May 18, 1965 R. H. KOZLOWSKI ETAL 3,184,402

HYDROCRACKING PROCESS

Filed April 8, 1964 3 Sheets-Sheet 1

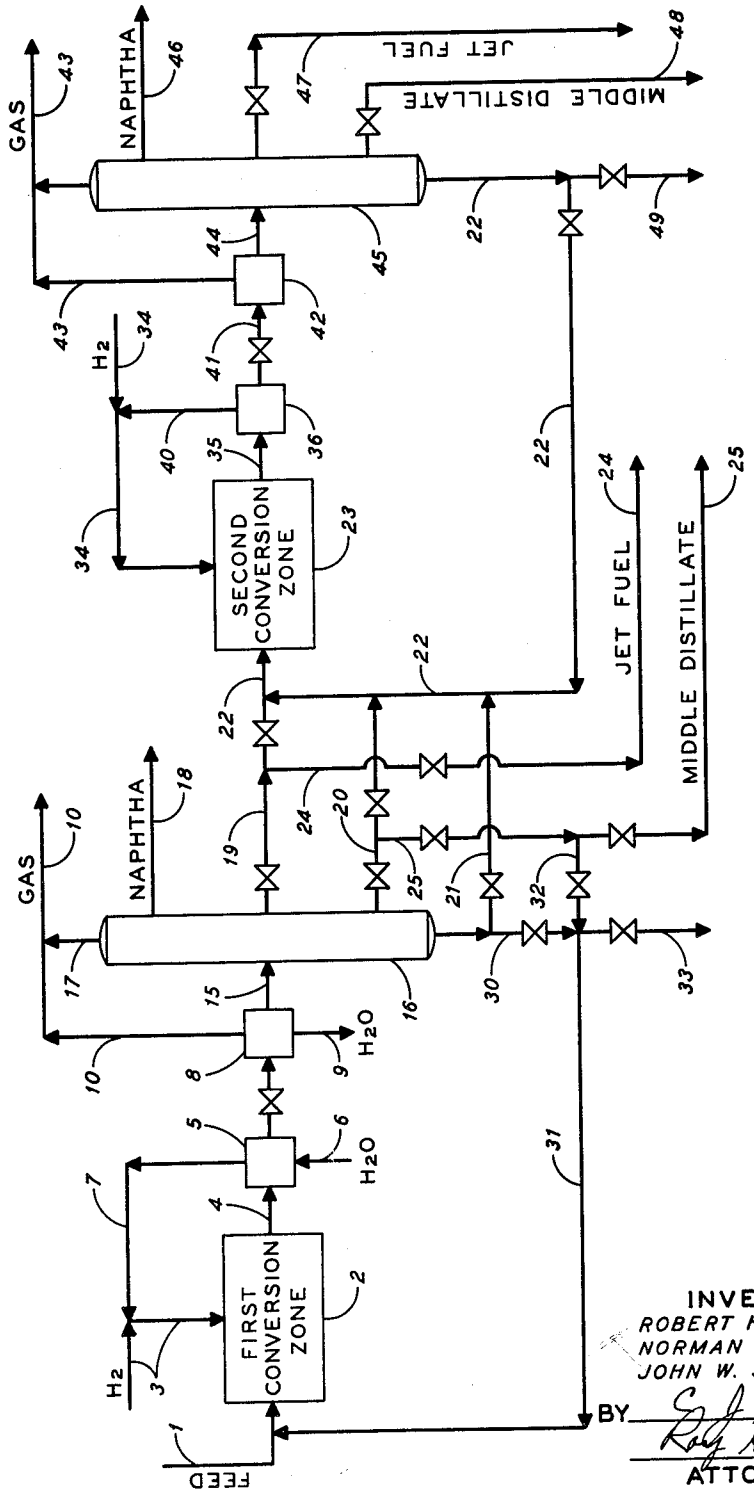


FIG. 1

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HYDROCRACKING PROCESS

Filed April 8, 1964 3 Sheets-Sheet 2

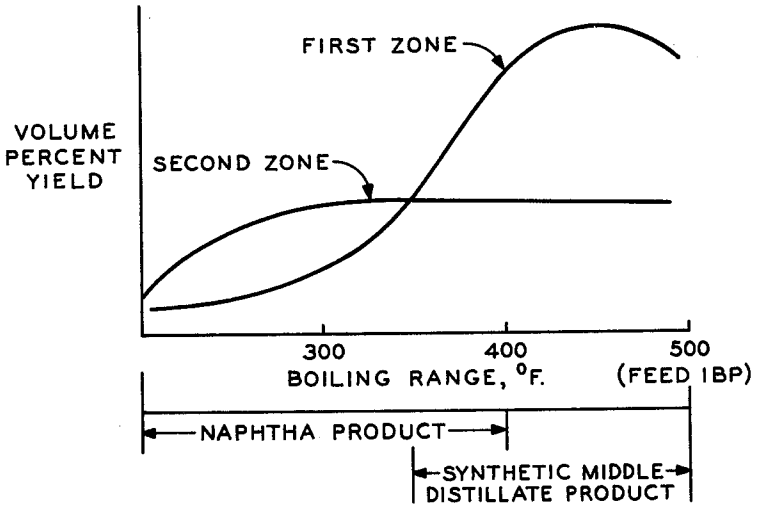


FIG. 2

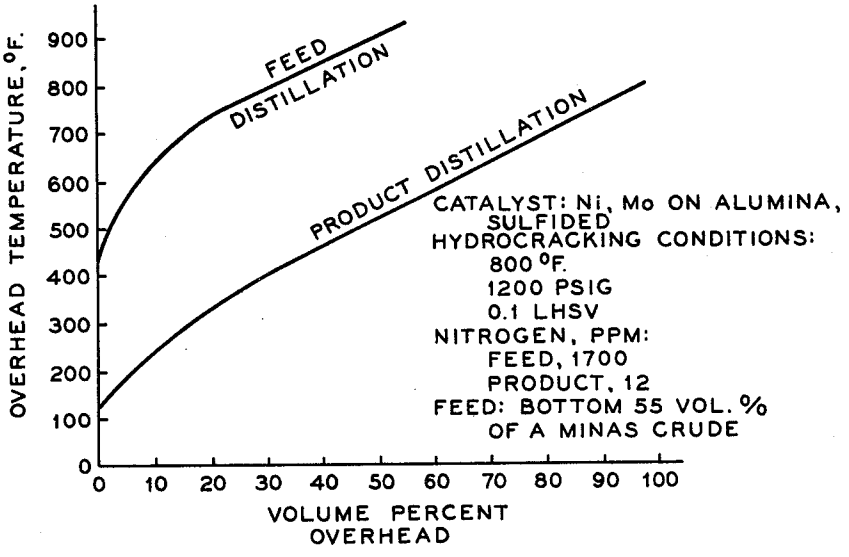


FIG. 3

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HYDROCRACKING PROCESS

Filed April 8, 1964 3 Sheets-Sheet 3

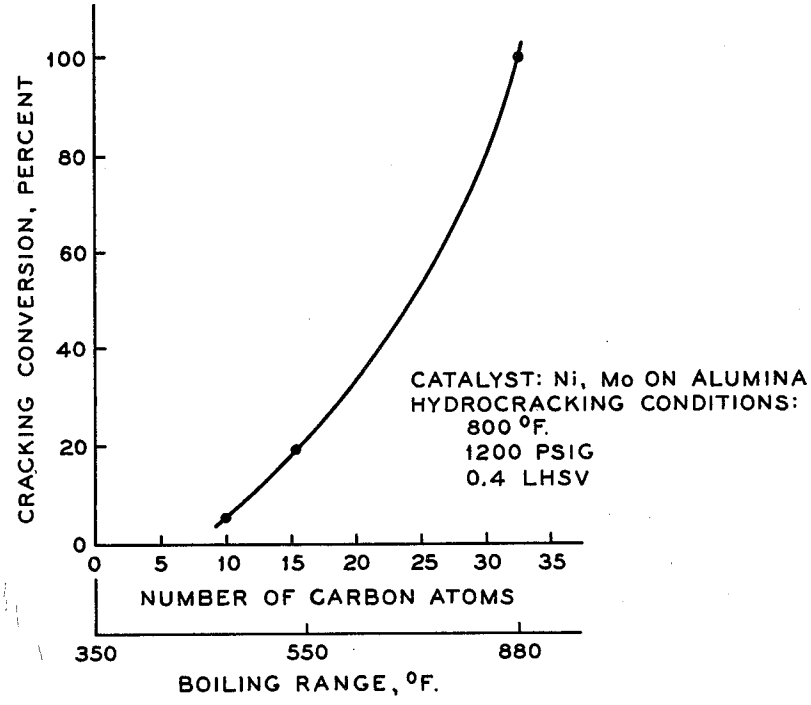


FIG. 4

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3,184,402

HYDROCRACKING PROCESS

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Filed Apr. 8, 1964, Ser. No. 359,548
4 Claims. (Cl. 208—59)

INTRODUCTION

This application is a continuation-in-part of application Serial No. 113,759, filed May 31, 1961, now abandoned.

This invention relates to a hydrocarbon conversion process, more particularly to a hydrocarbon conversion process for converting petroleum distillates and residua to various valuable products, and, still more particularly, to a flexible staged catalytic conversion process capable of producing both gasoline and middle distillates in widely varying ratios to meet demand fluctuations resulting from seasonal or other causes.

PRIOR ART PROBLEMS AND SOLUTIONS

It has been well known heretofore that seasonal fluctuations exert a heavy influence on the ratio of gasoline and middle distillates that refiners are called upon to produce. Further, particularly in recent years in which the supplies of crude have been adequate or in excess of needs in most areas, there has been an incentive for increasing the ratio of middle distillates to gasoline; particularly, this incentive has been heightened by jet fuel requirements and by the lack of need in certain foreign crude producing areas for large quantities of gasoline.

Even though a refiner increases the ratio of middle distillates to gasoline production in response to factors such as the foregoing, there are other factors, particularly seasonal changes, that frequently require him to reverse this trend to decrease the ratio of middle distillates to gasoline production. Accordingly, a refiner is interested in a high degree of flexibility in order to show the required changes in these ratios promptly as the need arises. Conventionally, a refiner obtains the desired degree of flexibility by proper manipulation of the various feed streams and products from a large number of conversion processes including thermal cracking, catalytic cracking, hydrocracking, coking and reforming. However, it is obvious that manipulation of the feed or product related to any one such unit in an interrelated system of units will necessarily require careful consideration of the effect on the other units. Accordingly, a most desirable objective is the attainment of the highest degree of flexibility in products produced, with the minimum number of conversion units. Heretofore, such flexibility, particularly in obtaining widely varying ratios of middle distillates to gasoline production, has not been obtainable as a practical matter with a single or two-stage hydrocracking process.

OBJECTS

In view of the foregoing, it is a primary object of the present invention to provide a two-stage hydrocracking process capable of producing widely varying ratios of middle distillates to gasoline in response to the effects on demand of seasonal or other changes.

THE PRESENT INVENTION

In accordance with the present invention, there is provided a two-stage hydrocarbon conversion process wherein catalysts of different acidities are used in the two stages and wherein wide variations in the ratio of middle distillates to gasoline produced are obtained by interstage fractionation and proper manipulation of operating conditions, fractionation cut points, and recycle streams.

More particularly, in accordance with the present invention there is provided a process for converting a hydrocarbon feed selected from the group consisting of hydrocarbon distillates boiling from about 500° to 1100° F. and hydrocarbon residua boiling above about 1050° F. which comprises converting in a first conversion zone from 10 to 50 volume percent of said feed per pass to fractions boiling below the initial boiling point of said feed, said first zone being operated at about 550° to 900° F., a space velocity of from about 0.1 to 3.0, and a hydrogen partial pressure of 500 to 3000 p.s.i.g., with a catalyst comprising a hydrogenating-dehydrogenating component and a cracking component having no more than weak acidity, withdrawing reaction products from said first zone, separating said reaction products in a fractionating zone to produce at least one bottoms fraction boiling above 320° F. and a naphtha fraction boiling below 400° F., withdrawing said naphtha fraction from the system as a product, passing at least a portion of said bottoms fraction to a second conversion zone, converting in said second zone at least 20 volume percent of said portion per pass to products boiling below the initial boiling point of said portion, said second zone being operated at about 450° to 850° F., a space velocity of from about 0.2 to 5.0, and a hydrogen partial pressure of at least 350 p.s.i.g., wtih a catalyst comprising a hydrogenating-dehydrogenating component and an active, strongly acid cracking component, withdrawing an effluent from said second zone, and recovering desired products from said effluent.

DRAWINGS

The novel features of the present invention are set forth with particularity in the appended claims. The invention will best be understood and additional objects and advantages thereof will be apparent from the following description of an exemplary process for producing middle distillates, gasoline and other products from petroleum distillate and residua feed and for achieving wide variations in the middle distillates-to-gasoline ratio, when read in connection with the accompanying drawings, in which:

FIGURE 1 is a flow diagram illustrating a preferred arrangement of process units and flow paths for use in practicing the present invention;

FIGURE 2 is a graphical qualitative representation of the differences in product distribution obtained with the different catalysts in the two conversion zones in the process of the present invention;

FIGURE 3 is a graphical representation of the product distribution obtained when hydrocracking a specific feed stock in the presence of a representative catalyst used in the first stage of the process of the present invention;

FIGURE 4 is a graphical representation of the effect of the feed boiling range on the percent cracking conversion in the first stage of the process of the present invention.

OVERALL PROCESS

Referring now to FIGURE 1, there shown is an exemplary overall process flow diagram suitable for carrying out the process of the present invention.

The hydrocarbon feed to be converted is passed through line **1** into first converion zone **2**, where it is hydrocracked and, if it contains nitrogen, also is at least partially denitrified. The feed may be any petroleum distillate boiling within a range of 500° to 1100° F. and any petroleum resduum boiling above 1050° F., or mixtures thereof. Satisfactory feed stocks include heavy gas oils and catalytic cycle oils, conventional 650° to 1050° F. FCC feed stocks, and the 650° to 850° F. portion of such FCC feed stocks. First conversion zone **2** is discussed in detail below. Hydrogen for the hydrocracking and any denitrification reactions in zone **2** is supplied to that zone through line **3**. Conversion products from zone **2** are withdrawn through line **4** where they are contacted in high pressure separator **5** with water supplied through line **6**. From high pressure separator **5** a hydrogen stream is recycled through line **7**. From high pressure separator **5** conversion products are passed to low pressure separator **8**, from which water is removed through line **9**. A gas stream is separated through line **10** from the conversion products in separator **8**, and the remainder of the conversion products are passed through line **15** to distillation column **16**.

From distillation column **16** a gas stream is withdrawn through line **17**, and a naphtha stream is removed from the system through line **18**, either as a product or for further processing, for example in a reforming zone. A stream is passed from column **16** through at least one of lines **19**, **20** and **21** to line **22** and thence to second conversion zone **23**. Jet fuel and middle distillate products may be withdrawn through lines **24** and **25**, respectively. A stream may be recycled through lines **30** and **31** and may be a bottoms stream remaining after streams are withdrawn from column **16** through lines **19** and/or **20** and/or **21**. or, if all but one of lines **19**, **20** and **21** are closed, may include the streams that otherwise would have passed through those closed lines. For further flexibility, a middle distillate stream may be recycled through line **32**, for example where it is desired to close line **30** and recycle middle distillate only to first conversion zone **2**. A net product stream may be removed through line **33** and may be further processed if desired, for example, by being sent to a catalytic cracking zone.

The feed entering second conversion zone **23** through line **22** is converted there in the presence of hydrogen supplied through line **34**. Second conversion zone **23** is discussed in detail below. The effluent from second conversion zone **23** is withdrawn through line **35** and passed to high pressure separator **36** from which a hydrogen stream is recycled through line **40**. The conversion products from high pressure separator **36** are passed through line **41** to low pressure separator **42** from which a gas stream is removed through line **43**. The conversion products remaining in low pressure separator **42** are passed through line **44** to distillation column **45**. From distillation column **45** a naphtha stream is withdrawn from the system through line **46** for use as a product or for further processing, for example by reforming. A jet fuel stream may be withdrawn through line **47** and a middle distillate stream may be withdrawn through line **48** or either or both of these streams may be combined with the bottoms stream that may be recycled through line **22**. A net bottoms stream may be withdrawn through line **49** and, if desired, may be passed to a catalytic cracking zone for further conversion.

Referring now to FIGURE 2, there shown is a qualitative graphical representation of the differences in product distribution between the products of the first and second conversion zones of the process of the present invention. It will be noted that the product from the first conversion zone is concentrated in the middle distillate range, whereas the product from the second conversion zone is spread more evenly over the whole boiling range below the initial boiling point of the feed, with a large yield in the naphtha range. The reason for these differences in product distribution are discussed in the detailed discussion below relating to the first and second conversion zones, respectively. These differences are drawn upon as one of the main bases for the remarkable flexibility of the process of the present invention for producing middle distillates and gasoline in widely varying ratios.

FEED TO FIRST CONVERSION ZONE

As discussed above in connection with the detailed description of FIGURE 1, the feed to the first conversion zone may be any petroleum distillate boiling from 500° to 1100° F., any petroleum residuum boiling above 1050° F., and mixtures thereof. Heavy gas oils and catalytic cycle oils are excellent feeds to the process, as well as conventional FCC feeds and portions thereof. Residua feeds may include Minas paraffinic residua, which may boil above 1100° F., and other paraffinic-type residua boiling above about 1050° F.

The feeds to the process are limited to those having an initial boiling point of 500° F. or above because it is only with such feeds that middle distillates, including jet fuels, can be produced which are highly naphthenic, low in aromatics (therefore having high smoke points), and low in normal paraffins (therefore having low freezing points). Where the feed has an initial boiling point above 500° F., it may be converted in the first conversion zone directly to a synthetic material (i.e., one boiling below the feed initial boiling point), which is a preferred jet fuel having a high naphthene content, low normal paraffin content and therefore low freeze point, and low aromatics content and therefore acceptably high smoke point. It has been found that feeds having lower initial boiling points, for example around 400° F., tend to produce excessive quantities of non-synthetic products having a high aromatics content and therefore an unacceptably low smoke point, although the freeze point may be satisfactory. Such non-synthetic product also tends to have a high pour point.

The nitrogen content of the feed to the first conversion zone is dependent upon the nitrogen content requirements of the feed to the second conversion zone. The nitrogen content of the feed to the second zone generally should be below 1000 parts per million, preferably below 100 parts per million, and still more preferably below 10 parts per million. The nitrogen content of the feed to the first conversion zone can be anything consistent with these requirements. However, it should be noted in connection with high nitrogen-content feeds that, even though the first conversion zone could be operated to reduce the nitrogen content to some minimum level without exceeding the permissible limit of cracking severity, it may be found very desirable not to accomplish this much denitrification, but rather to accomplish some lesser amount and permit the excess nitrogen to pass through to the second conversion zone. This method of operation will require an increase in pressure in the second conversion zone; however, particularly with heavy feeds, it will frequently permit a much greater decrease in pressure in the first conversion zone. A most desirable objective is to operate both of the zones at substantially the same pressure. Because pressure is nitrogen-dependent, this type of operation may be facilitated by controlling the amount of nitrogen passing to the second conversion zone and where necessary, deliberately permitting nitrogen to pass to that zone. This method of handling the nitrogen contents of the feeds to the two zones is applicable even in the absence of the interstage fractionation which is an essential feature of the present invention. The catalyst used in the first conversion zone generally has a high degree of de-

nitrification activity and accordingly where nitrogen-containing feeds are supplied to the process the first conversion zone will accomplish a substantial amount of denitrification concurrently with the hydrocracking in that zone.

FIRST CONVERSION ZONE

The first conversion zone in the process of the present invention produces a high quality product that has a low sulfur content, that has a high degree of saturation and therefore good burning qualities, and that is stable to oxidation and storage. The appropriate portions of the product have utility as superior heating oils, diesel fuels and jet fuels.

In the first conversion zone conditions are used in conjunction with the first zone catalyst that are only severe enough to convert naphthenes and aromatics, but not severe enough to crack substantial quantities of paraffins. A desired objective is to crack only the naphthenes boiling above the middle distillate range and to conserve the naphthenes boiling in the middle distillate boiling range. This objective is achieved with ease in the present process and the product from the first conversion zone in the middle distillate range is highly naphthenic and therefore very desirable for middle distillate uses requiring a low freeze point, low pour point, high cetane number, good heating value and/or comparatively high smoke point.

The catalyst in the first conversion zone, which as discussed below must be non-acidic or substantially non-acidic, must be a hydrocracking catalyst that is capable of converting the feed at a per-pass conversion of from 10 to 50 volume percent of said feed, under the operating conditions in the first zone in large part to reaction products in the synthetic middle distillate boiling range, i.e., products boiling not only in the middle distillate boiling range but also below the initial boiling point of the feed.

It has been found that a non-acidic or substantially non-acidic catalyst capable of accomplishing the foregoing conversion must comprise a hydrogenating-dehydrogenating component, alone or together with a separate cracking component, comprising at least one metal, metal oxide, metal sulfide, metal selenide or combination thereof, preferably oxides and sulfides of metals of both Groups VI and VIII of the Periodic Table. The most preferred catalyst will comprise combinations of sulfides of cobalt and/or nickel with sulfides of molybdenum and/or tungsten. Examples are nickel sulfide and molybdenum sulfide together with alumina, nickel sulfide and tungsten sulfide together with a cracking component that does not have strong acidity. Tungsten sulfide alone is inoperable because it is known to be strongly acidic when not modified by other components.

The aforesaid non-acidic or substantially non-acidic catalyst generally will comprise the aforesaid hydrogenating-dehydrogenating component associated with a separate cracking component. It is essential to the process of the present invention, where a separate cracking component is used, that it be substantially non-acidic, or at the most only weakly acidic. Exemplary cracking components include silica, charcoal, kieselguhr, titania, zirconia, bauxite and alumina, with alumina being especially preferred. While alumina sometimes is considered to be weakly acidic, its acidity is so low compared with silica-alumina for example, that it may be considered for purposes of the present process to be non-acidic, particularly in view of the markedly different product distribution it provides as compared with a silica-alumina support. For purposes of the present process, the cracking component particularly cannot be a strongly acidic mixed oxide, such as the well-known silica-alumina support conventionally used in hydrocracking catalysts and used as such as a catalytic cracking catalyst.

An outstanding catalyst composite fulfilling the aforesaid requirements both as to hydrogenating-dehydrogenating component and cracking component is a sulfided catalyst comprising 4 to 10 weight percent nickel, as metal, and 15.5 to 30 weight percent molybdenum, as metal, and a substantially non-acidic base consisting essentially of alumina. The preferred method of preparing the catalyst is by impregnating the cracking component in a solution of the hydrogenating-dehydrogenating component. However, catalysts prepared by various types of cogellation procedures are fully operable.

The aforesaid catalyst combination results in a significantly different product distribution from that obtained with acidic-type hydrocracking catalysts; it does not exhibit the high cracking activity of these catalysts even at higher temperatures and accordingly the maximum yield of products is in a higher molecular weight range than in the case of acidic-type hydrocracking catalysts. Further, the catalyst combination tends to give a much wider boiling range spectrum of products than does an acidic-type hydrocracking catalyst. Still further, the maximum total yield of synthetic products, i.e., those products boiling below the initial boiling point of the feed, occurs in a molecular weight range adjacent to and immediately below the initial boiling point of the feed, whereas in the case of an acidic-type hydrocracking catalyst this maximum yield occurs in a lower boiling range. Clearly, of the multitude of possible compounds in a given feed, many of these compounds must undergo different cracking and other reactions in the presence of the aforesaid non-acidic-type hydrocracking catalyst than they do in the presence of acidic-type hydrocracking catalysts; otherwise, the substantial differences in yield structure obtained with the two types of catalyst could not be accounted for.

A corollary feature of the use of the aforesaid non-acidic or substantially non-acidic-type hydrocracking catalyst in the process of the present invention is that such a catalyst generally has excellent denitrification activity and, where nitrogen is present in the feed to the process, the catalyst efficiently converts it in the reaction zone to ammonia, which may be removed from the reaction zone effluent by conventional procedures, such as the water scrubbing illustrated in FIGURE 1 hereof. As discussed under "Feed to First Conversion Zone" above, the nitrogen content of the feed to the first conversion zone is dependent upon the nitrogen content requirements of the feed to the second conversion zone.

The hydrocracking accomplished in the first conversion zone facilitates denitrification because, upon the breaking of carbon-to-carbon bonds, nitrogen is more easily removed. At higher levels of cracking conversion, the nitrogen is more easily removed than at lower levels. At higher levels of cracking conversion higher pressures are required to prevent rapid fouling and deactivation of the catalyst.

The nitrogen compounds tend to concentrate in the heavier portions of the feed; accordingly, such heavier portions as such are more difficult to denitrify. However, it will be noted from the foregoing that such heavier portions also are easier to crack in the first conversion zone. Accordingly, the first conversion zone operates to reduce the work load on the catalyst in the second conversion zone and also operates to reduce the nitrogen content of the feed to the second conversion zone, which is a desirable objective.

Particularly with heavy feeds it may be desirable to operate the first conversion zone in a counterflow manner, that is with the hydrogen being passed through the first conversion zone in a direction counter to the direction of the feed. Another desirable method of operation may be to operate the first conversion zone as two reaction systems in series with intermediate stripping of H_2S and NH_3. These types of operation will improve the hydrodenitrification efficiency of the zone.

The first conversion zone is operated at combinations of conditions selected from within the following ranges that will produce the desired degree of hydrocracking:

temperature of about 550° to 900° F., preferably 650° to 850° F., a hydrogen partial pressure of 500 to 3000 p.s.i.g., more preferably 1000 to 2500 p.s.i.g., and a liquid hourly space velocity of about 0.1 to 3.0, preferably 0.4 to 1.0. The hydrogen flow to the first conversion zone is at least 1000 s.c.f. per barrel of feed, and preferably 1500 to 6000 s.c.f. per barrel of feed. The hydrogen partial pressure, of course, will depend upon a number of factors, including type of feed stock and nitrogen content thereof, degree of denitrification required, etc.; however, in general a hydrogen partial pressure of 1000 to 1500 p.s.i.g. is highly desirable if practicable in any given instance. Further, it is desirable that the hydrogen partial pressures in both the first and second conversion zones be maintained at substantially the same level.

Referring now to FIGURE 3, there shown is an exemplary graphical representation of the product distribution obtained when hydrocracking a specific feed stock in the first conversion zone in the presence of a representative catalyst, namely, sulfided nickel-molybdenum on alumina. It will be noted from the graph that the feed stock had a nitrogen content of 1700 parts per million and that, at the operating conditions of 800° F., 1200 p.s.i.g. and 0.1 LHSV, the feed stock was denitrified down to a level of 12 parts per million nitrogen. It will also be noted from the graph that the upper curve is the distillation curve of the feed before being subjected to hydrocracking and that the lower curve is the distillation curve of the products obtained from the hydrocracking. From the upper curve it is seen that approximately 70 volume percent of the feed boiled above 800° F. From the lower curve it is seen that about 35 volume percent of the products boiled below the initial boiling point of the feed and that the remaining 65 volume percent of the products boiled below the boiling range of approximately 70 volume percent of the feed.

Referring now to FIGURE 4, there shown is an exemplary graphical representation of the feed boiling range on the cracking conversion in the first stage of the process of the present invention. The curve is a plot of the results of hydrocracking various stocks of various boiling ranges at the identical operating conditions of 800° F., 1200 p.s.i.g. and 0.4 LHSV over a catalyst comprising nickel-molybdenum on alumina. It will be seen that the rate of cracking decreases rapidly as the molecular weight of the feed decreases. When cracking a molecule containing 30 carbon atoms, for example, once it is cracked down to 15 carbon atoms, the chance of it cracking again over the catalyst used in the first conversion zone in the present process is small, whereas in the presence of an acidic-type hydrocracking catalyst it is very likely to crack again. Accordingly, the catalyst used in the first conversion zone of the present process produecs a much higher yield of middle distillates from a given feed stock than does the acidic-type catalyst.

INTERSTAGE FRACTIONATION AND CUT POINTS

As indicated in FIGURE 1, interstage fractionation zone or distillation column **16** is operated to separate the effluent from the first conversion zone into various streams, including a naphtha stream which is removed from the system through line **18**, and higher boiling streams which are maintained in the system. The following discussion will indicate variations in process operation as influenced by the various boiling points at which cuts may be made on column **16** and the resulting fractions subsequently manipulated, whether by being withdrawn as product, passed to the second conversion zone, or recycled to the first conversion zone.

(1) So long as at least a naphtha fraction boiling below 400° F. is withdrawn from the system as a product through line **18**, all remaining material from column **16** that boils above 320° F. may be passed to the second conversion zone.

(2) Instead of passing to the second conversion zone all remaining material boiling above 320° F., the material passed to the second conversion zone may be limited to material boiling above 500° F.

(3) The process may be operated as in (1), above, except that instead of passing all of the material boiling above 320° F. to the second conversion zone, at least a portion of that material is recycled to the first conversion zone.

(4) The process may be operated as in (1), above, with the additional feature of recycling to the second conversion zone at least a portion of the effluent therefrom that boils above the initial boiling point of the feed thereto.

(5) The process may be operated as in (1), above, except that at least a portion of the materials from the interstage fractionation zone boiling above about 320° F. is recycled to the first conversion zone, and with the additional feature of recycling to the second conversion zone at least a portion of the effluent therefrom that boils above the initial boiling point of the feed thereto.

(6) The process may be operated as in (3), above, but with the portion of the material recycled from the interstage fractionation zone to the first conversion zone being limited to material boiling above about 500° F.

(7) The process may be operated as in (4), above, but with the material passed from the interstage fractionation zone to the second conversion zone being limited to material boiling above about 500° F.

(8) The process may be operated as in (5), above, but with the material recycled from the interstage fractionation zone to the first conversion zone being limited to material boiling above about 500° F.

It will be readily seen from the above possible types of operation of the process of the present invention that the great variety of cut points and types of recycle that may be employed permit the widest flexibility in process operation, particularly in permitting wide variations in the ratio of gasoline to middle distillate production to meet seasonal swings in demand and demand changes for other reasons. It will be noted, particularly in view of FIGURE 2 herein, that the first conversion zone produces a maximum amount of middle distillates and the second conversion zone produces the maximum amount of product in the naphtha boiling range. Accordingly, the ratio of middle distillates to gasoline production from the overall process can be varied between two wide extremes:

(1) Middle distillate production can be maximized by removing middle distillate range materials from the interstage fractionation zone as a product and recycling higher boiling materials from the interstage fractionation zone to the first conversion zone; and

(2) Gasoline production can be maximized by passing to the second conversion zone all effluent from the fractionation zone boiling above the naphtha boiling range, and by recycling to the second conversion zone from the effluent thereof all materials boiling above the naphtha boiling range.

It has been found that at the first of the foregoing extremes the ratio of middle distillates to gasoline production, as a volume percent of the initial distillate feed, can be quite large, for example 51.7/28.5, while at the second extreme the ratio can be as low as zero.

It is within the purview of the present invention to use a common fractionation zone to handle the effluent from the first and second conversion zones, rather than using separate fractionation zones as illustrated in FIGURE 1. Those skilled in the art, upon reading the present specification, will be aware of the various factors that will require consideration in deciding to use a common fractionation zone rather than two fractionation zones, and will be aware of the possible differences in process results, including operational flexibility and ease of product separation involved in the use of two fractionation zones instead of one.

The aforesaid flexibility is further illustrated by the following specific variations in the manner of manipulating the process cut points and recycle streams.

Table I

Recycle to first conversion zone	Net product removed from interstage fractionation zone	Feed to second conversion zone	Recycle to second conversion zone	Purpose
(A) None	Below 300 to 400° F.	Above 300 to 400° F.	Above 300 to 400° F.	Maximize gasoline production.
(B) None	Below 500 to 800° F.	Above 500 to 800° F.	Above 500 to 800° F.	Produce gasoline and middle distillates.
(C) Above 600 to 900° F.	Below 500 to 800° F.	500-800° F. to 600-900° F.	Above 500 to 800° F.	Maximize middle distillates with recycle to first coversion zone.
(D) Above 600 to 900° F.	Below 300 to 400° F.	300-400° F. to 650-900° F.	Above 300 to 400° F.	Maximize gasoline with recycle to first conversion zone.
(E) None	Below 300 to 600° F. and above 600 to 800° F.	Between 300 to 600° F. and 600 to 800° F.	Above 300 to 600° F.	Maximize gasoline production, while removing from system heavy product from first oonversion zone.

FEED TO SECOND CONVERSION ZONE

The foregoing discussion of the feed to the first conversion zone and of the various possible inter-stage fractionation cut points and methods of product removal and recycle, together with the previous discussion of nitrogen contents, adequately defines the feed to the second conversion zone.

SECOND CONVERSION ZONE

The catalyst in the second conversion zone comprises a hydrogenating-dehydrogenating component and an active acidic cracking component. In the light of the present disclosure, those skilled in the art will be able to select specific catalysts suitable for the particular instances with which they are concerned. For purposes of the present invention, it will be sufficient if any of the well-known solid active acidic cracking components used for hydrocracking are selected, including silica-alumina, activated alumina, alumina-BF_3 combinations, and various fluorided or selenided catalyst supports. The hydrogenating-dehydrogenating component may comprise at least one metal, metal oxide, metal sulfide, metal selenide, or combination thereof, preferably selected from metals of Group VIII and compounds thereof, including nickel, platinum and palladium and compounds thereof. As in the case of first stage catalyst, the second stage catalyst is preferably prepared by impregnation, but various cogelation procedures are fully operable. The entire preferred catalyst composite of Scott U.S. Patent No. 2,944,-006 will be especially suitable in the process of the present invention. A very desirable method of operating the second conversion zone is to recycle to that zone a hydrogen-rich gas stream from which ammonia has been removed. As discussed above, various hydrocarbon fractions may be recycled to the second conversion zone. The product fractions from the second conversion zone that boil below the initial boiling point of the feed constitute excellent gasoline blending stocks for certain purposes; however, where they are desired for gasoline purposes, it will generally be found more desirable to send at least the heavier portions of them to a catalytic reformer where they will serve as a most excellent preferred feed for catalytic reforming operations.

The second conversion zone is supplied with at least 1500 s.c.f. of hydrogen per barrel of feed thereto. At least 500, and normally from about 1000 to 2000 s.c.f. of hydrogen are consumed in the second conversion zone per barrel of feed thereto that is converted to synthetic products, i.e., products boiling below the initial boiling point of the feed thereto.

Operating conditions in the second conversion zone will include a temperature of 450 to 850° F., preferably 500 to 800° F., a liquid hourly space velocity of 0.2 to 5.0, preferably 0.4 to 3.0, and a hydrogen partial pressure of at least 350 p.s.i.g., preferably 500 to 2000 p.s.i.g. In the second conversion zone there is converted at least 20 volume percent per pass of the feed thereto to products boiling below the initial boiling point of said feed.

While some nitrogen can be tolerated in the second conversion zone, as discussed above, nitrogen is an undesirable ingredient of the feed thereto and should be kept within the aforementioned limits.

EXAMPLES

The following examples further illustrate the advantages of the present invention over a conventional hydrocracking process wherein a heavy gas oil feed is hydrofined only in a first stage to remove nitrogen, and is then hydrocracked in a second stage without interstage product removal.

EXAMPLE NO. 1

Feed: 650-800° F. Arabian gas Oil
Gasoline cut point: 400° F.
Recycle (2nd stage) cut point: 650° F.
Yields, first stage feed basis:

	Conventional process	Process of present invention
Weight percent C_1-C_3	2.1	2.0
Weight percent i-C_4	6.5	5.9
Weight percent n-C_4	2.2	2.0
LV percent C_5-400° F. gasoline	76	67
LV percent 400-650° F. middle distillate:		
First stage	0	16
Second stage	30	22
Total, 400-650° F.	30	38
Middle distillate/gasoline	0.395	0.568

EXAMPLE NO. 2

Feed: 510°-800° F. California heavy cycle oil
Gasoline cut point: 320° F.
Recycle cut point (2nd stage): 510° F.
Yields, first stage feed basis:

	Conventional process	Process of present invention
Weight percent C_1-C_3	1.5	1.8
Weight percent i-C_4	5.6	6.0
Weight percent n-C_4	1.4	1.6
LV percent C_5-180° F. gasoline	21	22
LV percent 180-320° F. gasoline	57	44
LV percent 320-510° F. middle distillate:		
First stage	0	20
Second stage	37	26
Total, 320-510° F.	37	46
Middle distillate/gasoline	0.475	0.695

COMBINATIONS WITH OTHER CONVERSION PROCESSES

As discussed above in connection with FIGURE 1, there may be withdrawn from the system through lines 33 and 49 either net product streams or feed streams for catalytic cracking. A particularly excellent catalytic feed stock is so obtained when a heavy gas oil or heavy cycle oil feed is supplied to the first conversion zone, and the 650° F. and heavier portions of the effluent therefrom are sent to catalytic cracking. Any naphtha stream

removed from the system during the practice of the present invention is an excellent reformer feed stock.

CONCLUSION

From the foregoing it may be seen that the novel methods of the present invention are effective in providing a large degree of operational flexibility in the type of two-stage hydrocracking process to which the invention relates, and are effective in accomplishing the production of superior products, including naphthas, heating oils, diesel fuels and jet fuels.

Although only specific arrangements and modes of operation of the present invention have been described and illustrated, numerous changes could be made in these arrangements and modes without departing from the spirit of the invention, and all such changes that fall within the scope of the appended claims are intended to be embraced thereby.

We claim:

1. In a two-stage process for producing valuable fuel products from a hydrocarbon feed selected from the group consisting of hydrocarbon distillates having an initial boiling point of at least 500° F. and an end point below about 1100° F. and hydrocarbon residua boiling above about 1050° F., which comprises converting in a first conversion zone from 10 to 50 vol. percent of said feed per pass to fractions boiling below the initial boiling point of said feed, said first zone being operated at about 550°–900° F., a space velocity from about 0.1–3.0 and a hydrogen partial pressure of 1000–2500 p.s.i.g., withdrawing an effluent from said first zone, separating said effluent into fractions in a separation zone, withdrawing from said separation zone at least one of said fractions as a product, converting in a second conversion zone at least one of said fractions at a conversion of at least 20 vol. percent per pass to products boiling below the initial boiling point of said fraction passed to said second zone, said second zone being operated at about 450°–850° F., a space velocity from about 0.2–5.0 and a hydrogen partial pressure of at least 350 p.s.i.g. with a catalyst comprising a hydrogenating-dehydrogenating component and an active acidic cracking component, withdrawing an effluent from said second zone and recovering the desired products from said effluent, the improvement which comprises:

(*a*) using as the catalyst in said first zone a catalyst comprising 4–10 wt. percent of a component selected from the group consisting of nickel and compounds thereof, and 15.5–30 wt. percent of a component selected from the group consisting of molybdenum and compounds thereof and a substantially non-acidic component essentially of alumina,

(*b*) withdrawing from said separation zone a naphtha fraction boiling between C_5 and 400° F., a middle distillate fraction boiling between about 400° and 650° F., and a bottoms fraction boiling above about 650° F.,

(*c*) recovering said naphtha fraction as a product,

(*d*) recovering a portion of said middle distillate fraction as a product,

(*e*) passing at least a portion of said bottoms fraction and the remainder of said middle distillate fraction to said second zone, said feed to said second zone being passed through the entire catalyst bed in said second zone, and

(*f*) recycling to said second zone at least a portion of said effluent from said second zone boiling above the initial boiling point of said feed to said second zone.

2. A process as in claim 1 wherein at least a portion of the effluent from said separation zone boiling above about 400° F. is recycled to said first zone.

3. A process as in claim 1 wherein at least a portion of said fraction boiling above about 650° F. from said first zone is passed to a satalytic cracking zone.

4. A process as in claim 1 wherein at least a portion of said effluent from said second zone boiling above about 650° F. is passed to a catalytic cracking zone.

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