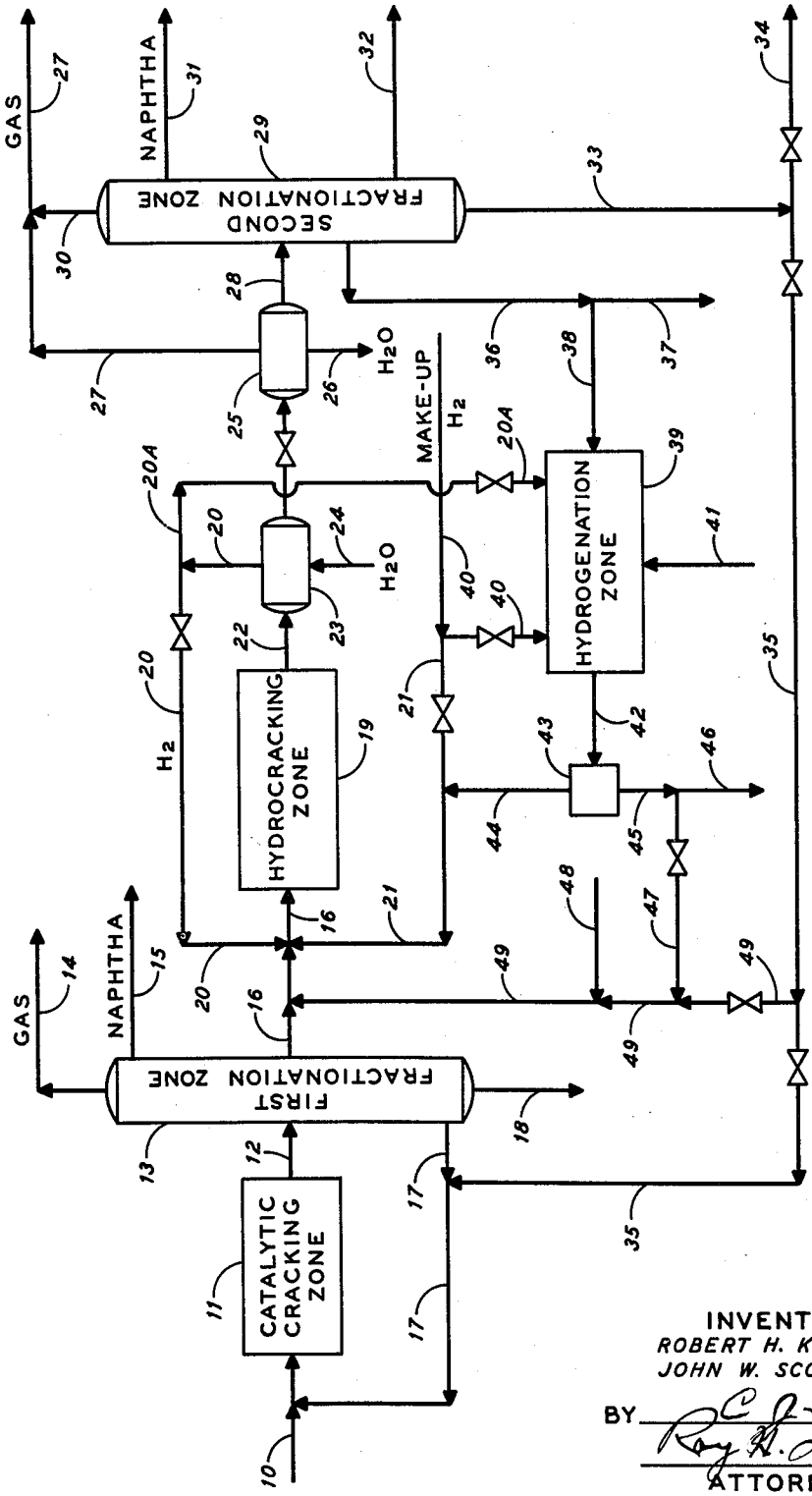
March 9, 1965 R. H. KOZLOWSKI ETAL 3,172,833

CATALYTIC CONVERSION PROCESS FOR THE PRODUCTION OF LOW LUMINOSITY FUELS

Filed Dec. 27, 1961




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United States Patent Office 3,172,833 Patented Mar. 9, 1965



3,172,833

# CATALYTIC CONVERSION PROCESS FOR THE PRODUCTION OF LOW LUMINOSITY FUELS

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Filed Dec. 27, 1961, Ser. No. 162,518
6 Claims. (Cl. 208—58)

## INTRODUCTION

This invention relates to a hydrocarbon conversion process, and, more particularly, to a process for the catalytic conversion of petroleum distillates to produce fuels characterized by high luminometer numbers, high smoke points, and low freezing points.

## PRIOR ART

It is well known that high smoke points and low freeze points are desirable characteristics of middle distillate boiling range fuels, particularly jet fuels. Only recently it has been discovered that another desirable characteristic of such fuels that can be critical to proper engine operation is a high luminometer number, indicating a fuel that burns with a low luminosity. Two different fuels can burn equally hot and yet one can be more luminous than the other. The luminosity of the more luminous flame is caused by incandescence of molecular fragments in the flame; these glowing fragments give off radiant heat, which increases the temperature of the surrounding engine parts without adding to engine power. Luminosity of a fuel is determined by a luminometer number (LN) rating, according to how little radiant heat the fuel gives off during burning. The higher luminometer numbers indicate less radiant heat given off and a more desirable fuel. Most jet fuels to date have luminometer numbers of 45 to 65.

Heretofore, in producing jet fuels by hydrocracking a feed stock of a particular boiling range, the luminometer number of the jet fuel products has been essentially fixed by crude source and feed boiling range, and little improvement in the luminometer number has been obtainable by varying the process operation. Heretofore, in such an operation, it has been possible, by various process techniques, to lower the freezing point and raise the smoke point of the jet fuel product to some extent; however, there has been a continuing need for process improvement in these respects.

## OBJECTS

In view of the foregoing, it is an object of the present invention to provide a method for operating a process for hydrocracking particular hydrocarbon distillate stocks to produce jet fuels which will result in a higher luminometer number jet fuel product than heretofore obtainable in such a process with the same feeds, and which will also result in reducing and therefore improving the freezing point of the jet fuel product.

It is a further object of the present invention to provide a method for operating a hydrocracking process for producing jet fuels which will result in raising the jet fuel product smoke point, particularly in those situations in which the jet fuel product obtained when hydrocracking a particular stock does not quite meet smoke point specifications because of the character of the feed.

## DRAWING

This invention will be more clearly understood, and further objects and advantages thereof will be apparent, from the following description when read in connection with the accompanying drawing. The drawing is a diagrammatic illustration of an embodiment of process units and flow paths suitable for carrying out the process of the invention.



## STATEMENT OF INVENTION

In accordance with the present invention, there is provided a hydrocracking process for producing jet fuels of high luminometer number which comprises contacting a hydrocarbon feed selected from the group consisting of hydrocarbon distillates boiling above about 350° F. and hydrocarbon residua boiling above about 1050° F. in a hydrocracking zone in the presence of at least 1000 standard cubic feet (s.c.f.) of hydrogen per barrel of said feed with a catalyst comprising a hydrogenating-dehydrogenating component and an active cracking support at a temperature of about from 400° to 900° F., a pressure of at least 500 p.s.i.g., and a liquid hourly space velocity (LHSV) of about from 0.1 to 15.0, withdrawing from said zone at least a normally gaseous fraction, at least one naphtha fraction, and a jet fuel fraction boiling in the range of about from 320° to 550° F. and hydrogenating in a pressure vessel located in the high pressure hydrogen system supplying the hydrocracking zone, at least 5 volume percent of the portion of said jet fuel fraction boiling below the initial boiling point of said feed, to produce the final jet fuel product.

In a preferred embodiment of the present invention, the hydrocarbon feed boils in the range of about from 500° to 1050° F., the feed is contacted in the presence of about at least 1000, preferably 1500 to 30,000, and still more preferably 1500 to 6000 s.c.f. of hydrogen per barrel of feed at a temperature of from about 500° to 800° F., a pressure of about from 800 to 3000 p.s.i.g., preferably 1200 to 3000 p.s.i.g., and an LHSV of about from 0.2 to 3.0, and there is hydrogenated in said pressure vessel about from 50 to 100 volume percent, preferably from 80 to 100 volume percent, of the portion of said jet fuel fraction boiling below the initial boiling point of said feed, to produce the final jet fuel product.

It is advantageous in operating the process of the present invention to return to the hydrocracking zone a hydrogen-rich recycle stream obtained from the effluent from said zone, along with the make-up hydrogen necessary to replace that consumed in the process, which operates with a net consumption of hydrogen.

## FEED

The feed stocks employed in the process of the present invention preferably boil over a range of at least 50° F. within the aforesaid boiling ranges; suitable feed stocks include those heavy distillates normally defined as heavy straight run gas oils and heavy cracked cycle oils, as well as conventional FCC feeds and portions thereof. Cracked stocks may be obtained from thermal or catalytic cracking of various stocks, including those obtained from petroleum, gilsonite, shale and coal tar. Residual feeds may include Minas paraffinic residua, which may boil above 1100° F., and other paraffinic-type residua boiling above about 1050° F.

The most preferred feeds to the present process are those having an initial boiling point of at least 500° F., particularly when the feeds are to be hydrocracked in the presence of a non-acidic or only weakly acidic catalyst. With such feeds the middle distillate products, including jet fuels, tend to have more superior properties, in that they are more naphthenic, less aromatic (therefore having higher smoke points), and lower in normal paraffins (therefore having lower freeze points), than products from feeds having a lower initial boiling point. Feeds having lower initial boiling points tend to produce excessive quantities of nonsynthetic products having a high aromatics content and therefore an unacceptably low

smoke point, although the freeze point may be satisfactory. More of the product in the jet fuel boiling range is satisfactory for jet fuel purposes when the initial boiling point of the feed is at least 500° F. than when it is lower.

## NITROGEN CONTENT OF FEED

While the invention can be practiced with utility in connection with hydrocarbon feeds to the hydrocracking zone which contain relatively large quantities of nitrogen, the operation becomes much more economical with stocks containing less than 200 parts per million (p.p.m.), preferably less than 100 p.p.m., and much more preferably less than 10 p.p.m. of total nitrogen. A reduction in feed nitrogen level generally permits the hydrocracking reaction to be conducted at lower temperatures than with feeds containing relatively large amounts of nitrogen compounds. Therefore, in the case of feeds which are not inherently low in nitrogen, acceptable levels can be reached by hydrofining the feed prior to passing it into the hydrocracking zone.

In general, the effect of a total nitrogen content in excess of 10 p.p.m. in the hydrocracking step is a reduction in catalyst activity which is reflected in reduced operational efficiency and poorer product distribution. As the nitrogen content increases above the specified maximum, higher reaction temperatures are necessary to maintain an economic per-pass conversion level. These higher reaction temperatures cause a disproportionate increase in the amount of product converted to gases and carbonaceous residues deposited on the catalyst surface and thus further decrease catalyst activity. Such further decrease in catalyst activity must be compensated for by resort to still higher operating temperatures if acceptable conversion is to be maintained; therefore, nitrogen causes the on-stream life of the catalyst to be shortened because unacceptable operating temperatures are reached sooner when nitrogen is present.

The effect of nitrogen upon the hydrocracking reaction is marked at low operating temperatures, for example, 500° to 800° F., but minor at higher operating temperatures, for example, above 850° F. Accordingly, where a feed to be processed in accordance with the present invention contains more than 10 p.p.m. total nitrogen, and particularly where an acidic-type hydrocracking catalyst is used in the hydrocracking zone, denitrification of the feed will be desirable, because the process, at least for substantial portions of the on-stream period, desirably is conducted at those low temperatures within the ranges disclosed herein that are sufficient to maintain desired per-pass conversions. Where a non-acidic-type hydrocracking catalyst is used in the hydrocracking zone, dentirification tends to take place in that zone along with hydrocracking, as discussed hereinafter, and there is less need for a previous hydrofining step.

As noted above, feed stocks containing more than about 10 p.p.m total nitrogen preferably are subjected to a pretreating operation that is relatively selective for the removal of nitrogen compounds. The desired low nitrogen levels may be reached, for example, by intimately contacting the feed stocks with various acidic media, such as $H_2SO_4$ or other liquid acids, or, in the case of feeds that are comparatively low in nitrogen compounds, with such solid acidic materials as acid ion exchange resins and the like. However, it is preferred to carry out denitrification by catalytic hydrogenation (hydrofining) of the feed. This entails contacting the feed at temperatures of from about 400° to 900° F., preferably from 500° to 800° F., pressures of at least 300 p.s.i.g., liquid hourly space velocities of from about 0.3 to 5.0, along with at least 500 s.c.f. of hydrogen per barrel of feed, with a sulfur-resistant hydrogenation catalyst. Any of the known sulfactive hydrogenation catalysts may be used in the hydrofining pretreatment. The preferred catalysts have as their main active ingredient one or more oxides or sulfides of the transition metals, such as cobalt, molybdenum, nickel and tungsten. These various materials may be used in a variety of combinations with or without such stabilizers and promoters as the oxides and carbonates of K, Ag, Be, Mg, Ca, Sr, Ba, Ce, Cu, Bi, Cr, Th, Si, Al and Zr. These various catalysts may be unsupported or disposed on various conventional supporting materials, for example charcoal, fuller's earth, kieselguhr, silica gel, alumina, bauxite and magnesia. While any of the noted classes of conventional sulfactive hydrogenation catalysts may be employed, it has been found that particularly desirable catalysts are: (1) a molybdenum oxide catalyst promoted by a minor amount of cobalt oxide and supported upon an activated alumina; (2) tungsten sulfide on activated alumina: and (3) a molybdenum sulfide catalyst promoted by a minor amount of nickel sulfide supported on activated alumina. The catalyst may be in the form of fragments or formed pieces such as pellets, extrudates and cast pieces of any suitable form or shape.

An effective hydrofining catalyst comprises cobalt impregnated on a coprecipitated molybdena-alumina (e.g., prepared in accordance with the disclosures of U.S. Patent 2,432,286 to Claussen et al., or U.S. Patent 2,697,006 to Sieg), combined with cobalt oxide, the final catalyst having a metals content equivalent to about 2% cobalt and 7% molybdenum.

Operable hydrofining conditions are temperatures of 700° to 800° F., pressures of 200 to 3000 p.s.i.g., space velocities of 0.5 to 3.0, and 1000 to 15,000 s.c.f. of hydrogen per barrel of hydrocarbon feed.

## OPERATING CONDITIONS IN HYDROCRACKING ZONE

The hydrocarbon feed and hydrogen are contacted in the hydrocracking zone at pressures of at least 500 p.s.i.g., preferably about from 800 to 3000 p.s.i.g. The contacting temperature is about from 400° to 900° F., preferably 500° to 800° F. The operating temperature during the on-stream period preferably is maintained at as low a value as possible consistent with maintaining adequate per-pass conversions as catalyst fouling progresses. While those skilled in the art will realize that the desired initial and terminal temperatures will be influenced by various factors including character of feed and catalyst, generally speaking it will be desirable to operate the process with an initial on-stream temperature of about from 500° to 650° F., with a progressive increase to about 750° to 800° F., to maintain substantially constant conversion of at least 25 volume percent, preferably 35 to 90 volume percent per pass, of the hydrocarbon feed to products boiling below the initial boiling point of that feed. Higher conversions generally are possible with more acidic catalysts; however, such catalysts give a different product distribution than less acidic catalysts, as discussed below.

## HYDROCRACKING CATALYST, GENERAL

The catalyst employed in the hydrocracking zone comprises a material having hydrogenating-dehydrogenating activity, and either: (1) deposited or otherwise disposed on an active acid cracking catalyst support, or (2) unsupported, or deposited or otherwise disposed on an active cracking support that is either non-acidic or only weakly acidic.

Where the catalyst comprises a non-acidic or only weakly acidic support, it tends to produce greater amounts of products boiling in the middle distillate boiling range than does a catalyst comprising an acidic support.

## ACIDIC HYDROCRACKING CATALYSTS

Where the support is acidic, the cracking component may comprise any one or more of such acidic materials as silica-alumina, silica-magnesia, silica-alumina-zirconia composites, alumina-boria, fluorided composites, and the like, as well as various acid-treated clays and similar ma-

terials. Preferred catalysts will comprise silica-alumina supports having silica contents in the range of from about 30 to 99 percent by weight. The hydrogenating-dehydrogenating components of the catalyst can be selected from any one or more of the various Groups VI and VIII metals, as well as the oxides, sulfides and selenides thereof, alone or together with promoters or stabilizers that may have by themselves small catalytic effect, representative materials being the oxides, sulfides and selenides of molybdenum, tungsten, vanadium, chromium and the like, as well as of metals such as iron, nickel, cobalt, platinum and palladium. If desired, more than one hydrogenating-dehydrogenating component can be present, and good results have been obtained with catalysts containing composites of two or more of the oxides of molybdenum, cobalt, nickel, chromium, copper, silver and zinc, and with mixtures of said oxides with fluorides. The amount of the hydrogenating-dehydrogenating component present can be varied within relatively wide limits of from about 0.5 to 30% based on the weight of the entire catalyst.

Exemplary acidic-type catalysts having satisfactory characteristics as aforesaid include those containing (*a*) about 1 to 12% molybdenum oxide, (*b*) a mixture of from 1 to 12% molybdenum oxide and from 0.1 to 10% cobalt oxide or nickel oxide, (*c*) mixtures of from about 0.5 to 10% each of cobalt oxide and chromium oxide, (*d*) 0.1 to 10% nickel, nickel oxide or nickel sulfide, (*e*) 0.1 to 10% cobalt, cobalt oxide or cobalt sulfide, (*f*) mixtures of from 0.1 to 10% each of nickel and cobalt, as metal, oxide or sulfide, (*g*) 0.1 to 5% platinum or palladium, in each case the said hydrogenating-dehydrogenating component being deposited on an active cracking support comprising silica-alumina beads having a silica content of about 70 to 99%. Thus, the molybdenum oxide catalyst can be prepared readily by soaking the beads in a solution of ammonium molybdate, drying the catalyst for 24 hours at 220° F., and then calcining the dried material for 10 hours at 1000° F. If cobalt oxide is also to be present, the calcined beads can then be similarly treated with a solution of a cobalt compound, whereupon the catalyst is again dried and calcined. Under favorable operating conditions, the hydrocracking catalyst will maintain high activity over periods of 50 to 300 or more hours. The activity of the used catalyst can then be increased, if desired, by a conventional regeneration treatment involving burning off catalyst contaminants with an oxygen-containing gas.

## NON-ACIDIC HYDROCRACKING CATALYSTS

When a non-acidic, or only weakly acidic, hydrocracking catalyst is used in the hydrocracking step of the present process, the catalyst should be one that is capable of converting the feed at a per-pass conversion of at least 10 to 50 volume percent of said feed, under operating conditions in the hydrocracking 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.

A suitable catalyst comprises a hydrogenating-dehydrogenating component alone or on a support comprising at least one metal, metal oxide, metal sulfide, metal selenide or combination thereof, preferably oxides or sulfides of of metals of 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.

The catalyst generally will comprise the aforesaid hydrogenating-dehydrogenating component disposed on a support that is substantially non-acidic or at the most only weakly acidic. Exemplary supports include silica, charcoal, kieselguhr, titania, zirconia, bauxite and alumina, with alumina being an especially preferred support. 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 silica-alumina support. For purposes of the present process, the support particularly cannot be an acidic-mixed oxide, for example silica-magnesia, alumina-boria or silica-alumina.

An outstanding catalyst composite fulfilling the aforesaid requirements both as to hydrogenating-dehydrogenating component and support, is the sulfided catalyst comprising 4 to 10 weight percent nickel, as metal, and 15.5 to 30 weight percent molybdenum, as metal, on a substantially non-acidic base consisting essentially of alumina.

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 those 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 catalysts; otherwise, the substantial difference 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-type or substantially non-acidic-type hydrocracking catalysts 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 by water scrubbing.

The cracking accomplished in the hydrocracking zone facilitates denitrification because, upon the breaking of carbon-to-carbon bonds, nitrogen is more easily removed. At higher levels of cracking conversion, 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.

## PROCESS OPERATION

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

As discussed above, the feed supplied to the hydrocracking zone 19 through line 16 includes heavy straight run gas oil and heavy cracked cycle oils. The drawing illustrates an embodiment wherein a catalytically cracked stock containing nitrogen is supplied to the hydrocracking zone 19 through line 16. In the embodiment shown, a hydrocarbon fraction suitable for use as a catalytic cracking feed stock is passed through line 10 to catalytic cracking zone 11, wherein it is contacted with a conventional cracking catalyst under conventional cracking conditions.

From catalytic cracking zone 11 an effluent is passed through line 12 to first fractionation zone 13 where it is separated into fractions of various boiling ranges.

A normally gaseous stream is withdrawn through line **14**, and a naphtha stream is withdrawn through line **15** either as a product or for further processing, for example in a reforming zone. A heavy cycle oil is recycled to catalytic cracking zone **11** through line **17**. A tarry bottoms fraction is removed through line **18**.

A hydrocarbon stock boiling in the range of about 350° to 1050° F., in this embodiment a cracked stock, is passed through line **16** into hydrocracking zone **19**, where it is hydrocracked and, if it contains nitrogen, may also be at least partially denitrified. Hydrogen for the hydrocracking and any denitrification reactions in zone **19** is supplied to that zone through lines **20** and **21**. Conversion products from zone **19** are withdrawn through line **22**, where they are contacted in high pressure separator **23** with water supplied through line **24** to facilitate nitrogen removal. From high pressure separator **23**, a hydrogen stream is recycled through line **20**. From high pressure separator **23**, conversion products are passed to low pressure separator **25** from which water is removed through line **26**. A gas stream is separated through line **27** from the conversion products in separator **25**, and the remainder of the conversion products are passed through line **28** to second fractionation zone **29**.

From second fractionation zone **29**, a gas stream is withdrawn through line **30**, and a naphtha stream is removed from the system through line **31**, either as a product or for further processing, for example in a reforming zone. If desired, a liquid product boiling above the naphtha boiling range and within the feed boiling range may be withdrawn as a product from second fractionation zone **29** through line **32**. A bottoms stream may be withdrawn through lines **33** and **34** as a product, for example as a diesel fuel, or all or a portion thereof may be recycled through lines **35** and **17** to catalytic cracking zone **11** for further processing, and/or through lines **35** and **49** to hydrocracking zone **19** for further processing.

From second fractionation zone **29**, a synthetic middle distillate stock, i.e., a middle distillate product boiling below the boiling range of the feed, more particularly one boiling in the range of about 320° to 550° F., is withdrawn through line **36** and at least 5 volume percent thereof may be withdrawn through line **37** as a jet fuel product. At least 5 volume percent, and up to 100 volume percent, preferably from 80 to 100 volume percent, of the stock withdrawn through line **36** is passed through line **38** to hydrogenation zone **39**, where it is hydrogenated in the presence of hydrogen supplied to zone **39** through line **40** and/or **20A**. The valves shown on lines **20**, **20A** and **40** may be adjusted as desired to supply zone **39** with any desired amount of fresh make-up hydrogen and/or recycle hydrogen. Additional stock from an external source may be passed through line **41** for hydrogenating in hydrogenation zone **39**.

It will be noted that only the desired product from hydrocracking zone **19** is hydrogenated in zone **39**, and therefore: (*a*) the hydrogenation vessel can be kept smaller than if other product fractions passed through it, and (*b*) said other product fractions are not affected by the hydrogenation.

Hydrogenation zone **39** may be a conventional hydrogenation vessel operated under conventional hydrogenation conditions with such conventional hydrogenation catalysts as supported platinum, palladium, nickel or rhodium, with platinum and nickel being preferred. Particularly effective results will be obtained when using a platinum catalyst comprising 0.5 weight percent platinum supported on alumina at temperatures of 300° to 650° F., liquid hourly space velocities of 0.1 to 10.0, and hydrogen feed rate of from 1500 to 4000 s.c.f. of hydrogen per barrel of stock contacted in zone **39**. The operating pressure and hydrogen feed rate will be determined by the pressure of the hydrocracking zone and the make-up hydrogen rate and/or recycle hydrogen rate to the hydrocracking zone, respectively. Generally, the operating pressure is at least 500 p.s.i.g. and preferably about from 800 to 3000 p.s.i.g. It will be noted that hydrogenation zone **39** is a high pressure vessel located in the high pressure hydrogen system supplying the hydrocracking zone **19**; therefore: (*a*) hydrogenation zone **39** may be a small, compact, simple, high pressure reactor, thereby dispensing with the need for larger and more expensive equipment that would be necessary if hydrogenation were accomplished in separate conventional hydrogenation facilities; and (*b*) the hydrogen gas rate through hydrogenation zone **39** may be large enough to maintain adequate hydrogen partial pressure without the need of additional compression because the hydrogen rates to the hydrocracking zone may be relatively large compared to that necessary for hydrogenating the middle distillate product fraction; (*c*) hydrogenation zone **39** may be operated at low temperatures so that the heat required may be provided by the hot distillate stream from fractionation zone **29**; (*d*) hydrogenation zone **39** may be used to purify an impure hydrogen stream to the hydrocracking zone by absorption of the impurities, such as methane, in the middle distillate product fraction stream at high pressure. It should also be noted that in some cases it might be advantageous to remove impurities such as $H_2S$ from the hydrogen supplied to zone **39** through line **20** to avoid poisoning of the hydrogenation catalyst.

From hydrogenation zone **39** an effluent is passed through line **42** to gas-liquid separator **43**, from which a hydrogen stream is passed to line **21** through line **44** and a hydrogenated middle distillate fuel fraction is withdrawn through line **45**. The hydrogenated jet fuel fraction is withdrawn through line **46** as a net product. If desired, a portion of this fraction is recycled to hydrocracking zone **19** through lines **47**, **49** and **16**. If it is desired to pass to hydrocracking zone **19** additional stock from an external source without prior catalytic cracking or hydrogenation, such stock may be passed to that zone through lines **48**, **49** and **16**.

If it is desired to add additional quantities of feed to the system from an external source, but it is not desired to catalytically crack, hydrogenate, or otherwise treat these additional portions first, they may be introduced into the system through line **44**.

## INCREASED LUMINOMETER NUMBER AND SMOKE POINT, AND LOWER FREEZE POINT, OF JET FUEL PRODUCT WHEN OPERATING IN ACCORDANCE WITH PRESENT INVENTION

Luminometer numbers are in inverse relation to the luminosity of a jet flame in a jet engine. Accordingly, jet flame will have a lower luminosity when the luminometer of the jet fuel is raised. It has been found that with increasing concentration or normal paraffins in a jet fuel the luminometer number increases more rapidly than with increases in concentration of isoparaffins, aromatics or naphthenes; however, this advantageous effect generally is outweighed by the adverse effect that normal paraffins have on jet fuel freeze point. It has been found that aromatics and naphthenes in a jet fuel have an adverse effect in that the luminometer number of the jet fuel is lowered as the ratio of aromatics and naphthenes to paraffins increases. It has been found that isoparaffins, while not having as great a tendency to increase the luminometer number of jet fuel as do normal paraffins, nevertheless do exert a markedly beneficial effect on luminometer number, as compared with aromatics and naphthenes. This markedly beneficial effect can be obtained by increasing the volume percentage of isoparaffins in a jet fuel, and such increase is not accompanied by the deleterious effect on freeze point that is produced with normal paraffins. Accordingly, as among aromatics,

naphthenes, normal paraffins and isoparaffins, the latter are the best species for use in improving jet fuel luminometer number without undue deleterious effect on freeze point.

In the operation of the present process, as described above, it has been found that the synthetic middle distillate fraction withdrawn from second fractionation zone **29** through line **36** has a high content of isoparaffins and accordingly is especially adapted for the production of a superior jet fuel product by hydrogenation in zone **39** to further increase the luminometer number and to raise the smoke point. Further, by recycling through line **47** at least 5 volume percent of the hydrogenated jet fuel, the volume percent of isoparaffins in said net jet fuel product withdrawn through line **46** is caused to build up, and the luminometer number of that product increases. It has further been found that hydrogenation in hydrogenation zone **39** of the recycle synthetic middle distillate product, by reducing the aromatic content of that product, not only causes a desirable increase in the smoke point of the ultimate end jet fuel product by converting aromatics to naphthenes, but is accompanied by a still further increase in the luminometer number of the ultimate end jet fuel product, because aromatics have a lower luminometer number than do naphthenes.

## TYPES OF OPERATION TO WHICH PROCESS IS ADAPTED

While the invention will be described more particularly in connection with the method of fixed hydrocracking catalyst bed operation wherein the hydrocracking catalyst bed may be periodically regenerated in situ, the process is also well adapted to be carried out in a moving catalyst bed, or in a slurry-type reaction system, or in one of the fluidized catalyst type. However, since in carrying out the process of this invention the catalyst retains its activity over long periods of time, it is normally preferable, from an economic standpoint, to employ the fixed catalyst bed method of operation or some modification thereof.

The feed may be introduced into the hydrocracking zone as a liquid, vapor, or mixed liquid-vapor phase, depending upon the temperature, pressure, proportions of hydrogen and boiling range of the charge stocks utilized.

## EXAMPLES

In the following examples of a preferred embodiment of the present invention, the operating variables and conversion factors have been determined by correlation of experimental data where necessary. Thus, in the examples, the results that can be expected from a 10,000 barrel per day (b.p.d.) hydrocracking zone feeding 500° to 850° F. petroleum distillates under specified operating conditions are shown in Table I. For comparative purposes only, Cases I and III show hydrocracking operations where there is no hydrogenation zone in the high pressure hydrogen system supplying the hydrocracking zone for hydrogenating the 320° to 525° F. synthetic middle distillate product. Cases II and IV show operations in accordance with the present invention wherein all of the 320° to 525° F. synthetic middle distillate from the hydrocracking zone is hydrogenated in a pressure vessel located in the fresh hydrogen make-up system with that product being withdrawn from the system as a jet fuel with high luminometer number.

Cases I and II are examples of operation with a 500° to 800° F. hydrofined straight run petroleum distillate and Cases III and IV are examples of operation with a 500° to 845° F. hydrofined cycle oil from a catalytic cracking unit. In all four cases the hydrocracking catalyst is a sulfided catalyst comprising 6% nickel on silica alumina, and the hydrogenation catalyst comprises 0.5% platinum on alumina.



*Table I*

| | Case III | Case IV | Case I | Case II |
|---|---|---|---|---|
| Hydrocracking Zone: | | | | |
| Fresh Feed Rate, b.p.d. | 6,000 | 6,000 | 6,000 | 6,000 |
| Recycle Feed Rate, b.p.d. | 4,000 | 4,000 | 4,000 | 4,000 |
| Total Feed Rate, b.p.d. | 10,000 | 10,000 | 10,000 | 10,000 |
| $H_2$ Recycle Rate, s.c.f./b. total feed | 6,500 | 6,500 | 6,500 | 6,500 |
| $H_2$ Consumption, s.c.f./b. fresh feed | 900 | 900 | 860 | 860 |
| $H_2$ Consumption, M s.c.f./d. | 5,400 | 5,400 | 5,560 | 5,560 |
| Catalyst Temperature, ° F. | 550 | 550 | 570 | 570 |
| Pressure, p.s.i.g. | 1,200 | 1,200 | 1,200 | 1,200 |
| LHSV | 0.8 | 0.8 | 0.8 | 0.8 |
| Hydrogenation Zone: | | | | |
| Feed Rate, b.p.d. | | 2,620 | | 2,580 |
| $H_2$ Rate, M s.c.f./d. out | | 5,400 | | 5,560 |
| $H_2$ Rate, s.c.f./b. feed out | | 2,060 | | 2,160 |
| $H_2$ Rate, s.c.f./b. feed in | | 2,510 | | 2,560 |
| $H_2$ Rate, M s.c.f./d. in | | 6,680 | | 6,600 |
| Catalyst Temperature, ° F. | | 520 | | 520 |
| Pressure, p.s.i.g. | | 1,200 | | 1,200 |
| LHSV | | 3.0 | | 3.0 |
| Jet Fuel (320–525° F.) Product, b.p.d. | 2,620 | 2,680 | 2,580 | 2,630 |
| Luminometer Number, CRC method [1] | 49 | 65 | 60 | 75 |
| Smoke Point (ASTM), mm. | 22 | 28 | 26 | 32 |
| Isoparaffin Content, Vol. percent | 39 | 39 | 45 | 45 |
| Aromatic Content, Vol. percent | 23 | 0 | 21 | 0 |
| Freezing Point, ° F. | below −76 | below −76 | below −76 | below −76 |

[1] Coordinating Research Council method.

We claim:

1. The process of producing a jet fuel of high luminometer number, which comprises:

passing a mixture of a hydrocarbon distillate feed boiling over a range of at least 50° F. in the range of from about 500° F. to about 1050° F. and containing less than about 100 p.p.m. of total nitrogen, in the presence of at least 1500 s.c.f. of compressed hydrogen per barrel of said feed at a pressure of at least 500 p.s.i.g., a temperature between 400° and 900° F., and a liquid hourly space velocity of about 0.2 to 3.0 v./v./hr., through a hydrocracking zone in contact with a hydrocracking catalyst comprising a cracking component selected from the group consisting of silica-alumina and silica-magnesia and a hydrogenating component selected from the group consisting of compounds of nickel, tungsten, molybdenum and cobalt and mixtures thereof, the reaction in said hydrocracking zone being characterized by a net consumption of hydrogen and a substantially constant conversion of at least about 25 volume percent per pass of said hydrocarbon feed to product boiling below the initial boiling point of said feed;

withdrawing the resulting hydrocracked mixture under pressure from said hydrocracking zone;

separating said hydrocracked mixture into a compressed hydrogen stream, as well as at least one hydrocarbon gas fraction, a relatively light synthetic liquid fraction boiling over the range of from about 320° to about 550° F. and below the initial boiling point of said hydrocarbon feed, and a relatively heavy liquid fraction boiling above the initial boiling point of said hydrocarbon feed;

passing from about 5 to about 100 volume percent of said relatively light synthetic liquid fraction and from 1500 to 4000 s.c.f., per barrel of said synthetic fraction, of hydrogen through a high pressure catalytic hydrogenation zone in contact with a hydrogenation catalyst at a pressure of at least 500 p.s.i.g. and at a temperature between about 300° and 650° F.;

separating hydrogen gas from the resulting hydrogenated synthetic liquid fraction in a high pressure separation zone and passing this separated hydrogen gas with said compressed hydrogen stream separated from said hydrocracked mixture through

a high pressure hydrogen system to said hydrocracking zone;

recycling at least 5 volume percent of said hydrogenated synthetic liquid fraction from said separation zone to said hydrocracking zone to increase its isoparaffin content; and

recovering a substantial portion of said hydrocracked and hydrogenated synthetic liquid fraction from said separation zone as net jet fuel product.

2. A process according to claim 1 wherein said hydrocracking catalyst comprises sulfided nickel on silica-alumina and wherein the conversion of the hydrocarbon feed in the hydrocracking zone is from about 35 to 90 volume percent per pass.

3. A process according to claim 1 wherein said distillate feed is catalytically cracked cycle oil containing less than about 10 p.p.m. total nitrogen.

4. A process according to claim 1 wherein said distillate feed is a straight-run gas oil.

5. A process according to claim 1 wherein the hydrogen fed to said hydrogenation zone is fresh make-up hydrogen.



6. A process according to claim 1 wherein the pressure in said hydrogenation zone is determined by the pressure of said hydrocracking zone.

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