

[54] **PRODUCTION OF JET FUEL**  
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 3,484,496 12/1969 Carruthers et al..... 208/57  
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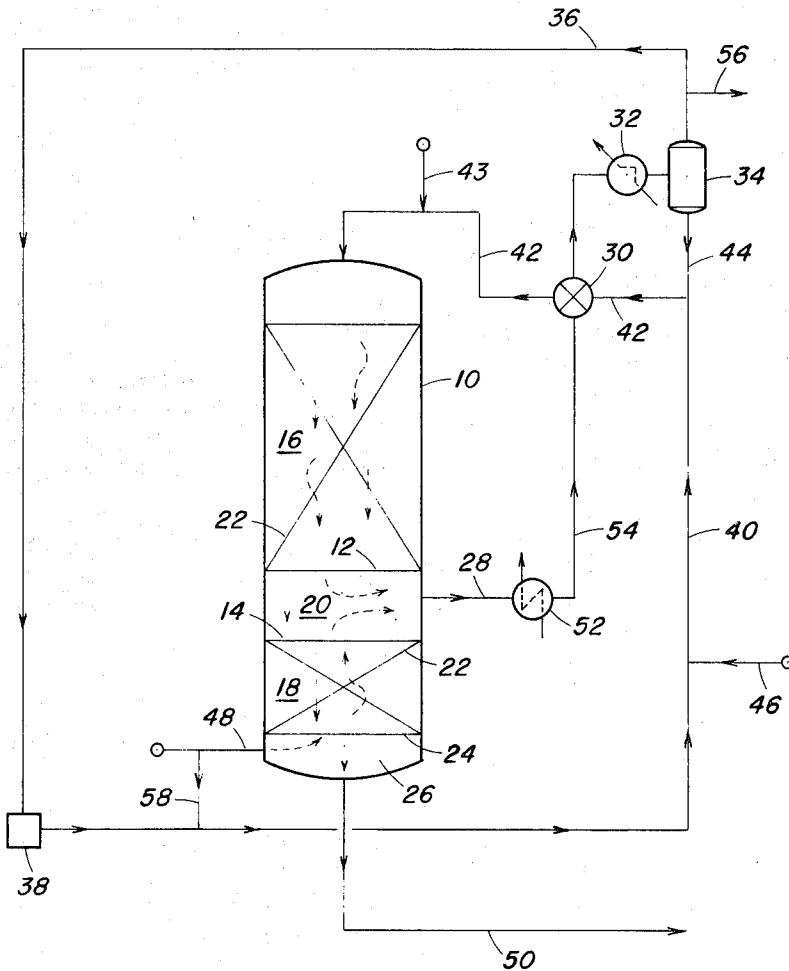
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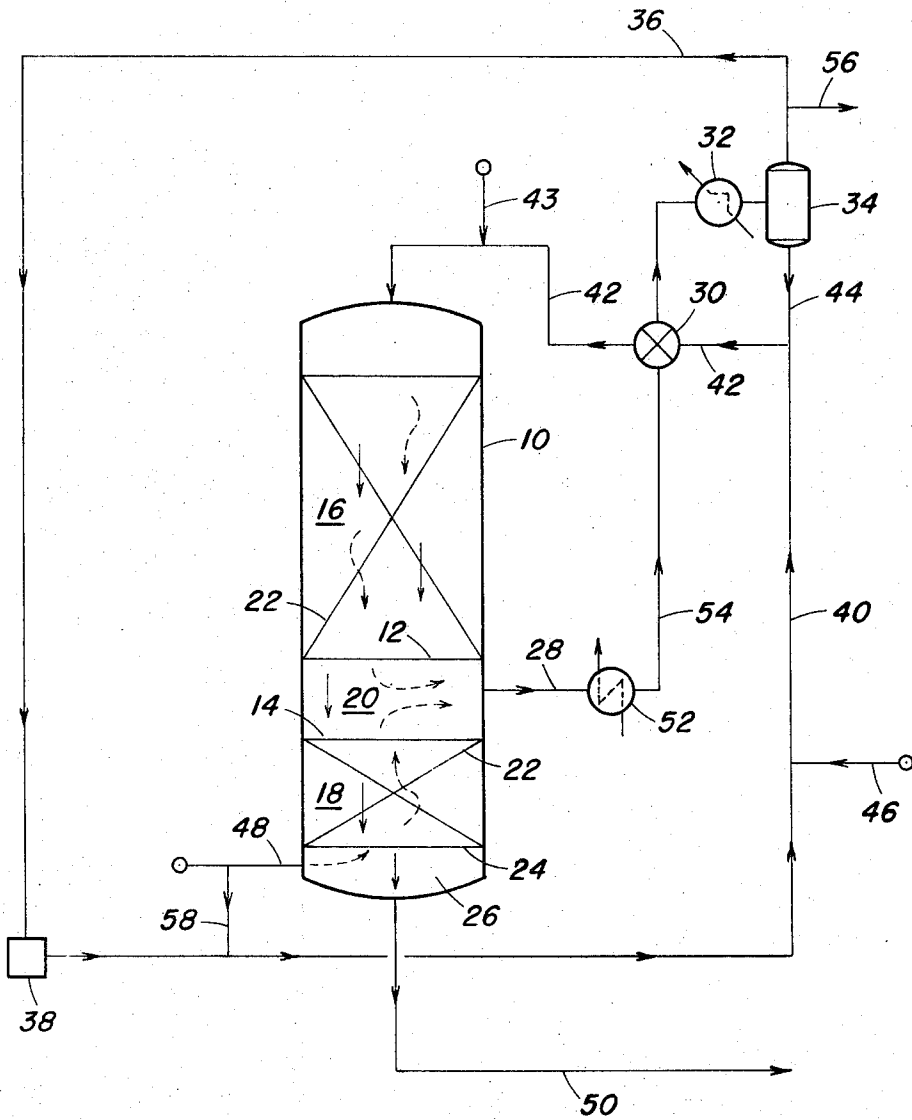
[57] **ABSTRACT**

A process for producing jet fuel from a petroleum fraction having a boiling range within the temperature range of about 135°F. to about 550°F., such as kerosene. The feed is mixed with hydrogen, and liquid recycle, preheated if necessary, and subjected to two-stage hydrogenation of aromatics to reduce the aromatics content and improve the smoke point.

Temperature in the reactor is also controlled by the operation of the process.

**13 Claims, 1 Drawing Figure**





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## PRODUCTION OF JET FUEL

### 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. No. 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. No. 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 ppm (0.2 percent) by weight, a minimum IPT Smoke Point of 25 mm and a maximum aromatics content of 20 volume per cent. 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.

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

### SUMMARY OF THE INVENTION

In brief, the invention contemplates the production of jet fuel from an aromatics-containing petroleum

feedstock 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-stock in cocurrent contact with a hydrogen-rich gas through a first reaction zone operated at a temperature of from about 250°F. to about 575°F. at elevated pressure in contact with a hydrogenation catalyst; (b) removing from said first reaction zone a gas phase effluent comprising hydrogen and vaporized liquid materials, and a partially hydrogenated liquid effluent; (c) passing said liquid effluent into a second reaction zone operated at a temperature of from about 200°F. to about 500°F. at elevated pressure; (d) passing a hydrogen-rich gas into said second reaction zone countercurrently to said liquid phase effluent in contact with a hydrogenation catalyst, and (e) drawing off from said second reaction 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

As shown in the FIGURE, the hydrogenation zones are preferably contained in one hydrogenation vessel, which has the form of a vertical cylinder having disched 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 a suitable hydrogenation catalyst 22, which may be of any of the well known hydrogenation-dehydrogenation 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 catalyst in zone 16 is supported on partition 12. The catalyst 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 is 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 1,500 psi, 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 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 and 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 per cent, 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 first 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 vented partially, 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 must be prevented or coke and 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 58 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. No. 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 percent aromatics. Because of the 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 factors, including hydrogen partial pressure and purity, desired temperature in the reactor, etc.

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 fraction; 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 of 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; consequently most feedstocks should be desulfurized prior to being introduced into the process, generally 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 42, 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 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 percent of the stoichiometric 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 percent of the aromatics is usually more than sufficient to reach this standard; as pointed out herein above, the product may have a residual aromatics content of up to 1.5 volume per cent. However, much lower aromatics contents can be achieved, as illustrated in the Example.

Most of the fuels produced by the process of this invention, from the feedstocks mentioned while meeting the specifications for standard jet fuel, will not possess a low enough freezing point to be suitable for use in supersonic aircraft (-57°F. or less). However, in the case of certain feedstocks, even this specification can be met. It has been found, for example, that such a jet fuel can be produced from a desulfurized kerosene obtained from a Bachaquero crude by utilizing the process described herein.

In order to illustrate more fully the nature of this invention, and the manner of practicing the same, the following specific example is presented.

#### EXAMPLE

A desulfurized straight run kerosene having the following properties:

ASTM Distillation, ASTM D-86-62

I.B.P., °F.—345

50 vol.%, °F.—390

E.P., °F.—460

Vol. % Aromatics, ASTM D-1319-65T—16.0

Smoke Point, mm ASTM D-1322-64—18.2

was mixed with hydrogen, then combined with recycled liquid in a ratio of 16 parts recycle to 100 parts fresh feed, preheated in heat exchanger 30 and introduced into the top of reactor 10. The inlet temperature at the top of section 16 was 400°F; the maximum overall catalyst bed temperature was 525°F. The reaction was conducted at an overall L.H.S.V. of 2.40 and a pressure of 900 psig. The hydrogenated product recovered in line 50 had an aromatics content of 0.55 volume percent. The smoke point was improved to 36 mm, well above the minimum acceptable limit of 25 mm.

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 300°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 an elevated pressure in contact with a hydrogenation catalyst 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 liquid;

c. hydrogenating the liquid hydrocarbon effluent in a second hydrogenation zone operated at a temperature of from about 200°F to about 500°F and at an elevated pressure by passing a hydrogen-rich gas having a temperature substantially lower than that of the liquid hydrocarbon effluent into the second hydrogenation zone countercurrently to the effluent, in contact with a hydrogenation catalyst; and

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

2. 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.

3. A process according to claim 1 wherein the feed to the first hydrogenation zone is preheated prior to being introduced into said zone.

4. A process according to claim 3 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.

5. A process according to claim 1 wherein the gas phase effluents from the first and second hydrogenation zones are cooled sufficiently to condense the va-

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porized 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.

6. A process according to claim 5 wherein a major portion of the remaining gas components is returned to the first hydrogenation zone.

7. A process according to claim 5 wherein the ratio of recycled liquid to fresh feed is between 0.05:1 and 0.75:1.

8. 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.

9. A process according to claim 1 wherein the second hydrogenation zone is operated at a temperature of

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from about 250°F to about 500°F.

10. 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.

11. 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.

12. 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.

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

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