage that boil below the initial boiling point of the feed to that first stage. These materials, termed synthetic materials because they do not contain any materials boiling within the boiling range of the original feed to the stage in which they are produced, contain a very low concentration of nitrogen despite the fact that the higher boiling materials have a substantially higher nitrogen concentration. This may be illustrated by the following examples:

Example 1

A 700° to 900° F. boiling range petroleum distillate containing 2450 parts per million nitrogen was hydrocracked over a nickel-tungsten on silica-magnesia catalyst under conditions within the aforesaid first conversion zone ranges. The whole hydrocracked product contained 50 parts per million nitrogen; however, it was found that only 2 parts per million of the said 50 parts per million nitrogen appeared in the 550° to 700° F. synthetic portion of the hydrocrackate.

Example 2

A hydrocarbon feed boiling between 550° and 1000° F., and containing 4050 p.p.m. total nitrogen is separated into two portions, boiling above and below about 775° F., respectively.

The heavier of the aforesaid feed portions, containing 5650 p.p.m. total nitrogen, is hydrofined-hydrocracked in a first conversion zone in the presence of a catalyst comprising nickel sulfide, tungsten sulfide and silica-magnesia at a temperature of 750° F. and a pressure of 2000 p.s.i.g., at a per-pass conversion of 50 liquid volume percent of said feed to materials boiling below the initial boiling point of said feed. From the effluent from said zone materials boiling above about 700° F. are recycled to said zone. The total nitrogen content of the 500–700° F. portion of said effluent is 0.12 p.p.m.

The lighter of the aforesaid feed portions, containing 2450 p.p.m. total nitrogen, is hydrofined on a once-through basis in a second conversion zone in the presence of a catalyst comprising nickel sulfide, tungsten sulfide and silica-magnesia at a temperature of 750° F. The effluent from said second conversion zone boils from 550 to 800° F. and has a total nitrogen content of 0.14 p.p.m.

The effluent from said second conversion zone is blended with said 500°–700° F. portion of the effluent from said first conversion zone. The resulting blended product has a total nitrogen content of 0.13 p.p.m.

Example 3

For comparison purposes, the same feedstock used in Example 2 instead of being separated into two portions as in Example 1 is passed without separation into contact in a conversion zone with the same catalyst used in both conversion zones in Example 2, on a once-through basis at a temperature of 750° F. and a pressure of 2000 p.s.i.g. The effluent from said conversion zone boils from 550° to 1000° F. and has a total nitrogen content of 6.3 p.p.m.

In order to obtain a nitrogen content of 0.13 p.p.m., as is obtained in the operation in Example 2, the temperature for the operation in this Example 3 would have to be raised 20° F., which would cause a substantial increase in catalyst fouling rate.

Example 4

Referring now to the drawing, there shown is an exemplary diagrammatic illustration of an embodiment of process units and flow paths suitable for carrying out the process of the present invention.

A hydrocarbon feed which may be, and in this example is, a petroleum distillate feed boiling above 350° F. and containing materials boiling above 560° F. is passed through line **1** to distillation column **2** where it is separated into various fractions as shown. A gaseous fraction may be removed from column **2** through line **3**, and a residum fraction boiling above 1100° F. may be removed through line **4**, if desired. Fraction A, having an initial boiling point above 560° F., is passed from distillation column **2** through line **5** to hydrofining-hydrocracking zone **6**. Fraction B, boiling from approximately the initial boiling point of the feed in line **1** to the initial boiling point of fraction A, is passed from distillaton column **2** through line **7** to hydrofining zone **8**.

Fraction A is hydrofined and hydrocracked in zone **6** with the aforesaid hydrofining-hydrocracking catalyst having no more than weak acidity and with hydrogen entering zone **6** through line **9** under the hydrocracking conditions previously discussed, including a per-pass conversion above about 40 volume percent of fraction A to products boiling below the initial boiling point of fraction A. From zone **6**, an effluent is passed through line **10** to separation zone **15** from which hydrogen is recycled through line **16**, ammonia is withdrawn through line **17**, and remaining materials are passed through line **18** to separation zone **19**. From separation zone **19** a product stream boiling below about 550° F., for example including gasoline and jet fuel components, is withdrawn through line **20**. From separation zone **19**, materials boiling above the initial boiling point of fraction A, i.e., materials boiling within the range of the feed entering zone **6** through line **5**, are returned to zone **6** through line **25**. From separation zone **19** a fraction boiling from about 550° F. to the initial boiling point of fraction A, i.e., approximately above the jet fuel boiling range and below the initial boiling point of the feed to zone **6**, is passed through line **26** into contact in hydrocracking zone **27** with the aforesaid highly acidic hydrocracking catalyst and with hydrogen entering zone **27** through line **28** under the hydrocracking conditions previously discussed, including a per-pass conversion above about 40 percent.

Fraction B is contacted in hydrofining zone **8** with the aforesaid hydrofining catalyst and with hydrogen enternig zone **8** through line **29** under the hydrofining conditions previously discussed, including a per-pass conversion of less than about 30 volume percent of fraction B to products boiling below the initial boiling point of fraction B. From zone **8** an effluent is passed through line **30** to separation zone **35** from which hydrogen is recycled through line **36** to zone **8**, ammonia is withdrawn through line **37**, and remaining materials are passed through line **38** into contact in hydrocracking zone **27** with the aforesaid highly acidic hydrocracking catalyst and with hydrogen entering zone **27** through line **28**, under the hydrocracking conditions previously discussed, including a per-pass conversion of above about 40 percent of said remaining materials to products boiling below the initial boiling point of said remaining materials. The hydrocrackate effluent from zone **27** is passed through line **39** to separation zone **40** for separation into products boiling below about 550° F., which are passed through line **45**, and materials boiling above about 550° F. which are returned to zone **40** through line **46** for further processing.

The nitrogen concentration in the stream passed through line **26** to conversion zone **27** is lower than the nitrogen concentration in the stream returned through line **25** to conversion zone **6**, and accordingly a given volume of the stream in line **26** will be less deleterious to the hydrocracking catalyst in zone **27** from the standpoint of nitrogen poisoning than the same volume of the stream in line **25**, even though the total nitrogen concentration of the stream in line **18** may be higher than permissible for a suitable feed stock to zone **27**.

From the foregoing, it will be seen that the process of the present invention is effective in producing both middle distillates, in particular jet fuels, and gasoline in varying ratios from heavy, nitrogen-containing feed stocks. It will also be seen that the process embodies a discovery which permits the production in the zone containing the hydrofining-hydrocracking catalyst having no more than weak acidity under surprisingly mild hydrofining conditions of fractions, having adequately low nitrogen contents to be suitable feed stocks for the subsequent conversion zone containing a catalyst having a high acidity.

Although only specific embodiments of the present invention have been described, numerous variations can be made of those embodiments without departing from the spirit of the invention, and all such variations that fall within the scope of the appended claims are intended to be embraced thereby.

We claim:

1. A process for producing gasoline and middle distillates from a hydrocarbon feed stock selected from the group consisting of nitrogen-containing petroleum distillates and petroleum residua boiling above 350° F., which comprises selecting two feed fractions each having different boiling ranges, the higher boiling of said fractions boiling above 560° F., hydrocracking said higher boiling fraction in the presence of from 1000 to 10,000 s.c.f. of hydrogen per barrel thereof in a first conversion zone at a temperature of from 500° to 950° F., a pressure above 500 p.s.i.g., an LHSV of from 0.1 to 4.0, and a per-pass conversion of more than about 40 volume percent of said higher boiling fraction to products boiling below the initial boiling point thereof, with a hydrofining-hydrocracking catalyst having no more than weak acidity comprising at least one hydrogenating component selected from the Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals in intimate association with a silica-containing support, recovering at least one product boiling below 550° F. from said first conversion zone, hydrofining the lower boiling of said fractions with a hydrofining catalyst in a second conversion zone to reduce the nitrogen content thereof under conditions that accomplish in said second zone a concurrent hydrocracking conversion of less than 30 volume percent of the feed thereto to products boiling below the boiling range of said feed, passing to a third conversion zone from said first zone a fraction boiling above 550° F. and below the initial boiling point of the feed to said first zone, removing ammonia from the hydrofined fraction from said second conversion zone and passing the resulting hydrofined fraction to said third conversion zone, and hydrocracking in said third conversion zone said fractions passed thereto to produce additional products boiling below 550° F.

2. A process as in claim **1**, wherein said third conversion zone contains a hydrocracking catalyst comprising at least one hydrogenating component in intimate association with an active, acid support, and wherein said third conversion zone is operated at a temperature of from 550° to 900° F., a pressure above 500 p.s.i.g., and an LHSV of 0.1 to 4.0.

3. A process as in claim **1**, wherein a fraction boiling within the range of the feed to said first conversion zone is recycled to said first conversion zone from the effluent thereof.

4. A process as in claim **1**, wherein a fraction boiling within the boiling range of said fractions passed to said third conversion zone is recycled to said third conversion zone from the effluent thereof.

5. A process for producing gasoline and middle distillates from a hydrocarbon feed stock selected from the group consisting of nitrogen-containing petroleum distillates and petroleum residua boiling above 350° F., containing materials boiling above 560° F., and also containing materials boiling below 560° F., which comprises separating said feed into two feed fractions each having different boiling ranges, the higher boiling of said fractions boiling above 560° F., hydrocracking said higher boiling fraction in the presence of 1000 to 10,000 s.c.f. of hydrogen per barrel thereof in a first conversion zone at a temperature of from 500° to 950° F., a pressure above 500 p.s.i.g., an LHSV of from 0.1 to 4.0, and a per-pass conversion of more than about 40 volume percent of said higher boiling fraction to products boiling below the initial boiling point thereof with a hydrofining-hydrocracking catalyst having no more than weak acidity comprising at least one hydrogenating component selected from the Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals in intimate association with a support substantially less acidic than a conventional silica-alumina hydrocracking support, recovering at least one product boiling below 550° F. from said first conversion zone, hydrofining the lower boiling of said fractions by contacting said fraction in a second conversion zone with a hydrofining catalyst comprising a hydrogenating component selected from the Group VI metals and compounds of Group VI metals and a hydrogenating component selected from the Group VIII metals and compounds of Group VIII metals in intimate association with a support substantially comprising alumina at 500° to 800° F., 500 to 4,000 p.s.i.g., an LHSV of 0.2 to 10, and a per-pass conversion of less than 30 volume percent of said lower boiling fraction to products boiling below the initial boiling point thereof, in the presence of 500 to 10,000 s.c.f. of hydrogen per barrel of said lower boiling fraction, passing to a third conversion zone from said first zone a fraction boiling above 550° F. and below the initial boiling point of the feed to said first zone, removing ammonia from the hydrofined fraction from said second conversion zone and passing the resulting hydrofined fraction to said third conversion zone and hydrocracking in said third conversion zone said fractions passed thereto to produce additional products boiling below 550° F.

References Cited by the Examiner

UNITED STATES PATENTS

3,026,260	3/1962	Watkins	208—59
3,159,568	12/1964	Price et al.	208—111
3,175,966	3/1965	Burch	208—79

DELBERT E. GANTZ, *Primary Examiner.*