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**SMOKE POINT IMPROVEMENT OF JET FUEL
KEROSENE FRACTIONS****Robin J. Parker, Western Springs, and Ernest L. Pollitzer,
Skokie, Ill., assignors to Universal Oil Products Com-
pany, Des Plaines, Ill.****No Drawing. Filed Feb. 10, 1969, Ser. No. 798,179****Int. Cl. C10g 23/02****U.S. Cl. 208—89****5 Claims****ABSTRACT OF THE DISCLOSURE**

A process for improving the jet fuel characteristics of sulfurous kerosene boiling range fractions. The improvement is especially noticeable in the IPT Smoke Point, the concentration of aromatic hydrocarbons and the concentration of sulfur. A two-stage process wherein desulfurization of a sulfurous charge stock is effected in the first reaction zone at relatively mild severities which result in a normally liquid product effluent containing from about 15 to about 35 p.p.m. of sulfur by weight. Aromatic saturation is the principal reaction effected in the second reaction zone having disposed therein a catalytic composite of alumina, a halogen component, a Group VIII noble metal component and a Group VII-B metallic component.

APPLICABILITY OF INVENTION

Suitable charge stocks, for utilization in the present process, are commonly referred to as kerosene fractions. As generally defined in petroleum technology, a kerosene fraction can have an initial boiling point as low as about 300° F., and an end boiling point as high as about 575° F., and, in some instances, up to 600° F. Typical kerosene fractions are those boiling from about 300° F. to about 550° F., from 330° F. to about 500° F., from 330° F. to about 530° F., etc. Although the particular source of the kerosene fraction, for use as charge stock herein, is not material, a highly olefinic/aromatic kerosene is probably the least desirable—i.e. catalytically cracked cycle oil fractions.

Typical of those charge stocks, visualized as having their jet fuel characteristics improved through the process of our invention, is a Lake Superior kerosene having a gravity of about 42.3° API, an initial boiling point of about 337° F., an end boiling point of about 513° F., and containing about 1500 p.p.m. of sulfur, about 3.8 p.p.m. of nitrogen and having an IPT Smoke Point of about 20 mm.; and, a Redwater kerosene having a gravity of about 40.9° API, an initial boiling point of 361° F., an end boiling point of 518° F., an IPT Smoke Point of 21.9 mm., containing about 1450 p.p.m. of sulfur and 18.5% by volume of aromatics. While these kerosene fractions are straight-run kerosenes derived from full boiling range crude oils, suitable charge stocks also include those product fractions derived from a prior conversion process. For example, a kerosene obtained from hydrocracking a Mid-Continent slurry oil, having a gravity of about 30.5° API, an initial boiling point of about 388° F., an end boiling point of about 522° F., has an IPT Smoke Point of 17.1 mm., and contains 530 p.p.m. of sulfur and 24.8% by volume of aromatic hydrocarbons.

Through the utilization of the present process, kerosene fractions of the type hereinabove described, can be converted into kerosenes of enhanced, improved jet fuel characteristics. The improvement in the quality of the kerosene fraction is most significant with respect to the IPT Smoke Point, the concentration of sulfur and the quantity of aromatic hydrocarbons. With respect to motor fuel gasoline fractions utilized in internal combustion engines, the

critical properties are generally considered to be a high octane rating, indicative of the anti-knock quality of the motor fuel, a specified volatility, generally dependent upon locale and/or climate, a low concentration of olefinic hydrocarbons and low concentrations of contaminating influences. By contrast, many more criteria are utilized in describing a fuel suitable for use in jet engines, and even these are further restricted depending upon engine complexity, speed, cruising altitude, distance, etc. Since about 1960, the quality and classification of jet fuels has generally followed the development of the jet engine. Thus, specifications for jet fuels of particular physical and/or chemical characteristics, have resulted in fuels designated as JP-1, JP-3, JP-4, JP-5, JP-6, JP-8, Jet-A, Jet-B and Jet-A1. Although the allowable limits of the characteristics, employed as criteria in determining the grade of the foregoing jet fuels, differ one from the other, the selected characteristics are generally the same. These include, for example, the gravity in ° API, particular volumetric distillation temperatures, including the initial and end boiling points, the freeze point, the flash point, luminosity number, thermal stability, aromatic concentration, the IPT Smoke Point, the Aniline Point and, most certainly, the concentration of contaminating influences, particularly sulfur.

It is important to note that the above-designated jet fuels are described in the literature as standard, or sonic jet fuels. It has already been anticipated that although a jet fuel fraction may conform to the specifications for a given standard jet fuel, the same will not be considered suitable for use in future supersonic jet transports. It is contemplated that the jet fuel specifications necessitated by supersonic jet transports will be further limiting.

A comparison of the detailed requirements for sonic jet fuels may be found in the ASTM Specifications for Aviation Turbine Fuels, ASTM designation, D-1655-67T. The comparison is made for the jet fuels commonly referred to as Jet-A, Jet-A1 (both of which are also referred to as JP-5) and Jet-B (also designated as JP-8). With respect to the more critical properties, that is, properties which require something other than mere distillation and/or fractionation to achieve, it is noted that the specifications called for a sulfur concentration of 0.3% by weight maximum (3000 p.p.m.), a minimum IPT Smoke Point of 25 mm. and a maximum aromatic concentration of about 20.0 vol. percent. In view of the fact that the specifications for the various standard jet fuels, as well as the limitations imposed upon the various physical and chemical characteristics, and the methods for determining the quality of any given characteristic, are thoroughly defined in the literature, further discussion thereof is not deemed necessary.

OBJECTS AND EMBODIMENTS

An object of the present invention is to provide a process for improving the jet fuel characteristics of kerosene fractions. A corollary objective is to provide a two-stage flow system for producing jet fuel kerosenes from sulfur contaminated kerosene fractions.

Another object of our invention is to increase the stability of the overall process, while simultaneously reducing the contaminant level, particularly with respect to the concentration of aromatic hydrocarbons.

With respect to high sulfur-containing kerosene feed stocks, it is an object of our invention to provide a two-stage process in which the catalytic composite in the second stage has a degree of sulfur tolerability to the extent that the desired reactions in the first stage can be effected at relatively mild operating severities.

Therefore, in one embodiment, our invention involves a process for improving the jet fuel characteristics of

a sulfurous kerosene boiling range fraction, which process comprises reacting said kerosene fraction and hydrogen in a catalytic reaction zone containing a catalytic composite of an alumina-containing inorganic oxide, halogen, a Group VIII noble metal component and a Group VII-B metallic component having an atomic number greater than 25; and, separating the resulting reaction zone effluent, to provide a hydrogen-rich vapor phase and to recover a normally liquid kerosene fraction having improved jet fuel characteristics.

A more limited embodiment encompassed by the present invention affords a process for improving the jet fuel characteristics of a sulfurous kerosene boiling range fraction, which process comprises the steps of: (a) desulfurizing said kerosene fraction in a first catalytic reaction zone at a pressure less than about 1500 p.s.i.g. and at a maximum catalyst bed temperature below about 725° F., said temperature and pressure selected to convert sulfurous compounds to hydrogen sulfide and hydrocarbons; (b) separating the resulting reaction zone effluent to provide a first vaporous phase and a normally liquid phase containing from about 15 to about 35 p.p.m. of sulfur by weight; (c) reacting said normally liquid phase and hydrogen in a second catalytic reaction zone, in contact therein with a catalytic composite of alumina, from about 0.1% to about 1.5% by weight of halogen, from about 0.01% to about 1.0% by weight of a platinum group metallic component and about 0.01% to about 1.0% by weight of a Group VII-B metallic component having an atomic number greater than 25, calculated as the elements; and, (d) separating the resulting second catalytic reaction zone effluent, to provide a second vapor phase and to recover a normally liquid kerosene fraction having improved jet fuel characteristics.

Other embodiments of our invention involve preferred processing techniques and operating conditions, as well as the catalytic composites for utilization in the two reaction zones. For example, one technique involves combining the first and second vapor phases, introducing the mixture into a hydrogen sulfide removal system, and recycling a portion of the remaining hydrogen enriched vaporous phase to both the first and second catalytic reaction zones. In another embodiment, the second catalytic reaction zone is maintained under an imposed pressure of at least about 400 p.s.i.g., and the hydrogen circulation rate therethrough is at least about 1500 standard cubic feet per barrel. An especially preferred catalytic composite for utilization in the second reaction comprises alumina, a platinum component, a rhenium component and chlorine. These, in addition to other objects and embodiments of our invention will be evident from the following detailed description thereof.

SUMMARY OF INVENTION

The purpose of the present invention, as hereinbefore set forth, is to improve the jet fuel characteristics of kerosene boiling range fractions. In essence, this purpose is accomplished through the use of a catalytic reaction system, containing a particular catalytic composite and functioning at particular conditions of operation, the latter including a kerosene feed stock containing sulfurous compounds in an amount of from about 15 p.p.m. to about 35 p.p.m. by weight of sulfur. Noble metal-containing catalysts, particularly those containing a platinum component, are notoriously sulfur-sensitive. As such, charge stocks intended for processing, in contact with a noble metal-containing catalyst, must necessarily be initially subjected to a treatment designed to effect desulfurization to a level less than about 10 p.p.m., and, with respect to particular reactions, to a level less than about 1 p.p.m. The catalytic composite utilized in the present invention, for the purpose of saturating aromatics and increasing the IPT Smoke Point, not only can tolerate feed stocks containing up to about 35 p.p.m. by weight of sulfur, but appears to possess a greater propensity for effecting the saturation of aromatic hydrocarbons in the presence of sulfur.

It must be recognized that many of the virgin, or raw fractions of petroleum crude oil, are too poor in smoke point, sulfur concentration and possess a quantity of aromatic hydrocarbons which prohibit their direct use in jet fuels. Although these jet fuel characteristics of various kerosene fractions may be improved through a suitable hydrogenation technique, or other treatment, it must further be recognized that all of the known hydrogenation-type catalytic composites are not suitable for this purpose. Thus, although the metals of Group VI-B and VIII of the Periodic Table exhibit excellent hydrogenation capabilities, the noble metals of Group VIII cannot be employed directly in view of the excessive sulfur contamination of the raw kerosene. On the other hand, metals from the Iron-Group and Group VI-B of the Periodic Table, although resistant to sulfur, require excessive pressures beyond about 2000 p.s.i.g., in order to convert sulfurous compounds into hydrogen sulfide and hydrocarbons, while simultaneously saturating a sufficient quantity of the aromatic hydrocarbons to meet the requirements of a jet fuel. Furthermore, excessive pressure enhance the possibility of effecting undesirable hydrocracking reactions inherently resulting in the overproduction of light gaseous material such as methane, ethane and propane.

In essence, our invention involves the catalytic treatment of a kerosene boiling range fraction, containing up to about 35 p.p.m. of sulfur by weight, through the use of a particular catalytic composite at particular conditions of operation. With respect to straight-run or virgin kerosene fractions, containing excessive amounts of sulfur, and generally quantities up to about 1.0% by weight, our invention provides a two-stage process. Since the catalytic composite employed in the second-stage exhibits a degree of sulfur tolerability, the first, or desulfurization stage can be maintained at comparatively mild operating severities.

Therefore, the present invention, in one of its embodiments, involves the utilization of a first catalytic reaction zone containing a catalyst comprising at least one metallic component from Group VI-B and the Iron-Group of the Periodic Table, for the principal purpose of effecting desulfurization at relatively low severities. The catalytic composite, utilized in the second reaction zone for the primary purpose of saturating aromatic hydrocarbons and increasing the IPT Smoke Point of the normally liquid product from the first stage, comprises a Group VIII noble metal component, a halogen component, a Group VII-B metallic component, having an atomic number greater than 25, and an alumina-containing refractory inorganic oxide.

DESCRIPTION OF CATALYTIC COMPOSITES

The catalytic composites utilized in the present process comprise metallic components selected from the metals, and compounds thereof, of Group VI-B, VII-B and VIII of the Periodic Table. Thus, in accordance with the Periodic Table of The Elements, E. H. Sargent & Co., 1964, suitable metallic components are selected from the group consisting of chromium, molybdenum, tungsten, technetium, iron, cobalt, nickel, rhenium, ruthenium, osmium, rhodium, iridium, palladium and platinum. It should be noted that the metals selected from Group VII-B, technetium and rhenium, have atomic numbers greater than 25, being 43 and 75 respectively. The use of manganese, in combination with the Group VIII noble metal component, does not result in the desired degree of aromatic saturation, accompanied by the noticeable sulfur tolerability, and stability of operation.

While neither the precise composition, nor the method of manufacturing the catalyst is essential to our invention, certain considerations are obviously preferred. For example, since the charge stocks to the process are kerosene fractions, and the normally liquid product is a kerosene fraction, it is preferred that neither catalytic composite exhibit a great degree of hydrocracking ac-

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tivity, under the operating conditions utilized herein, whereby the kerosene boiling range material is converted into lower-boiling hydrocarbon products. These catalytically active components are generally composited with a suitable refractory inorganic oxide, having little hydro-

cracking activity at the selected operating conditions, the inorganic oxides being selected from alumina, silica, zirconia, magnesia, titania, boria, hafnia, etc.

The catalytic composite disposed within the first reaction zone serves a dual function—it is non-sensitive to the presence of nitrogenous or sulfurous compounds, while at the same time is capable of effecting the destructive removal thereof. A catalyst comprising comparatively large quantities of molybdenum, calculated as the element, composited with a carrier of alumina and silica, is very efficient in carrying out the desired operation. A particularly preferred catalytic composite, for utilization in this reaction zone, comprises from about 4.0% to about 40.0% by weight of molybdenum, or other Group VI-B metallic component, and from about 1.0% to about 6.0% by weight of an Iron-Group metallic component. With respect to the alumina-silica composite, utilized as the carrier material for the foregoing catalytically active metallic components, generally has an alumina/silica weight ratio of from about 60/40 to about 90/10. The precise composition of this desulfurization catalyst is primarily dependent upon the characteristics of the fresh kerosene feed stock, particularly the sulfur and nitrogen concentration. Since the methods of manufacturing these catalysts, and various compositions thereof, are well-described within the prior art, further discussion thereof is not required herein.

The catalytic composite, utilized in the catalytic reaction zone for the purpose of saturating aromatic hydrocarbons and increasing the IPT Smoke Point, is a composite of an alumina-containing inorganic oxide, a halogen component, a Group VIII noble metal component and a Group VII-B metallic component, the latter having an atomic number greater than 25, all of which are calculated on the basis of the elements, regardless of the particular state in which they exist within the composite. With respect to the alumina-containing carrier material, alumina may be suitably employed in and of itself, or in combination with minor quantities of silica and/or the previously described refractory inorganic oxides. When combined with, for example silica, it is preferred that the alumina/silica weight ratio be within the range of from about 63/37 to about 90/10. Suitable carrier materials have physical characteristics indicating an apparent bulk density of about 0.30 to about 0.70 gram per cc., an average pore diameter from about 20 to about 150 angstroms, a pore volume from about 0.1 to about 1.0 ml./gm. and a surface area from about 100 to about 500 square meters per gram. The carrier material may be prepared in any suitable manner, and may be either synthetically-prepared, or naturally-occurring. Following its preparation, the carrier material may be formed into any desired shape including spheres, pills, cakes, extrudates, powders, granules, etc. Neither the form of, nor the method of manufacturing the carrier material is considered to be an essential feature of our invention.

One component of the catalyst, utilized to saturate aromatic hydrocarbons, is a halogen component. The precise form of the association of the halogen component with the carrier material is not accurately known; however, the prior art indicates that it is customary to refer to the halogen component as being combined therewith, or with the other ingredients of the composite, and is, therefore, conveniently referred to as combined halogen, or as combined halide. The halogen may be either fluorine, chlorine, iodine, bromine or mixtures thereof, with fluorine, and particularly chlorine being preferred. The halogen component may be added to the carrier material in any suitable manner, either during preparation of the carrier, or before or after the addition of

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the other catalytically active components. The halogen component will be composited with the alumina carrier material in such a manner as results in a final composite containing about 0.1% to about 1.5% by weight, and preferably from about 0.4% to about 0.9% by weight, calculated on an elemental basis.

The second-stage catalytic composite also contains a Group VIII noble metal component selected from ruthenium, rhodium, palladium, osmium, iridium and platinum. Of these, a palladium and/or platinum metallic component is preferred. This component may exist within the final catalytic composite as a compound, such as an oxide, sulfide, halide, etc., or in an elemental state. The Group VIII noble metal component generally comprises about 0.01% to about 1.0% by weight of the final catalytic composite, calculated on the basis of the element. Excellent results are obtained when the catalyst contains from about 0.3% to about 0.9% by weight of platinum. The Group VIII noble metal component may be incorporated within the catalytic composite in any suitable manner including coprecipitation with the carrier material, ion-exchange, or impregnation of the carrier material with a suitable water-soluble compound of the Group VIII metal. Following the incorporation of the Group VIII noble metal component, for example by way of impregnation, the carrier material is dried and subjected to a high temperature calcination technique, which technique is well-described in the prior art.

Another constituent of this catalytic composite is a metallic component from Group VII-B, having an atomic number greater than 25, and being technetium and/or rhenium. A manganese component is not suitable for use herein since the desired results with respect to aromatic saturation, sulfur tolerability and stability of operation are not obtained. As hereinabove stated with respect to the noble metal component, the Group VII-B component may be present within the catalytic composite as an elemental metal, a compound, including an oxide, sulfide, halide, or in some physical and/or chemical association with the carrier material, or the other components of the catalyst, generally, the rhenium, or technetium component is utilized in an amount sufficient to result in a final catalytic composite containing from about 0.01% to about 1.0% by weight, calculated as the elemental metal. While the Group VII-B component may be incorporated in any suitable manner, as a general rule it is preferable to introduce this component at a later step of the formulation in order that the expensive metal is not lost during subsequent processing techniques. In general, the Group VII-B component can be impregnated either prior to, simultaneously with, or after the Group VIII noble metal component.

Advantageous results are achieved with a catalytic composite having a Group VII-B/noble metal weight ratio in the range of about 0.05:1 to about 2.75:1. Exemplary of preferred catalytic composites are those containing: 0.1% by weight of rhenium and 0.65% by weight of platinum, 0.2% by weight of rhenium and 0.55% by weight of palladium, 0.375% by weight of rhenium and 0.375% by weight of platinum, 0.55% by weight of technetium and 0.20% by weight of platinum, 0.65% by weight of rhenium and 0.10% by weight of platinum, 0.10% by weight of technetium and 0.65% by weight of palladium, 0.20% by weight of technetium and 0.55% by weight of platinum, 0.375% by weight of rhenium and 0.375% by weight of palladium, 0.375% by weight of technetium and 0.375% by weight of platinum, 0.55% by weight of technetium and 0.20% by weight of platinum and, 0.65% by weight of technetium and 0.10% by weight of palladium, etc.

The final catalytic composite will generally be dried at a temperature of from about 200° F. to about 600° F., for a period of from about 2 to about 24 hours. The dried composite is then calcined at a temperature of about 700° F. to about 1100° F. for a period of about

0.5 to about 10 hours. In those instances where the catalytic composite is subjected to a presulfiding operation designed to incorporate from about 0.05% to about 0.50% by weight of sulfur, on an elemental basis, the presulfiding technique is effected on a reduced composite. That is, prior to sulfiding the catalytic composite, it is subjected to a substantially water-free reduction in a stream of substantially pure and dry hydrogen—i.e. containing less than about 30 p.p.m. by volume of water.

PROCESS CONDITIONS AND OPERATIONS

In practicing the present invention, the charge stock, for example a straight-run kerosene fraction from a sour Wyoming crude oil, having a sulfur concentration of 5580 p.p.m., an IPT Smoke Point of 19.9 mm. and containing about 21.7% by volume of aromatic hydrocarbons, is admixed with recycled hydrogen in an amount within the range of from about 500 to about 2000 standard cubic feet per barrel. Following suitable heat-exchange with various hot product effluent streams, the hydrogen/hydrocarbon mixture is heated to a temperature level necessary to control the maximum catalyst bed temperature below about 725° F., and preferably not above 700° F., with a minimum of about 600° F. The catalyst, containing about 2.2% by weight of cobalt and about 5.7% by weight of molybdenum, calculated as the elemental metals, and composited with alumina, is disposed in a reaction zone which is maintained under an imposed pressure of about 500 to about 100 p.s.i.g. The quantity of catalyst disposed within the reaction zone, and the charge stock rate, is such that the liquid hourly space velocity (defined as volumes of liquid hydrocarbon charge per hour per volume of catalyst) is in the range of from about 0.5 to about 10.0, and preferably from about 0.5 to about 5.0. In view of the fact that the principal reactions are exothermic in nature, a temperature increase will be experienced as the charge stock flows through the catalyst bed. A preferred technique limits the temperature increase to about 50° F., as measured at the outlet of the catalyst bed; therefore, as will be recognized by those having skill in the art, it is sometimes advisable to utilize conventional quench streams at intermediate loci of the reaction zone.

The total product effluent from this first catalytic reaction zone is separated in a manner which provides a hydrogen-rich gaseous phase and a normally liquid hydrocarbon stream containing 15 p.p.m. to about 35 p.p.m. of sulfur by weight. The vaporous phase may, where desired, be treated in any manner well known to the art, for the purpose of removing constituents other than hydrogen. Similarly, the normally liquid phase from the cold separator may be fractionated to the degree necessary to remove liquid hydrocarbons boiling below a particular kerosene boiling range. In those instances where the fresh kerosene charge stock is contaminated by nitrogenous compounds, a conventional technique involves admixing the product effluent with water prior to the introduction thereof into the cold separator, and providing the latter with a dip leg for the removal of sour water containing the ammonia formed as a result of the decomposition of the nitrogenous compounds.

In any event, the normally liquid phase from the cold separator is utilized as the fresh feed charge stock to the second catalytic reaction zone. With this particular Wyoming kerosene, processed at the foregoing conditions, the first reaction zone has decreased the sulfur concentration to about 25 p.p.m., the aromatic concentration to about 16.3% by volume and has increased the IPT Smoke Point to a level of about 21.5 mm.

The catalyst disposed in the second catalytic reaction zone comprises alumina, 0.30% by weight of platinum, 0.25% by weight of technetium and about 0.70% by weight of combined chloride. The reaction zone is maintained at an imposed pressure of at least about 400 p.s.i.g., with an upper limit of about 1500 p.s.i.g. The

hydrogen circulation rate is at least about 1500 standard cubic feet per barrel, with an upper limit of about 10,000 standard cubic feet per barrel. The liquid hourly space velocity, hereinabove defined, is in the range of from about 0.5 to about 5.0, and preferably from about 0.5 to about 3.0. Although some aromatic saturation will be effected at a catalyst bed temperature of about 800° F., it is preferred to limit the catalyst temperature to a maximum level of about 750° F. With a catalyst of this particular chemical and physical characteristics, optimum aromatic saturation, processing a feed stock containing from about 15 p.p.m. to about 35 p.p.m. of sulfur, is effected at maximum catalyst bed temperatures in the range of about 625° F. to about 750° F. The total product effluent from the second catalytic reaction zone is introduced into a second cold separator at a temperature in the range of from about 60° F. to about 140° F. With respect to the normally liquid kerosene fraction, recovered from the condensed liquid removed from the cold separator, the sulfur concentration is effectively "nil," being about 0.1 p.p.m. The quantity of aromatic hydrocarbons has been decreased to a level of about 1.0% by volume, or less, and the IPT Smoke Point has been increased to above about 35.0 mm. The principally vaporous phases, from the cold separators utilized to concentrate the normally liquid hydrocarbons from the first and second reaction zones, may be combined and introduced into a common hydrogen sulfide removal system. The hydrogen-rich vaporous phase is utilized, after addition thereto of make-up hydrogen from a suitable external source, as recycle to both the first and second catalytic reaction zones.

As hereinbefore set forth, the first catalytic reaction zone, or desulfurization zone, is maintained under the various aforesaid operating conditions specifically selected within the indicated ranges, to convert sulfurous compounds into hydrogen sulfide and hydrocarbons, while simultaneously providing a normally liquid hydrocarbon fraction containing up to about 35 p.p.m. by weight of sulfur. In view of the fact that the necessity for further decreasing the sulfur concentration of the "desulfurized" feed stock, to a level less than about 10 p.p.m., and often to about 1.0 p.p.m., has been eliminated, the first catalytic reaction zone can carry out its intended function at lower operating severities. The severity of a given operation is generally based on the temperature and liquid hourly space velocity under which the reactions are effected. Although pressure and hydrogen circulation rate have an effect, greater consideration is given to the operating temperature and liquid hourly space velocity. In general, a higher temperature and/or a lower space velocity alludes to a "high" severity operation, while a lower temperature and/or higher space velocity connotes a "low" severity operation. One of the attended advantages of the low operating severity within the first catalytic reaction zone, afforded through the utilization of the present invention, is the fact that a commercially-scaled unit can be designed with relatively narrow limitations imposed upon pressure, hydrogen circulation rate and catalyst bed temperature, the principal operating variable then becoming the liquid hourly space velocity. Another advantage resides in the fact that the catalyst utilized herein has a greater propensity for aromatic saturation and increasing the IPT Smoke Point, as a result of its sulfur tolerability.

EXAMPLE

The kerosene boiling range charge stock employed in this illustrative example is a Redwater kerosene, characteristics of which are: a gravity of 40.9° API, an initial boiling point of 361° F., a 50% volumetric distillation temperature of 425° F. and an end boiling point of 518° F.; an IPT Smoke Point of 20.8 mm., a sulfur concentration of 1480 p.p.m. and an aromatic hydrocarbon content of 18.5 vol. percent. The kerosene fraction is processed with about 1500 standard cubic feet

per barrel of hydrogen, in contact with a catalytic composite of about 2.2% by weight of cobalt and 5.7% by weight of molybdenum, combined with alumina. The pressure imposed upon the reaction zone is about 900 p.s.i.g., the catalyst bed inlet temperature about 600° F. and the liquid hourly space velocity therethrough is of the order of 0.75. The normally liquid portion of the product effluent indicates an IPT Smoke Point of about 22.5 mm., an aromatic hydrocarbon concentration of about 17.7 vol. percent and a sulfur concentration of about 22 p.p.m. by weight.

The normally liquid product effluent is processed in a second catalytic reaction zone at a pressure of about 850 p.s.i.g. and a maximum catalyst bed temperature of about 725° F. The liquid hourly space velocity is about 1.25, and the hydrogen circulation rate is about 6000 standard cubic feet per barrel. The catalytic composite disposed within the second catalytic reaction zone is a composite of alumina, 0.375% by weight of platinum, 0.35% by weight of rhenium and about 0.70% by weight of combined chloride. Following separation and distillation to concentrate the kerosene fraction, analyses indicate that the Smoke Point has been increased to a level of about 36.5 mm., the aromatic concentration has been lowered to about 0.8% by volume and the sulfur concentration is "nil."

The foregoing specification, and particularly the example, indicate the benefits to be afforded through the utilization of the process encompassed by the present invention. Through the use of the present invention, the jet fuel characteristics of a kerosene fraction, particularly the IPT Smoke Point, aromatic concentration and sulfur content, have been improved significantly.

We claim as our invention:

1. A process for improving the jet fuel characteristics of a sulfurous kerosene boiling range fraction containing in excess of 35 p.p.m. by weight of sulfur, which process comprises the steps of:

(a) desulfurizing said kerosene fraction in a first catalytic reaction zone in the presence of a catalyst comprising a Group VI-B metallic component and an iron-group metallic component under relatively mild severity operating conditions, including a temperature of from about 600° F. to about 725° F., to re-

duce the sulfur content of said kerosene fraction to between about 15 and 35 p.p.m. by weight of sulfur; (b) separating the resulting reaction zone effluent to provide a first vaporous phase and a normally liquid phase containing from about 15 to about 35 p.p.m. of sulfur by weight;

(c) reacting said normally liquid phase and hydrogen in a second catalytic reaction zone containing a catalytic composite of an alumina-containing inorganic oxide, halogen, a Group VIII noble metal component and a Group VII-B metallic component having an atomic number greater than 25 at a higher temperature, in the range of about 625–800° F., than is maintained in said first reaction zone; and

(d) separating from the effluent of said second reaction zone a normally liquid kerosene fraction of improved jet fuel characteristics.

2. The process of claim 1 further characterized in that the hydrogen circulation rate to said catalytic reaction zone is at least about 1500 standard cubic feet per barrel.

3. The process of claim 1 further characterized in that said catalytic reaction zone is maintained under an imposed pressure of at least about 400 p.s.i.g.

4. The process of claim 1 further characterized in that said catalytic composite in said second zone comprises alumina, a platinum component, a rhenium component and chlorine.

5. The process of claim 1 further characterized in that said catalytic composite in said second zone comprises alumina, a platinum component, a technetium component and chlorine.

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