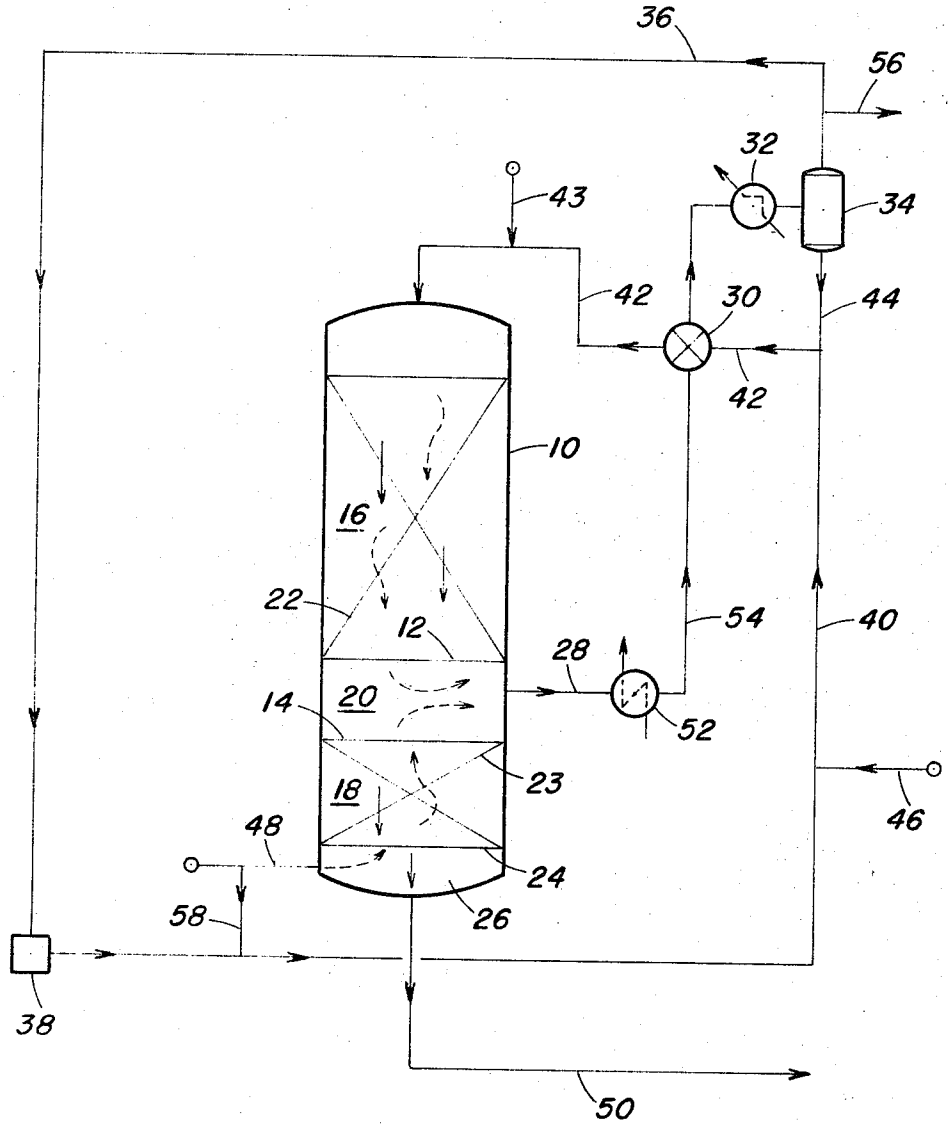
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PRODUCTION OF JET FUEL
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PRODUCTION OF JET FUEL

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Continuation-in-part of application Ser. No. 177,362, Sept. 2, 1971, now Patent No. 3,767,562. This application July 12, 1973, Ser. No. 378,617

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U.S. Cl. 208—57 20 Claims

ABSTRACT OF THE DISCLOSURE

Jet fuel is produced from a petroleum fraction boiling from about 135° F. to about 550° F., such as kerosene, by a two-stage hydrogenation process. A platinum group catalyst is utilized in the first stage, a nickel catalyst in the second.

This application is a continuation-in-part of our application, Ser. No. 177,362, filed Sept. 2, 1971 now Pat. No. 3,767,562 and copending herewith, the disclosure of which is incorporated by reference herein.

BACKGROUND OF THE INVENTION

This invention relates to the production of jet fuel from hydrocarbon feedstocks. In general, a number of methods have been proposed for jet fuel production, from a wide range of feedstocks. In some processes, various petroleum fractions or products have been subjected to hydrocracking, reforming, alkylation and other processes in various combinations. U.S. Pat. 3,513,085, which discloses jet fuel production from coal liquids and petroleum oils by hydrocracking, solvent extraction, fractionation and hydrogenation is typical of such processes. Other methods of producing jet fuel have involved the hydrogenation of aromatics-containing feeds in various ways, sometimes in combination with such other processes as hydrocracking. For example, U.S. Pat. 3,147,210 discloses the production of jet fuel by catalytic hydrogenation of high boiling aromatic hydrocarbons, preceded by a hydrofining or hydrodesulfurization step. The feedstock is desulfurized in cocurrent flow with added hydrogen in the first stage, hydrogen sulfide is stripped after the first stage; the stripped liquid is then subjected to catalytic hydrogenation in countercurrent flow with hydrogen in a second stage.

Detailed specifications for various types of jet fuels have been published by the Armed Forces and ASTM. Three jet fuels in common use today are those designated JP–4, JP–5 and ASTM D–1655 Jet A–1 fuel. With respect to the more critical properties, the specifications call for a maximum sulfur concentration of 2,000 p.p.m. (0.2%) by weight, a minimum IPT Smoke Point of 25 mm. and a maximum aromatics content of 20 volume percent. In addition to methods such as are described in the preceding paragraphs, attempts have been made to use various kerosene fractions directly as jet fuels. However, while these fractions may meet many of the specifications for such fuels, they often do not meet the IPT Smoke Point specification. Additionally, some kerosenes contain a higher aromatics content than the specifications permit.

Application 177,362 discloses a process for production of jet fuel by a two-stage hydrogenation of a petroleum-derived fraction boiling in the range of about 135° F. to about 550° F., prefereably about 300° F. to about 550° F., in which the feed is passed cocurrently with hydrogen over a hydrogenation catalyst in the first stage, and countercurrently to hydrogen over a hydrogenation catalyst, in the second stage. It is disclosed that the hydrogenation catalyst may be any of the well-known hydrogenation catalysts, including such as Raney nickel, or nickel, platinum or palladium, preferably on a support such as alumina, silica, kieselguhr, diatomaceous earth, magnesia, zirconia or other inorganic oxides, alone or in combination.

The choice of a proper catalyst for the conduct of this reaction will depend, of course, on a balancing of the advantages and disadvantages of the catalysts, as well as the feedstocks and operating conditions. Platinum group catalysts, particularly platinum and palladium, have been found to possess the advantages of having a comparatively long catalyst life under the operating conditions generally employed, as well as being less sensitive to sulfur poisoning.

Platinum group catalysts, however, may not always result in as high a conversion rate of aromatics as may be desirable.

It is an object of this invention, therefore, to provide a method for producing jet fuel from a hydrocarbon feedstock without the need for expensive processing steps such as hydrocracking.

It is a further object of this invention to provide a method for producing jet fuel from a hydrocracking feedstock having a boiling range within the temperature range of about 135° F. to about 550° F.

It is a still further object of this invention to provide a process for producing jet fuel from a hydrocarbon fraction boiling substantially within the kerosene boiling range, and more particularly, from a hydrocarbon fraction boiling within the range of from about 300° F. to about 550° F.

A yet further object of this invention is to provide a method for producing a jet fuel with a low aromatics content. Additionally, it is an object of this invention to provide a method for producing a jet fuel which exceeds the minimum IPT Smoke Point of 25 mm.

A still further object of this invention is to provide an optimum catalyst system for such a process.

Other objects and advantages of this invention will become apparent from the specification, drawings and claims thereof.

SUMMARY OF THE INVENTION

In brief, the invention contemplates the production of jet fuel by the two-stage hydrogenation of a hydrocarbon feed having a boiling range within the temperature range of from about 135° F. to about 550° F. comprising the steps of: (a) passing the feed in cocurrent contact with a hydrogen-rich gas through a first hydrogenation zone operated at a temperature of from about 250° F. to about 575° F., at elevated pressure in contact with a catalyst comprising a platinum group metal to at least partially hydrogenate the feed; (b) removing from said first hydrogenation zone a gas phase effluent comprising hydrogen and vaporized liquid materials, and a partially hydrogenated liquid hydrocarbon effluent; (c) further hydrogenating the partially hydrogenated liquid hydrocarbon effluent in a second hydrogenation zone operated at a temperature of from about 200° F. to about 500° F. at elevated pressure by passing a hydrogen-rich gas into said second hydrogenation zone countercurrently to said liquid hydrocarbon effluent in contact with a catalyst comprising nickel; and (d) drawing off from said second hydrogenation zone a gas phase effluent comprising hydrogen and vaporized liquid materials and a liquid phase effluent comprising jet fuel.

The Figure is a diagrammatic illustration of the process of this invention.

DETAILED DESCRIPTION OF THE INVENTION

As shown in the Figure, the hydrogenation zones are preferably contained in one hydrogenation vessel, which

has the form of a vertical cylinder having dished ends and pressure sustaining walls. The interior of the vessel is divided by horizontal partitions **12**, **14** and **24**, which are preferably perforated or foraminous plates or the like, into a plurality of chambers or zones including an upper reaction chamber **16**, an intermediate vapor-disengaging zone **20**, and a lower reaction chamber **18**.

The reaction chambers **16** and **18** are packed with hydrogenation catalysts **22** and **23** respectively, as discussed hereinafter. The catalyst **22** in zone **16** is supported on partition **12**. The catalyst **23** in zone **18** is supported on a similar partition **24**. Partition **24** is preferably spaced somewhat above the bottom of the converter, thus defining the upper boundary of an additional lower chamber or zone **26**.

Fresh aromatics-containing feed, such as is hereinafter described, is introduced into the system at line **46**, into a hydrogen stream in line **40**, and the mixture proceeds in line **40** as indicated by the arrows until it joins line **44**, from which may be added a condensed recycle liquid from separator **34**. The resulting mixture then passes through line **42** into the top of the hydrogenation vessel, at a temperature of from about 250° F. to about 575° F. and a pressure of from about 400 to about 1500 p.s.i., depending on the boiling range of the feedstock and the severity of the hydrogenation. The lower temperature and pressure correspond to lower boiling feeds and lower severity of treatment.

The mixture of feed, recycle liquid and hydrogen passes downwardly through the catalyst bed **22** in zone **16**, under adiabatic reaction conditions in which a substantial amount of the aromatics present in the total liquid charge are hydrogenated to the corresponding naphthenic compounds. The reaction mixture which passes out of zone **16** is a two-phase mixture. The liquid phase is a mixture of paraffins, naphthenes and some unreacted aromatics. The gas phase effluent is a mixture of hydrogen, inert gaseous impurities, and vaporized liquid hydrocarbons of a composition generally similar to that of the liquid phase effluent.

The liquid phase of the effluent passes downwardly through the vapor-disengaging zone **20** into the second hydrogenation zone **18** (through partition **14**, which serves as a distributor plate).

In reaction chamber **18**, hydrogen introduced through line **48** passing through chamber **26** contacts the liquid phase effluent countercurrently, hydrogenating the remaining aromatics to the corresponding naphthenes. The hydrogen is introduced without being preheated, at a relatively low temperature, compared to that of the liquid phase effluent from zone **16**; generally the hydrogen temperature is no higher than about 100–120° F.

The liquid portion which emerges from hydrogenation zone **18** is briefly accumulated in chamber **26** of the reactor, permitting disengagement of vapors and sealing the outlet to line **50** to prevent escape of hydrogen. The liquid product is collected in line **50** and contains a very minor portion, generally less than 1.5 volume percent, of residual unhydrogenated aromatics. The gas phase effluent from hydrogenation zone **18** contains excess hydrogen, inert gaseous impurities, and vaporized hydrocarbons of a composition similar to those contained in the gas phase effluent from hydrogenation zone **16**.

The gas phase effluents from both the first hydrogenation zone **16** and the second hydrogenation zone **18** collect in vapor-disengaging zone **20**. The combined gas phase fraction is withdrawn through line **28**, and is preferably cooled by being passed through heat exchanger or waste heat boiler **52**, in which some of the heat is used to produce steam for use in other processing steps, or in other processes, or for general purposes.

The still hot vapor mixture is then passed through line **54**, then preferably through condenser **30** in which it is used to preheat the mixture fed to the reactor, then through condenser **32**, where the vaporized liquid phase components remaining in the system are recondensed to liquids. The resulting two-phase system, consisting of gaseous hydrogen, inert gases, and reliquefied hydrocarbons, is passed into separator **34**, where the liquid and gaseous phases are separated. The liquid phase is passed through line **44** to be mixed with the feed to hydrogenation zone **16** as previously described. The gaseous phase, comprising hydrogen and inert gases, may be partially vented, as through line **56**, to prevent build-up of inert impurities in the system.

The remainder, and majority of this gaseous phase is recycled through line **36**, to be mixed with the feed to the first hydrogenation zone **16** in line **40**. Fresh feed hydrogen gas may be supplied from line **48** through line **58** into the recycle gas, in the event that the recycle hydrogen is insufficient to supply the needs in the first hydrogenation zone.

An important feature of this invention is a built-in temperature control. Reactions of the type contemplated are exothermic. The production of the desired jet fuel is favored by low outlet temperatures. Furthermore, runaway reactions much be prevented or coke and/or undesirable side products will be formed. Accordingly, external temperature control means are usually necessitated in processes for hydrogenating aromatics for jet fuel production. The present process, however, provides an inherent temperature control, particularly in the second hydrogenation zone **18**. As the hydrogen feed from line **48** passes upwardly through this zone, a portion of the heat present in that chamber is absorbed in the process of sensibly heating the hydrogen.

An additional amount of heat is absorbed by the vaporization of reaction product liquid in zone **18**, in an amount sufficient to saturate the gas stream emerging from this zone into vapor-disengaging zone **20**. Similarly, the temperature in the first reaction zone **16** is controlled by the absorption of heat in partially vaporizing the liquid feed. The vaporized liquid is removed from the vapor-disengaging zone **20** in conduit **28**, as previously described. A similar process for the production of cyclohexane from benzene, with this same built-in temperature control, is described in our U.S. Pat. 3,450,784.

The vaporized hydrocarbons recovered from the vapor-disengaging zone **20** and used as recycle comprise partially hydrogenated feed containing up to about 5% aromatics. Because of low concentration of aromatics, the ratio of recycle to fresh feed is less than 1:1, generally in the range of about 0.05:1 to about 0.75:1, and depends on a number of fractors, including hydrogen partial pressure and purity, desired temperature in the reactor, aromatic content of the feed, etc.

We have discovered that supported nickel-containing catalysts produce higher conversion rates of aromatics and lower residual aromatics content than catalysts of the platinum group. One disadvantage, however, of using nickel catalysts in a process of this type is that such catalysts are quite sensitive to sulfur and tend to become permanently poisoned or deactivated within a relatively short time unless the feed is substantially free of sulfur (less than about 1 p.p.m.). Consequently, to utilize nickel as the catalyst in both zones of the reactor, the feed must be either naturally very low in sulfur content or must be thoroughly desulfurized before utilization. Alternatively, other catalysts may be used, but the conversion levels and residual aromatics content will not be as satisfactory.

We have found, however, that the advantages of the higher conversion and lower residual aromatics content may still be achieved if a supported nickel catalyst is utilized in the second hydrogenation zone **18**, with a catalyst selected from the platinum group, more specifically platinum or palladium, with platinum being preferred, being utilized in the first hydrogenation zone **16**. Platinum group catalysts are only reversibly poisoned by sulfur at levels

where nickel catalysts would be permanently deactivated, and thus, in addition to having a higher sulfur tolerance, also possess a longer catalyst life.

Additionally, the use of the platinum group catalyst **22** in the first, or upper hydrogenation zone **16** permits the processing of feeds containing appreciably more sulfur than if a nickel catalyst were used in this zone. With this system feeds may be treated which contain generally up to about 5 p.p.m. sulfur, though sulfur contents as high as 10 p.p.m. and, in few cases, even 20 p.p.m. may be tolerated, though at these levels catalyst life may begin to decrease. Under ordinary operating conditions it would be expected that sulfur leaving the first hydrogenation zone **16** would be in the form of hydrogen sulfide and will be stripped out of the liquid effluent from the first zone by the hydrogen and gaseous products from the second zone **18** before coming into contact with the nickel catalyst **23**. However, as an extra precaution catalyst bed **23** may be covered with a layer of zinc oxide which acts as a scavenger of hydrogen sulfide.

The platinum group catalyst is preferably supported on a support such as alumina, silica, magnesia, zirconia or other inorganic oxides, alone or in combination or on activated charcoal. The nickel catalyst may be supported on such materials as various inorganic oxides, as above, diatomaceous earth or kieselguhr, alone or in combination.

The feed to the process comprises a petroleum fraction having a boiling range within the temperature range of from about 135° F. to about 550° F. Fractions, for example, with boiling ranges such as 135° F.–480° F., 350° F.–510° F. and 300° F.–520° F. are typical of those within this broad range which are suitable feedstocks for this process. The feed can be either a straight run or other petroleum fractions; such fractions as kerosenes, light and heavy naphthas, catalytically cracked cycle oils and furnace oils can be utilized. Particularly suitable is a feedstock generally boiling within the kerosene boiling range, that is, boiling within the range from about 300° F. to about 550° F.

When such a feed is utilized, the first hydrogenation zone **16** is operated at a temperature of from about 300° F. to about 575° F. and the second zone at about 250° F. to about 500° F., within the pressure ranges previously mentioned.

The process of this invention does not accomplish desulfurization for practical purposes except to the degree mentioned previously, consequently most feedstocks should be at least partially desulfurized prior to being introduced into the process, so that the sulfur content is not greater than about 20 p.p.m., preferably not greater than about 10 p.p.m. and most preferably not greater than about 5 p.p.m. This is generally performed in a separate unit (not shown).

If the feed is desulfurized just prior to its admission into the first hydrogenation zone, it will generally be sufficiently hot that no further heating is required to bring it up to reaction temperature. If, however, the feed has been obtained from a simple fractionation process or has been allowed to cool down prior to being passed into this process, or has been in storage, preheating is required. In any case, the hydrogen fed to the first hydrogenation zone **16** must be preheated prior to its introduction into this zone. The liquid recycle to this zone must also be preheated.

The preheating of the hydrogen, and feed if necessary, can be accomplished in a number of ways, and can be performed separately or together. A convenient method, in this process, is to utilize the heat contained in the vapors in lines **28** and **54** which have been removed from the vapor-disengaging zone **20**. The combined hydrogen (and feed, if necessary) in stream **40**, together with recycle liquid from line **44**, is passed through heat exchanger **30**, in which it is preheated to the desired inlet temperature by indirect heat exchange with the partially cooled vapors in line **54**. This heat exchange, under some conditions, may have the additional effect of partially condensing some of the hydrocarbons in the combined vapor stream, facilitating the separation of hydrocarbons for recycle from the hydrogen and other gases, in separator **34**.

If the fresh feed is already sufficiently hot so as not to require preheating, it should be by-passed around the preheater to avoid overheating and undesirable side reactions. The fresh feed will then enter the system, for example, through line **43** instead of through line **46**, or the by-pass can be accomplished in other ways known in the art. In this case, only the hydrogen and recycled liquid hydrocarbons will be preheated.

Alternatively, the preheating of the fresh feed, liquid recycle and hydrogen can be done in separate heat exchangers, and the heated materials mixed before being introduced into the reactor. This separate preheating can be done using any source of available heat, including the hot vapor mixture in line **54**.

The ratio of hydrogen to fresh feed in the mixture fed to reaction zone **16** may vary from a stoichiometric ratio of 1 mole of hydrogen per double bond to as much as about 300% of the stoichiomertic requirement, and the ratio of hydrogen to the liquid material entering reaction zone **18** may vary from about 0.3 to about 1.0 moles/mole.

The L.H.S.V. in the first zone **16** is preferably maintained between about 0.5 and about 6.0, based on fresh feed only, while that in the second zone **18** is generally at a higher level. The overall L.H.S.V. is maintained, however, between 0.5 and 6.0.

The temperature conditions in the second zone should be adjusted to maintain the temperature of the liquid product at the outlet between about 300° F. and about 500° F., depending on the boiling range of the fresh feed, to provide optimum conditions favoring hydrogenation of the aromatics to naphthenes and close equilibrium approach.

It should be noted that it is not necessary to saturate all aromatics in the feed to produce a jet fuel meeting the minimum smoke point requirement. Saturation of 90% of the aromatics is usually more than sufficient to reach this standard; as pointed out hereinabove, the product may have a residual aromatics content of up to 1.5 volume percent. However, much lower aromatics contents can be achieved, as illustrated in the Example.

In order to illustrate more fully the nature of this invention, and the manner of practicing the same, the following comparative examples are presented.

A desulfurized straight-run kerosene having a boiling range of 350°–500° F. was hydrogenated as shown in the following tabulation, illustrating the beneficial aspects of utilizing a supported nickel catalyst in the second hydrogenation zone.

	I	II
Catalyst:		
Top stage	Pt/alumina	Pt/alumina.
Bottom stage	do	Ni/kieselguhr.
L.H.S.V., hr.$^{-1}$:		
Top stage	2.40	2.40.
Bottom stage	8.09	8.07.
T_{FD}, ° F.:		
Top stage	421	421.
Bottom stage	512	513.
Pressure, p.s.i.g	900	900.
Aromatics, vol. percent:		
Top stage product	3.5	3.5.
Bottom stage product	1.4	0.5.
Fresh feed	16.5	16.5.
Conversion, vol. percent:		
Top stage	78.8	78.8.
Bottom stage	60.0	85.7.

While the above constitutes a description of our invention, it is by no means intended to limit the invention to the specific items disclosed herein, as alternatives and

equivalents will readily occur to those skilled in the art. The invention, therefore, is not to be construed as limited, except as set forth below in the claims.

We claim:

1. A process for producing jet fuels by the two-stage hydrogenation of a hydrocarbon feed having a boiling range within the temperature range of about 135° F. to about 550° F. and substantially free of sulfur-containing impurities, comprising the steps of:

(a) passing the feed in cocurrent contact with a hydrogen-rich gas through a first hydrogenation zone operated at a temperature of from about 250° F. to about 575° F. and at elevated pressure in contact with a catalyst comprising a platinum group metal to at least partially hydrogenate the feed;

(b) removing from the first hydrogenation zone a gas phase effluent comprising hydrogen and vaporized liquid materials, and a partially hydrogenated liquid hydrocarbon effluent;

(c) further hydrogenating the liquid hydrocarbon effluent in a second hydrogenation zone operated at a temperature of from about 200° F. to about 500° F. at elevated pressure by passing a hydrogen-rich gas into the second hydrogenation zone counter-currently to the liquid hydrocarbon effluent, in contact with a catalyst comprising nickel; and

(d) drawing off from the second hydrogenation zone a gas phase effluent comprising hydrogen and vaporized liquid material and a liquid phase effluent comprising jet fuel.

2. A process according to Claim 1 wherein the hydrogen-rich gas introduced into the second hydrogenation zone is at a temperature substantially lower than that of the liquid hydrocarbon effluent.

3. A process according to Claim 1 wherein the feed contains up to 5 p.p.m. sulfur.

4. A process according to Claim 1 wherein the feed contains up to 10 p.p.m. sulfur.

5. A process according to Claim 1 wherein the feed to the first hydrogenation zone is subjected to desulfurization prior to being introduced into said zone.

6. A process according to Claim 1 wherein the feed is preheated prior to being introduced into the first hydrogenation zone.

7. A process according to Claim 6 wherein the gas phase effluents from the first and second hydrogenation zones are combined and passed in indirect heat exchange relationship with the feed to the first hydrogenation zone, thereby cooling said gas phase effluents and preheating said feed.

8. A process according to Claim 1 wherein the gas phase effluents from the first and second hydrogenation zones are cooled sufficiently to condense the vaporized liquid components thereof, and said vaporized liquid components are separated from the remaining gas components and returned as liquid feed to the first hydrogenation zone.

9. A process according to Claim 8 wherein a major portion of the remaining gas components is returned to the first hydrogenation zone.

10. A process according to Claim 8 wherein the ratio of recycled liquid to fresh feed is between 0.05:1 and 0.75:1.

11. A process according to Claim 1 wherein the first hydrogenation zone is operated at a temperature of from about 300° F. to about 575° F.

12. A process according to Claim 1 wherein the second hydrogenation zone is operated at a temperature of from about 250° F. to about 500° F.

13. A process according to Claim 1 wherein the second hydrogenation zone is operated at temperature conditions such that the liquid outlet temperature from said zone is between about 300° F. and 500° F.

14. A process according to Claim 1 wherein the hydrocarbon feed has a boiling range within the temperature range of from about 300° F. to about 550° F.

15. A process according to Claim 1 wherein the hydrocarbon feed has a boiling range within the temperature range of from about 350° F. to about 510° F.

16. A process according to Claim 1 wherein the hydrocarbon feed has a boiling range within the temperature range of from about 300° F. to about 520° F.

17. A process according to Claim 1 wherein the hydrocarbon feed is a desulfurized straight-run kerosene.

18. A process according to Claim 1 wherein the catalyst of step (a) comprises a member selected from the group consisting of platinum and palladium.

19. A process according to Claim 16 wherein the catalyst of step (a) comprises platinum.

20. A process according to Claim 16 wherein the catalyst of step (a) comprises palladium.

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