

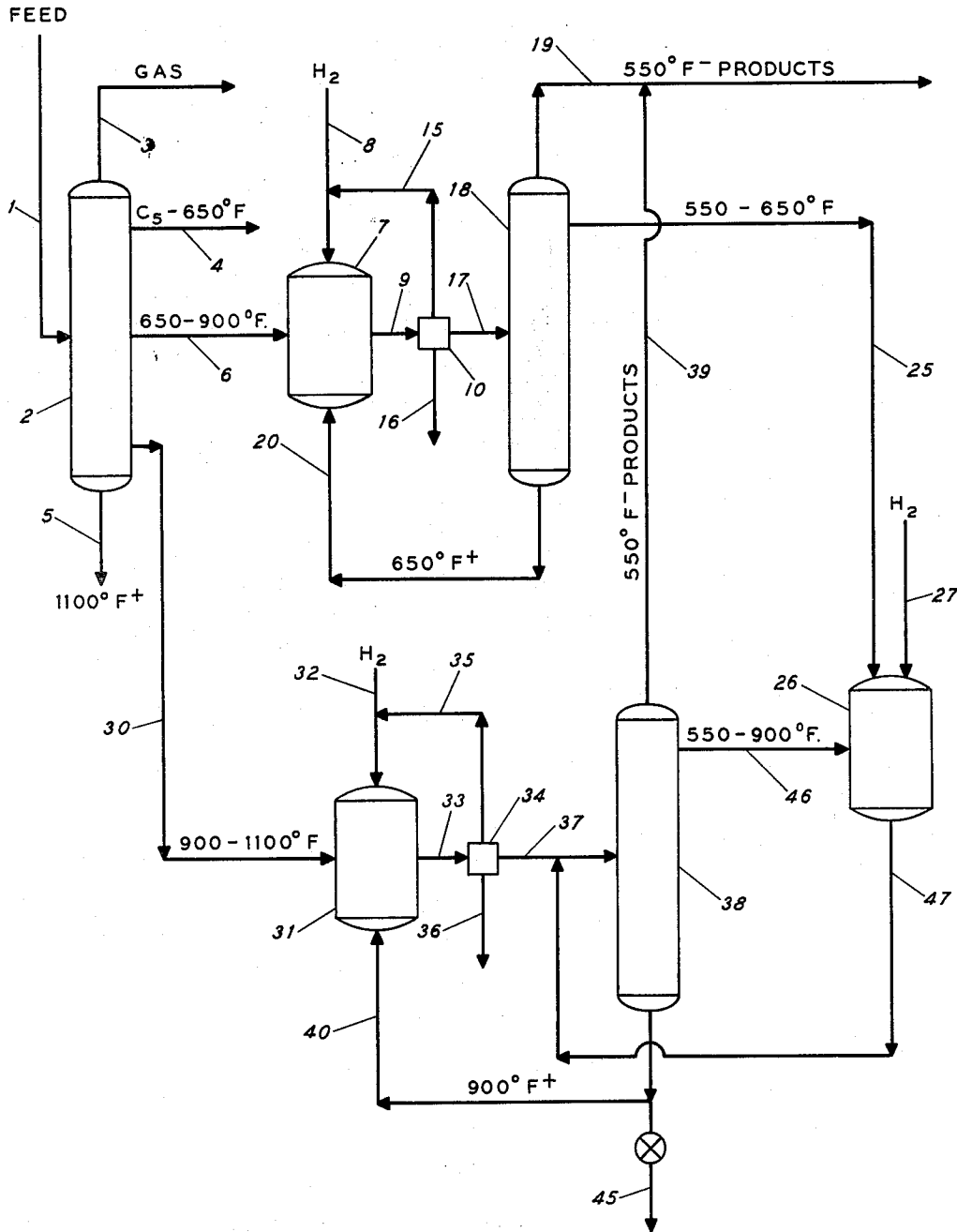
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MULTI-STAGE HYDROCRACKING PROCESS

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MULTI-STAGE 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 catalysts, 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. It is also well known that such highly acidic catalysts do not result in the production of substantial quantities of middle distillates and that where gasoline production and also substantial middle distillate production is desired a 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 the hydrofining-hydrocracking catalyst having no more than weak acidity is used in the first stage and an 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 a greater amount of hydrocracking, light gas production and catalyst fouling in the first stage than is desired. 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 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 selected from the group consisting of nitrogen-containing petroleum distillates and petroleum residua boiling above 650° F., which comprises selecting at least two feed fractions having different boiling ranges, separately hydrocracking each of said fractions in the presence of from 1,000 to 10,000 s.c.f. of hydrogen per barrel thereof in

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a conversion zone at a temperature from 500° to 950° F., a pressure above 500 p.s.i.g., a per-pass conversion above 40%, and an LHSV of 0.1 to 4.0 with a 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 zone, and separately hydrocracking that portion of the effluent from said zone boiling above 550° F. and below the initial boiling point of the feed to said zone 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 selected from the group consisting of nitrogen-containing petroleum distillates and petroleum residua boiling above 650° F. which comprises separating said feed into a first fraction and a second fraction of different boiling range, hydrocracking said first 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., a per-pass conversion above 40%, and an LHSV of from 0.1 to 4.0 with a 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, hydrocracking said second fraction in the presence of from 1000 to 10,000 s.c.f. of hydrogen per barrel thereof in a second conversion zone at a temperature of from 500° to 950° F., a pressure above 500 p.s.i.g., a per-pass conversion above 40%, and an LHSV of from 0.1 to 4.0 with a 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 second conversion zone, passing to a third conversion zone from said first conversion zone a fraction boiling above 550° F. and below the initial boiling point of the feed to said first conversion zone, passing to said third conversion zone a fraction boiling above 550° F. and below the initial boiling point of the feed to said second conversion zone, and hydrocracking in said third conversion zone at a per-pass conversion above 40%, said fractions passed thereto to produce additional products boiling below 550° F.

Suitable feeds for use in the process of the present invention are nitrogen-containing petroleum distillates and nitrogen-containing petroleum residua from which fractions can be selected boiling above 650° F., preferably fractions boiling between 650° F. and 1200° F., and mixtures of the foregoing. 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 as well as solvent decarbonized oils from a wide range of residua.

The aforesaid catalysts having no more than weak acidity comprise at least one hydrogenating component selected from the Group VI metals and compounds of the Group VI metals and at least one hy-

drogenating 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 catalysts having no more than weak acidity comprise 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 catalysts having no more than weak acidity are 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 5000 parts per million. 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 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.

Conversion zones in the process of the present invention containing said catalysts having no more than weak acidity are 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.g., preferably 1000 to 2500 p.s.i.g.; and an LHSV of from about 0.1 to 4.0, preferably 0.4 to 2.0. The hydrogen flow to said conversion zones may be from 1000 to 12,000 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. to hydrogen partial pressure.

A separate conversion zone may be used containing said catalyst having no more than weak acidity for each feed fraction of different boiling range that is to be processed, or, if desired, a single such conversion zone may be used to process each of said feed fractions alternately.

The catalyst in the conversion zone subsequent to the conversion zones containing catalysts having no more than weak acidity 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., and a temperature of from 550° to 850° F. Generally, at least 3000 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. It is apparent that 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 moderate acidity is used in a first stage and a highly acidic hydrocracking catalyst is used in subsequent stage, the first stage must be operated at severe enough hydrofining conditions to reduce the nitrogen content of the feed to the subsequent stage to an acceptable level. It is also apparent that there are frequent cases when such severe conditions in the first stage will result 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 plurality of first stages, each containing a catalyst having no more than weak acidity, at adequately mild hydrocracking conditions and permit the effluent from each of said stages 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 catalyst only those materials in the effluent from each 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 sulfide-tungsten sulfide 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 750° to about 1300° F. boiling range petroleum distillate containing 5475 parts per million nitrogen is distilled into two equal fractions, boiling above and below about 950° F., respectively. Each fraction is separately hydrocracked over a nickel sulfide-tungsten sulfide on silica-magnesia catalyst under conditions within the aforesaid first conversion zone ranges and at a per-pass conversion of 50 percent. In hydrocracking the fraction boiling from 750° to about 950° F., a synthetic product boiling from 500° to 700° F. is obtained and remaining higher boiling materials boiling above 700° F. are recycled. The 500° to 700° F. product had a nitrogen content of 0.12 part per million. In hydrocracking the fraction boiling above about 950° F. a synthetic product boiling between 500° and 950° F. is obtained and remaining higher boiling materials were recycled. The product boiling within the range of 500° to 950° F. has a nitrogen content of 5.1 parts per million. Upon blending the products obtained in the aforesaid separate hydrocracking operations the resulting product blend boiling within the range 400° to 950° F. have a nitrogen content of 2.6 parts per million.

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 containing materials boiling above 650° F., is passed through line 1 to distillation column 2, where it is separated into various fractions as shown. A gaseous fraction is removed from column 2 through line 3, a C₅-650° F. fraction is removed through line 4, and, if desired, a residuum fraction boiling above 1100° F. is removed through line 5. A 650° to 900° F. fraction is passed from separation zone 2 through line 6 into contact in hydrocracking zone 7 with the aforesaid hydrocracking catalyst having no more than weak acidity and with hydrogen entering zone 7 through line 8 under the hydrocracking conditions previously discussed, at a per-pass conversion preferably above about 40%. From zone 7, an effluent is passed through line 9 to separation zone 10, from which hydrogen is recycled through line 15, ammonia is withdrawn through line 16, and remaining materials are passed through line 17 to separation zone 18. From separation zone 18 a product stream boiling below about 550° F., for example including gasoline and jet fuel components, is withdrawn through line 19. From separation zone 18, materials boiling above about 650° F., i.e., materials boiling within the range of the feed entering zone 7 through line 6, are returned to zone 7 through line 20. If desired a portion of the materials in line 20 may be passed to a catalytic cracking zone, or used for any other desired purpose, for example as a lube oil stock. From separation zone 18 a fraction boiling from about 550° to 650° F., i.e., approximately above the jet fuel boiling range and below the initial boiling point of the feed to zone 7, is passed through line 25 into contact in hydrocracking zone 26 with the aforesaid highly acidic hydrocracking catalyst and with hydrogen entering zone 26 through line 27, at a per-pass conversion preferably above about 40%.

A 900° to 1100° F. fraction is passed from separation zone 2 through line 30 into contact in hydrocracking zone 31 with the aforesaid hydrocracking catalyst having no more than weak acidity and with hydrogen entering zone 31 through line 32 under the hydrocracking conditions previously discussed, at a per-pass conversion preferably above about 40%. From zone 31 an effluent is passed through line 33 to separation zone 34 from which hydrogen is recycled through line 35 to zone 31, ammonia is withdrawn through line 36, and remaining materials are passed through line 37 to separation zone 38. From separation zone 38, products boiling below about 550° F., including gasoline and jet fuel components, are recovered through lines 39 and 19, and materials boiling above about 900° F., i.e., within the boiling range of the feed entering zone 31 through line 30, are returned to zone 31 through line 40. A portion of the materials in line 40 may be passed through line 45 to a catalytic cracking zone, or used for any other desired purpose, for example as a lube stock. From separation zone 38 a fraction boiling between about 550° and 900° F., i.e., approximately above the jet fuel boiling range and below the initial boiling point of the feed entering zone 31 through line 30, is passed through line 46 into contact in hydrocracking zone 26 with the aforesaid highly acidic hydrocracking catalyst and with hydrogen entering zone 26 through line 27 under the hydrocracking conditions previously discussed, at a per-pass conversion above about 40%. The hydrocrackate effluent from zone 26 is passed through line 47 to separation zone 38 for separation into products boiling below about 550° F., which are passed through line 39, and materials boiling above about 550° F., which are returned to zone 26 through line 46 for further processing.

The nitrogen concentration in the stream passed through line 25 to conversion zone 26 is substantially lower than the nitrogen concentration in the stream returned through line 20 to conversion zone 7. The nitrogen concentration in the stream passed through line 46 to conversion zone 26 is substantially lower than the nitrogen concentration in the stream returned through line 40 to conversion zone 31.

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 zones containing catalysts 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 selected from the group consisting of nitrogen-containing petroleum distillates and petroleum residua boiling above 650° F., which comprises selecting at least two feed fractions having different boiling ranges, separately hydrocracking at a per-pass conversion above 40% each of said fractions in the presence of from 1000 to 12,000 s.c.f. of hydrogen per barrel thereof in a conversion zone at a temperature from 500° to 950° F., a pressure above 500 p.s.i.g. and an LHSV of from 0.1 to 4.0 with a 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 zone, and separately hydrocracking at a per-pass conversion above 40% that portion of the effluent from said zone boiling above 550° F. and below the initial boiling point of the feed to said zone to produce additional products boiling below 550° F.

2. A process for producing gasoline and middle distillates from a hydrocarbon feed selected from the group consisting of nitrogen-containing petroleum distillates and petroleum residua boiling above 650° F., which comprises separating said feed into a first fraction and a second fraction of different boiling range, hydrocracking said first fraction in the presence of from 1000 to 12,000 s.c.f. of hydrogen per barrel thereof in a first conversion zone at a temperature from 500° to 950° F., a pressure above 500 p.s.i.g., a per-pass conversion above 40%, and an LHSV of from 0.1 to 4.0 with a 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, hydrocracking said second fraction in the presence of from 1000 to 12,000 s.c.f. of hydrogen per barrel thereof in a second conversion zone at a temperature from 500° to 950° F., a pressure above 500 p.s.i.g., a per-pass conversion above 40%, and an LHSV of from 0.1 to 4.0 with a 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 second conversion zone, 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 conversion zone, passing to said third conversion zone a fraction boiling above 550° F. and below the initial boiling point of the feed to said second conversion zone, and hydrocracking in said third conversion zone at a per-pass conversion above 40%, said fractions passed thereto to produce additional products boiling below 550° F.

3. A process as in claim 2 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 from 500° to 950° F., a pressure above 500 p.s.i.g. and an LHSV of 0.1 to 4.0.

4. A process as in claim 2 wherein a fraction boiling within the boiling range of the feed to said first conversion zone is recycled to said first conversion zone from the effluent thereof.

5. A process as in claim 2 wherein a fraction boiling within the boiling range of the feed to said second conversion zone is recycled to said second conversion zone from the effluent thereof.

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