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**Engineering Company**, Annandale,  
NJ (US)(52) **U.S. Cl. .... 208/58; 208/144**(21) Appl. No.: **13/327,838**(57) **ABSTRACT**(22) Filed: **Dec. 16, 2011**

The present invention relates to processes for increasing smoke point of a fuel. The process can be carried out using an upgrading catalyst that contains at least one noble metal supported on an inorganic, porous crystalline phase material. The catalyst is particularly effective in increasing smoke point, while minimizing reduction in total aromatics content, particularly naphthalene content.

**Related U.S. Application Data**(60) Provisional application No. 61/425,053, filed on Dec.  
20, 2010.

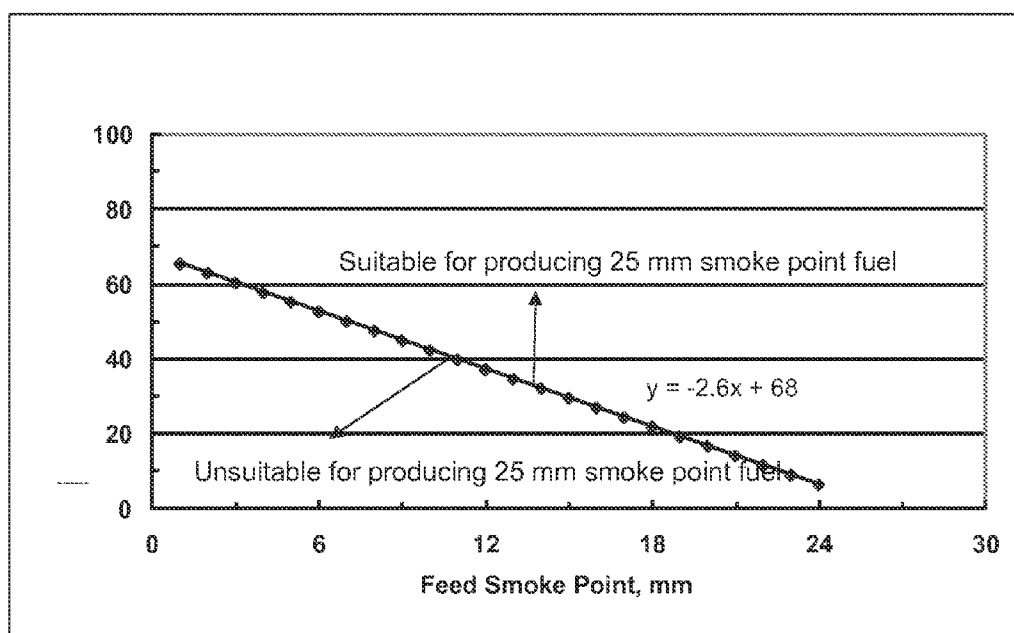


Fig. 1

## INCREASING FUEL SMOKE POINT

### FIELD OF THE INVENTION

[0001] This invention involves a process for increasing smoke point of a fuel. In particular, this invention has an aspect directed to a process for increasing smoke point of a fuel using an upgrading catalyst that contains at least one noble metal supported on an inorganic, porous crystalline phase material.

### BACKGROUND OF THE INVENTION

[0002] Fuels such as kerosene and aviation turbine fuels are required to meet smoke point requirements using standard test methods, such as by ASTM D 1322-08. Such a test method provides an indication of the relative smoke producing properties of the fuel in a diffusion flame.

[0003] The smoke point is quantitatively related to the potential radiant heat transfer from the combustion products of the fuel. Because radiant heat transfer exerts a strong influence on the metal temperature of combustor liners and other hot section parts of gas turbines, the smoke point provides a basis for correlation of fuel characteristics with the life of these components.

[0004] Smoke point is related to the hydrocarbon type composition of the fuel. Generally the more aromatic the fuel the smokier the flame. A high smoke point indicates a fuel of low smoke producing tendency, which is highly desirable.

[0005] The aromatics concentration of a fuel type hydrocarbon can be reduced by catalysts that have hydrogenation, dearomatization, and/or aromatic saturation functions. A number of such catalysts are known.

[0006] U.S. Patent Application Publication No. 2002/0112989, for instance, discloses a hydrocarbon hydrogenation process and a catalytic composition having such functionality. The catalytic composition includes at least two noble metals supported on an inorganic, porous crystalline phase support material. The crystalline support material includes the M41 S group of mesoporous crystalline materials, which is described in U.S. Pat. No. 5,102,643, and further includes MCM-41, which is described in U.S. Pat. No. 5,098,684, and MCM-48, which is described in U.S. Pat. Nos. 5,102,643 and 5,198,203. Similar support materials are indicated as being disclosed in U.S. Pat. No. 5,573,657. The noble metals are selected from the group consisting of Pd, Pt, Rh, and Ir, and the crystalline material is a metallosilicate or an aluminosilicate. The hydrocarbon hydrogenation process includes contacting a hydrocarbon feedstock containing aromatics, olefins, or aromatics and olefins with the catalytic composition under superatmospheric conditions, wherein the concentration of the aromatics, olefins, or aromatics and olefins in the product is reduced.

[0007] What is needed is a process for upgrading fuels that are already standard quality fuels to premium quality fuels. In particular, what is needed is a process for upgrading fuels to increase smoke point to premium quality standards, without negatively affecting already acceptable fuel properties.

### SUMMARY OF THE INVENTION

[0008] This invention provides processes air upgrading fuels to premium quality fuels. The process is particularly effective in increasing smoke point, without negatively affecting already acceptable fuel properties.

[0009] One aspect of the invention relates to a process for increasing smoke point of a fuel, comprising: providing a feedstock fuel having a smoke point from 18 mm to below 25 mm and a total aromatics content of  $A_r \geq 68 - 2.6S_m$ , wherein  $A_r$  is vol % total aromatics of the feedstock and  $S_m$  is the smoke point of the feedstock, provided that  $A_r$  is at least about 4 vol %; and contacting the feedstock fuel with a smoke point upgrading catalyst comprised of at least one noble metal hydrogenation component disposed on a support having an inorganic, porous crystalline phase material to provide a fuel product having a smoke point of at least 25 mm.

[0010] Another aspect of the invention relates to a process for increasing smoke point of a fuel, comprising: hydrocracking a mineral oil feedstock; providing from the hydrocracked mineral oil feedstock a first fuel having a smoke point from 18 mm to below 25 mm and a total aromatics content of  $A_r \geq 68 - 2.6S_m$ , wherein  $A_r$  is vol % total aromatics of the feedstock and  $S_m$  is the smoke point of the feedstock, provided that  $A_r$  is at least 4 vol %; and contacting the first fuel with a smoke point upgrading catalyst comprised of at least one noble metal hydrogenation component disposed on a support having an inorganic, porous crystalline phase material to provide a fuel product having a smoke point of at least 25 mm.

### BRIEF DESCRIPTION OF THE DRAWING

[0011] FIG. 1 is a graph showing characteristics of feedstock fuels suitable for producing at least 25 mm smoke point fuel product according to the invention.

### DETAILED DESCRIPTION OF THE INVENTION

#### Introduction

[0012] This invention provides a process for increasing the smoke point of a fuel. The process can be particularly effective in increasing the smoke point of fuels of standard quality to relatively high quality fuel.

[0013] The process can include contacting a feedstream that may already be of at least standard quality for alternately almost of standard quality) with a hydrogenation (aromatic saturation, dearomatization) catalyst that contains at least one noble metal supported on an inorganic, porous crystalline phase material. The catalytic process can be particularly effective in increasing smoke point, while minimizing reduction in naphthalene content, and at relatively mild hydrogenation conditions. This can be a particular advantage in upgrading fuels such as jet fuels that meet or come close to meeting standard fuel specifications, but need to have a higher smoke point in order to meet higher grade fuel specifications.

#### Feedstock Fuel Composition for Upgrading to Increase Smoke Point

[0014] The fuel provided as feedstock, or that can be treated according to this invention, to be upgraded to increase smoke point can be any one or more of kerosene, jet, and diesel grades of fuel, including mixtures within or overlapping the particular boiling ranges of each indicated fuel. The invention is particularly suited to producing jet fuel grades of fuel. Boiling point ranges are preferably determined according to ASTM D86-09e1 Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure.

[0015] In an embodiment, the fuel or feedstock that is treated according to this invention can have an initial and final boiling point within the range from about 90° C. to about 360° C., for example from about 100° C. to about 340° C., from

about 110° C. to about 320° C., or from about 120° C. to about 300° C. Additionally or alternately, the process can be carried out by contacting a catalyst with a feedstock fuel having an ASTM D86 10% distillation point (i.e., a T10, which represents the temperature at which ~10% of the feedstock would have boiled) within the range from about 110° C. to about 190° C., for example from about 115° C. to about 180° C. or from about 120° C. to about 60° C.

**[0016]** Further additionally or alternately, the process can be carried out by contacting a catalyst with a feedstock fuel having an ASTM D86 90% distillation point (i.e., a T90, which represents the temperature at which ~90% of the feedstock would have boiled) within the range from about 200° C. to about 290° C., for example from about 210° C. to about 280° C. or from about 220° C. to about 270° C.

**[0017]** The feedstock fuel to be upgraded to increase smoke point according to the present invention can typically already have a relatively high smoke point, but which may not be high enough to meet the minimum smoke point qualifications for Jet A or Jet A-1 aviation turbine fuels (according to ASTM D1655-09a Standard Specification for Aviation Turbine Fuels). Thus, in an embodiment, the feedstock fuel to be upgraded can have a smoke point of at least 18 mm, for example at least 19 mm, at least 20 mm, at least 21 mm, at least 22 mm, at least 23 mm, or at least 24 mm. Due to the fact that a feedstock fuel having a 25 mm smoke point or greater is considered of the highest grade, the feedstock fuel should typically also have a smoke point below 25 mm.

**[0018]** Due to the type of catalyst used to upgrade the feedstock according to this invention, there can be acceptable/minimal loss of naphthenics content during the upgrade process. However, since there should nevertheless be some loss of naphthenics, as well as total aromatics, due to saturation/hydrogenation of a portion of the aromatic components, the feedstock fuel to be upgraded to increase smoke point can preferably have a total aromatics content defined by the following inequality:  $A_r \geq 68 - 2.6S_m$ , wherein  $A_r$  is vol % total aromatics of the feedstock and  $S_m$  is the smoke point of the feedstock.

**[0019]** In any event, however, the feedstock should contain a sufficient level of aromatics compounds to allow for at least partial saturation/hydrogenation of aromatics and corresponding smoke point increase upon treatment in the presence of the catalyst according to the invention. As a result, the feedstock  $A_r$  can typically be at least about 4 vol %, based on the total feedstock volume. In some cases, the feedstock  $A_r$  can be at least about 6 vol %, for example at least about 10 vol %, at least about 15 vol %, or at least about 20 vol %, based on the total feedstock volume. Although there may not necessarily be an upper limit for  $A_r$ , limits on  $A_r$  can be desirable in some embodiments. For example, in various embodiments, the feedstock  $A_r$  can be no greater than about 50 vol %, based on the total weight of the feedstock, for example no greater than about 45 vol %, no greater than about 40 vol %, no greater than about 35 vol %, no greater than about 30 vol %, or no greater than about 25 vol %.

**[0020]** The feedstock to be upgraded according to the inventive process can generally have a relatively low sulfur content. However, the catalyst used according to this invention to upgrade the feedstock fuel can be relatively more tolerant of sulfur (and/or nitrogen), as compared to conventional catalysts capable of increasing smoke point. Thus, in an embodiment, the feedstock fuel to be upgraded according to this invention can have a sulfur content not greater than about

5000 wppm, for example not greater than about 3000 wppm, not greater than about 2000 wppm, or not greater than about 1000 wppm, as measured according to at least one of the following standard test methods: ATSMs D1266, D2622, D4294, and D5453.

#### Hydrocracked Mineral Oil as Feedstock

**[0021]** The feedstock provided according to this invention for upgrading to increase smoke point can be obtained from a mineral oil that has been hydrocracked. The term "mineral oil," as used herein, should be understood to represent a fossil/mineral fuel source, such as crude oil, and not the commercial organic product, such as sold under CAS number 8020-83-5, e.g., by Aldrich. Non-limiting examples of mineral oils can include straight run gas oils, vacuum gas oils, atmospheric gas oils, demetallized oils, coker distillates, cat cracker distillates (including light cycle oils and heavy cycle oils), atmospheric resids, vacuum resids, coal liquids, and combinations thereof that would be suitable for hydrocracking.

**[0022]** If desired, the present invention can include a step of hydrocracking (preferably through contact with hydrogen and an appropriate hydrocracking catalyst) a mineral oil feedstock, particularly in (but not limited to) the situation where the mineral oil feedstock had not been previously hydrocracked and/or where the mineral oil feedstock could benefit from being hydrocracked (again). The product of any hydrocracking of a mineral oil feedstock, whether within a step according to the invention or separately, can be referred to as a first fuel when it meets the feedstock fuel requirements as described herein. This first fuel can then be contacted with the catalyst according to the present invention to increase smoke point.

**[0023]** The mineral oil feedstock to be hydrocracked can generally contain some amount of nitrogen compounds (nitrogen content), which can in some embodiments be at least about 5 wppm, based on total weight of the feedstock, for example at least about 10 wppm, at least about 20 wppm, at least about 30 wppm, or at least about 50 wppm. Additionally or alternately, the mineral oil feedstock to be hydrocracked can have a nitrogen content of about 2.0 wt % or less, based on total weight of the feedstock, for example about 1.5 wt % or less, about 1.0 wt % or less, about 0.8 wt % or less, about 0.6 wt % or less, or about 0.5 wt % or less. In general, at least a majority of the nitrogen content can be in the form of organic nitrogen compounds.

**[0024]** Furthermore, the mineral oil feedstock to be hydrocracked can generally contain some amount of sulfur-containing compounds (sulfur content), which can in some embodiments be at least about 300 wppm, based on total weight of the feedstock, for example at least about 500 wppm, at least about 700 wppm, at least about 1000 wppm, at least about 1500 wppm, at least about 2000 wppm, or at least about 2500 wppm. Additionally or alternately, the mineral oil feedstock to be hydrocracked can have a sulfur content of about 6.0 wt % or less, based on total weight of the feedstock, for example about 4.0 wt % or less, about 2.5 wt % or less, about 1.5 wt % or less, about 1.0 wt % or less, or about 0.9 wt % or less.

**[0025]** In an embodiment, the mineral oil feedstock to be hydrocracked can have an initial boiling point of at least about 100° C., for example at least about 150° C., at least about 180° C., or at least about 200° C. Additionally or alternately, the mineral oil feedstock to be hydrocracked can have T5 boiling

point (i.e., the temperature below which about 5 wt % of the composition boils) of at least about 100° C., for example at least about 130° C., at least about 150° C., at least about 180° C., at least about 200° C., or at least about 210° C. Further additionally or alternately, the mineral oil feedstocks to be hydrocracked can have a final boiling point of about 600° C. or less, for example about 550° C. or less, about 500° C. or less, about 450° C. or less, about 425° C. or less, or about 400° C. or less. Additionally or alternately, the mineral oil feedstock to be hydrocracked can have T95 boiling point (i.e., the temperature below which about 95 wt % of the composition boils) of about 590° C. or less, for example about 550° C. or less, about 500° C. or less, about 450° C. or less, about 425° C. or less, about 400° C. or less, or about 375° C. or less. The basic test method of determining the boiling points/ranges of such feedstocks, as well as of fuel compositions produced according to the present invention, involves performing batch distillation according to ASTM D86-09e1, Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure.

**[0026]** It is noted that, although the feedstock (e.g., to be hydrocracked) is described herein as being a “mineral oil” feedstock, it may optionally contain an additional biocomponent portion. As used herein, an additional biocomponent portion refers to a hydrocarbonaceous component derived from a biological raw material component, from biocomponent sources such as higher plant (vegetable), animal, fish, and/or algae. Generally, these biocomponent sources can include higher plant (vegetable) fats/oils, animal fats/oils, fish oils, pyrolysis oils, and algae lipids/oils, as well as components of such materials, and in some embodiments can specifically include one or more type of lipid compounds. Lipid compounds are typically biological compounds that are relatively insoluble in water, but can be soluble in relatively nonpolar (or fat) solvents. Non-limiting examples of such solvents include alcohols, ethers, chloroform, alkyl acetates, benzene, and combinations thereof.

**[0027]** Major classes of lipids include, but are not necessarily limited to, fatty acids, glycerol-derived lipids (including fats, oils and phospholipids), sphingosine-derived lipids (including ceramides, cerebrosides, gangliosides, and sphingomyelins, steroids and their derivatives, terpenes and their derivatives, fat-soluble vitamins, certain aromatic compounds, and long-chain alcohols and waxes.

**[0028]** In living organisms, lipids generally serve as the basis for cell membranes and as a form of fuel storage. Lipids can also be found conjugated with proteins or carbohydrates, such as in the form of lipoproteins and lipopolysaccharides.

**[0029]** Examples of higher plant (vegetable) oils that can be used in accordance with this invention include, but are not limited to rapeseed (canola) oil, soybean oil, coconut oil, sunflower oil, palm oil, palm kernel oil, peanut oil, linseed oil, tall oil, corn oil, castor oil, jatropha oil, jojoba oil, olive oil, flaxseed oil, camelina oil, safflower oil, babassu oil, tallow oil and rice bran oil.

**[0030]** Higher plant (vegetable) oils as referred to herein can also include processed plant (vegetable) oil material. Non-limiting examples of processed vegetable oil material include fatty acids and fatty acid alkyl esters. Alkyl esters typically include C<sub>1</sub>-C<sub>5</sub> alkyl esters. One or more of methyl, ethyl, and propyl esters are preferred.

**[0031]** Examples of animal flits that can be used in accordance with the invention include, but are not limited to, beef fat (tallow), hog fat (lard), turkey fat, fish fat/oil, and chicken

fat. The animal fats can be obtained from any suitable source including restaurants and meat production facilities,

**[0032]** Animal fats as referred to herein also include processed animal fat material. Non-limiting examples of processed animal fat material include fatty acids and fatty acid alkyl esters. Alkyl esters typically include C<sub>1</sub>-C<sub>5</sub> alkyl esters. One or more of methyl, ethyl, and propyl esters are preferred.

**[0033]** Algae oils or lipids are typically contained in algae in the form of membrane components, storage products, and metabolites. Certain algal strains, particularly microalgae such as diatoms and cyanobacteria, contain proportionally high levels of lipids. Algal sources for the algae oils can contain varying amounts, e.g., from 2 wt % to 40 wt % of lipids, based on total weight of the biomass itself.

**[0034]** Algal sources for algae oils include, but are not limited to, unicellular and multicellular algae. Examples of such algae include a rhodophyte, chlorophyte, heterokontophyte, tribophyte, glaucophyte, chlorarachniophyte, euglenoid, haptophyte, cryptomonad, dinoflagellum, phytoplankton, and the like, and combinations thereof. In one embodiment, algae can be of the classes Chlorophyceae and/or Haptophyta. Specific species can include, but are not limited to, *Neochloris oleoabundans*, *Scenedesmus dimorphus*, *Euglena gracihiis*, *Phaeodactylum tricornutum*, *Pleurochrysis carterae*, *Prymnesium parvum*, *Toraelmis chui*, and *Chlamydomonas reinhardtii*. Additional or alternate algal sources can include one or more microalgae of the *Achnanthes*, *Amphiprora*, *Amphora*, *Ankistrodesmus*, *Asteromonas*, *Boekelovia*, *Borodinella*, *Botryococcus*, *Bracteococcus*, *Chaetoceros*, *Carteria*, *Chlamydomonas*, *Chloroecum*, *Chlorogonium*, *Chlorella*, *Chroomonas*, *Chgsosphaera*, *Cricosphaera*, *Copthecodinium*, *Cryptomonas*, *Cyclotella*, *Dunaliella*, *Ellipsoldon*, *Eremasphaera*, *Frnodesmius*, *Euglena*, *Francella*, *Eragilaria*, *Gloeothamnion*, *Haematococcus*, *Halocafeteria*, *Hymenomonas*, *Isochrysis*, *Lepocinclis*, *Ificractinium*, *Monoraphidium*, *Nannochloris*, *Nannochloropsis*, *Navicula*, *Neochloris*, *Nephrochloris*, *Nephroselmis*, *Nitzschia*, *Ochroinonas*, *Oedogonium*, *Oocystis*, *Ostreococcus*, *Pavlova*, *Parachlorella*, *Pascheria*, *Phaeodactylum*, *Phagus*, *Platymonas*, *Pleurochrysis*, *Pleurococcus*, *Prototheca*, *Pseudoehlorella*, *Pyramimonas*, *Pyrobrotys*, *Scenedesmus*, *Skeletonema*, *Spyrogyra*, *Stichococcus*, *Tetrayelmis*, *Thalassiosira*, *Viridiella*, and *Volvox* species, and/or one or more cyanobacteria of the *Agmenedurn*, *Anabaena*, *Anabaenopsis*, *Anacystis*, *Aphanizomenon*, *Arthrospira*, *Asterocapsa*, *Borzia*, *Calothrix*, *Chamaesiphon*, *Chlorogloeopsis*, *Chroococcidhpsis*, *Chroococcus*, *Crinallium*, *Cyanobacterium*, *Cyanobium*, *Cyanocylis*, *Cyanospira*, *Cyanothee*, *Cylindrospermopsis*, *Cylindrospermum*, *Dactylococcopsis*, *Dermocarpella*, *Fischerella*, *Fremyella*, *Geitleria*, *Geitlerinema*, *Gloeobacter*, *Gloeocapsa*, *Gloeotheca*, *Halospirulina*, *Iyengariella*, *Leptolyngbya*, *Limnithrix*, *Lyngbya*, *Microcoleus*, *Microcystis*, *Myxosarcina*, *Nodularia*, *Nosioc*, *Nostochopsis*, *Oseillatoria*, *Phormidium*, *Planktothrix*, *Pleurocapsa*, *Prochlorococcus*, *Prochloron*, *Prochlorothrix*, *Pseudanabaena*, *Rivularia*, *Sehizothrix*, *Scytonema*, *Spirulina*, *Stanieria*, *Starria*, *Stigonema*, *Symploca*, *Synechococcus*, *Synechocystis*, *Thlypothrix*, *Trichodesmium*, *Tychonema*, and *Xenococcus* species.

**[0035]** When present in mineral oil feedstocks, the biocomponent portion can comprise less than 50 wt %, based on the total weight of the feedstock material, for example about 40 wt % or less, about 30 wt % or less, about 25 wt % or less,

about 20 wt % or less, about 15 wt % or less, about 10 wt % or less, or about 5 wt % or less. Additionally, when present in mineral oil feedstocks, the biocomponent portion can optionally comprise at least about 0.1 wt %, for example at least about 0.5 wt %, at least about 1.0 wt %, at least about 1.5 wt %, at least about 2.0 wt %, at least about 2.5 wt %, or at least about 5 wt %.

**[0036]** Hydrocracking refers to a process by which certain hydrocarbon molecules in a provided feedstock are broken into simpler molecules to produce a fuel product. Typically, the feedstock to be upgraded can include one or more fuels such as gasoline, kerosene, jet fuel, and diesel, and these individual fuels can be separated into their component parts, if desired, e.g., by fractionation.

**[0037]** A hydrocracking step can be carried out by contacting the mineral oil feedstock with a hydrocracking catalyst in the presence of hydrogen to form the product. The addition of hydrogen can provide further benefit to the cracking aspect of the step in that the fuel product produced can be more saturated and/or reduced in aromatic content, and/or can typically have a reduced content of undesirable components such as heteroatoms nitrogen, oxygen, and/or sulfur.

**[0038]** In an embodiment, the hydrocracking catalyst can be comprised of an amorphous and/or zeolitic support/base and a hydrogenation component comprising one or more metals from Groups 6 and 8-10 of the Periodic Table of Elements (e.g., Fe, Co, Ni, Mo, and/or W). Zeolitic cracking supports/bases can also be referred to as molecular sieves, which may be composed of silica, alumina, and typically (but not necessarily) one or more exchangeable cations, such as sodium, magnesium, calcium, a rare earth metal, or a combination thereof. Examples of zeolitic molecular sieves that can be used in the hydrocracking catalyst can include, but are not limited to, Zeolite Beta, Zeolite X, Zeolite Y, faujasite, Ultrastable Y (USY), Dealuminized Y (Deal Y), Mordenite, ZSM-3, ZSM-4, ZSM-5, ZSM-18, ZSM-20, and combinations thereof.

**[0039]** In one embodiment, the hydrocracking catalyst can comprise a large pore crystalline molecular sieve, e.g., having a Constraint Index of less than 2, or less than 1. The method by which the Constraint Index can be determined is fully described in U.S. Pat. No. 4,016,218, which is incorporated herein by reference.

**[0040]** Additionally or alternately, the hydrocracking catalyst can comprise a molecular sieve having a pore size of at least about 7 Å, for example at least about 7.4 Å or at least about 8 Å. Further additionally or alternately, the hydrocracking catalyst can comprise a molecular sieve having a pore size of about 18 Å or less, for example about 15 Å or less.

**[0041]** It can be preferred in some embodiments for the hydrocracking catalyst to have at least some acidity. The alpha value is a measure of zeolite acidic functionality and is described in greater detail in U.S. Pat. No. 4,016,218 and in *J. Catalysis*, Vol. VI, pages 278-87 (1966). Thus, in various embodiments, the hydrocracking catalyst can have an alpha value greater than 1, for example greater than 5 or greater than 10. It is not necessary that the hydrocracking catalyst be highly acidic, although a highly acidic catalyst can be used. Therefore, additionally or alternately, the hydrocracking catalyst can have an alpha value of not greater than 200, for example not greater than 100.

**[0042]** Hydrocracking can be carried out under conditions effective for producing the desired fuel product, which can include one or more of: an average reaction temperature from

about 300° F. (about 149° C.) to about 900° F. (about 482° C.), for example from about 550° F. (about 289° C.) to about 800° F. (about 427° C.); an average reaction pressure from about 400 psia (about 2.8 MPaa) to about 3000 psia (about 20.7 MPaa), for example from about 500 psia (about 3.5 MPaa) to about 2000 psia (about 13.8 MPaa); a hydrogen-containing treat gas rate from about 300 scf/bbl (about 51 Sm<sup>3</sup>/m<sup>3</sup>) to about 5000 scf/bbl (about 850 Sm<sup>3</sup>/m<sup>3</sup>), for example from about 1000 scf/bbl (about 170 Sm<sup>3</sup>/m<sup>3</sup>) to about 4000 scf/bbl (about 680 Sm<sup>3</sup>/m<sup>3</sup>); and a liquid hourly space velocity (LHSV), in volumes/volume/hour (v/v/hr or hr<sup>-1</sup>), from about 0.1 hr<sup>-1</sup> to about 20 hr<sup>-1</sup>, for example from about 1 hr<sup>-1</sup> to about 10 hr<sup>-1</sup>.

**[0043]** Treat gas, as referred to in this invention, can be either pure hydrogen or a hydrogen-containing treat gas, so long as hydrogen is present in an amount at least sufficient for the intended reaction(s). If the hydrogen is not pure, other gas(es) can be present (e.g., nitrogen, light hydrocarbons such as methane, and the like, and combinations thereof), advantageously which gas(es) substantially do not adversely interfere with or affect either the reactions or the products. Impurities, such as H<sub>2</sub>S and NH<sub>3</sub>, can be generally undesirable and can thus be removed from the treat gas before it is conducted to the reactor. The treat gas stream can contain at least about 50 vol % hydrogen, preferably at least about 70 vol %, at least about 80 vol %, or at least about 90%.

**[0044]** Any type of reactor suitable for hydrocracking can be used to carry out the step. Examples of such reactors can include, but are not limited to, trickle bed, ebullating bed, moving bed, and slurry reactors.

**[0045]** One or more fractions can be removed/recovered from the hydrocracked product as the first fuel composition to be upgraded to increase smoke point according to the present invention. Like the mineral oil feedstock, the first fuel for upgrading to increase smoke point can be fractionated from hydrocracked product into at least one fractionated first fuel component, e.g., selected from the group consisting of gasoline, kerosene, jet fuel, diesel, and combinations thereof.

**[0046]** In one embodiment, the smoke point upgrading process can be carried out to produce and/or recover a kerosene type or a gasoline type jet fuel. For instance, a kerosene type jet fuel can be produced/recovered according to the inventive process so as to exhibit an ASTM D86 90% distillation point within the range from about 250° C. to about 290° C., for example from about 260° C. to about 280° C. Additionally or alternately in such an embodiment, a kerosene type jet fuel can be produced/recovered according to the inventive process so as to exhibit an ASTM D86 10% distillation point within the range from about 150° C. to about 200° C., for example from about 160° C. to about 180° C. In an alternate embodiment, a gasoline type jet fuel can be produced/recovered according to the inventive process so as to exhibit an ASTM D86 90% distillation point within the range from about 200° C. to about 240° C., for example from about 210° C. to about 230° C. Additionally or alternately in such an embodiment, a gasoline type jet fuel can be produced/recovered according to the inventive process so as to exhibit an ASTM D86 10% distillation point within the range from about 110° C. to about 40° C., for example from about 120° C. to about 130° C.

**[0047]** In another embodiment, the smoke point upgrading process can be carried out to produce and/or recover a diesel fuel. For instance, a diesel fuel can be produced/recovered according to the inventive process so as to exhibit an ASTM D86 90% distillation point within the range from about 260°

C. to about 350° C., for example from about 280° C. to about 340° C. Additionally or alternately, a diesel fuel can be produced/recovered according to the inventive process so as to exhibit an ASTM D86 10% distillation point within the range from about 200° C. to about 240° C., for example from about 210° C. to about 230° C.

#### Smoke Point Upgrading Catalyst

**[0048]** Highly active upgrading catalysts, which can be more sulfur and/or nitrogen tolerant than other, can be used to increase the smoke point of the feedstock fuel according to the process of the invention. Such upgrading catalysts can generally contain a hydrogenation component comprising at least one Group VIII noble metal (e.g., Pt, Pd, Ru, Rh, Ir, or a combination thereof), for example at least two Group VIII noble metals, disposed on a support having an inorganic, porous crystalline phase material.

**[0049]** Crystalline support materials suitable for use in the upgrading catalyst can include the M41S group of mesoporous crystalline materials, which are described in U.S. Pat. No. 5,102,643. Specific examples of such support materials can include, but are not limited to, MCM-41 and MCM-48. MCM-41, which is described in U.S. Pat. No. 5,098,684, is characterized by a microstructure with a relatively uniform, hexagonal arrangement of pores with diameters of at least about 13 Å. MCM-48 has a cubic structure and is described in U.S. Pat. Nos. 5,026,643 and 5,198,203.

**[0050]** In one preferred embodiment, the smoke point upgrading catalyst can comprise an MCM-41 support material on which both platinum and palladium hydrogenation metals are disposed. The Pt/Pd/MCM-41 catalyst can produce high-quality jet and diesel fuels by reducing smoke point highly efficiently.

**[0051]** Additionally or alternately, the upgrading catalytic material according to the invention can include an ultra-large pore size crystalline phase as a support for the hydrogenation component, which crystalline phase material can be characterized (in its calcined form) by an X-ray diffraction (XRD) pattern having at least one peak corresponding to a d-spacing greater than about 18 Å with a relative intensity normalized to about 100 (e.g., which can represent the largest resolvable peak in the XRD spectrum) and/or can be characterized by an equilibrium benzene sorption capacity of at least about 1.5 grams of benzene per 100 grams of material at about 50 torr (about 6.7 kPaa) and at about 25° C. Further additionally or alternately, the upgrading catalytic material according to the invention can include an inorganic, porous support material having a hexagonal pore with a maximum perpendicular cross-section pore dimension of not less than about 13 Å, for example from about 13 Å to about 200 Å (also termed “mesoporous”) or from about 15 Å to about 110 Å.

**[0052]** Equilibrium benzene adsorption capacity can be determined by contacting a material at about 25° C. and at about 50 torr (about 6.7 kPaa) with benzene until equilibrium is reached, after which the weight of sorbed benzene can then be determined. The material, e.g., usable as support material according to the invention, should generally be tested only after thermal treatment at a temperature of about 540° C. for at least one hour, e.g., in an attempt to remove any pore blocking contaminants.

**[0053]** Still further additionally or alternately, the upgrading catalytic material according to the invention can include

an inorganic mesoporous crystalline material as a support having the following composition:

$$M_{n/q}(W_aX_bY_cZ_dO_h) \quad (1)$$

wherein: W is an element having a divalent ion, such as a divalent first row transition metal (e.g., manganese, cobalt, iron, and/or magnesium, preferably containing cobalt); X is an element having a trivalent ion, such as aluminum, boron, iron, and/or gallium (preferably containing aluminum); Y is an element having a tetravalent ion, such as silicon and/or germanium (preferably containing silicon); Z is an element having a pentavalent ion, such as phosphorus; M is one or more ions whose valence is an integer multiple of n/q, and which can include, but is not limited to, ammonium, a mono-, di-, tri-, or tetra-alkylammonium, one or more ions of Groups IA, IIA, and VIIB of the Periodic Table of Elements (e.g., hydrogen, sodium, and/or fluoride); the subscript n represents the charge of the composition, excluding M, expressed as oxides; the subscript q represents the weighted molar average valence of M; the subscripts a, b, c, and d represent the mole fractions of W, X, Y and Z, respectively; the subscript h is a number of from 1 to 2.5; and (a+b+c+d)=1.

**[0054]** In one such embodiment, the inorganic mesoporous crystalline material defined by equation (1) can be further defined by (a+b+c) being greater than d, and by h being 2. Additionally or alternately, both a and d can be 0, and h can be 2. Examples of materials that satisfy such definitions can include aluminosilicates, although other metasilicates can be suitable for use according to the invention.

**[0055]** In the as-synthesized form, the support material having the composition defined by equation (1) can additionally have a composition, on an anhydrous basis, expressed empirically as follows:

$$rRM_{n/q}(W_aX_bY_cZ_dO_h) \quad (2)$$

wherein M, W, X, Y, Z, n, q, a, b, c, d, and h are defined as above; R is the total organic material not included in M as an ion; and r is the coefficient for R the number of moles, or mole fraction, of R). The M and R components can be associated with the material as a result of the presence during crystallization of components that may not be present in the dried and/or calcined product, and which can thus be easily removed or, in the case of M, replaced by post-crystallization.

**[0056]** To the extent desired, the original M (e.g., sodium and/or chloride) ions of the as-synthesized material can be replaced in accordance with conventional ion-exchange techniques. Examples of ions for replacing the original M can include, but are not limited to, metal ions, hydrogen ions, hydrogen precursor (e.g., ammonium) ions, and mixtures thereof. When utilized, the replacing ions can, in some embodiments, provide at least a significant portion of the desired metal (hydrogenation component) functionality in the final catalyst. Such ions can therefore include hydrogen, rare earth metals, Group 7 metals (e.g., Mn), Group 8-10 metals (e.g., Ni), Group 11 metals (e.g., Cu), Group 14 metals (e.g., Sn) (each from the Periodic Table of Elements), and mixtures thereof.

**[0057]** Such inorganic mesoporous crystalline materials can be distinguished from other porous inorganic solids by the regularity of its large open pores, whose pore size more nearly resembles that of amorphous or paracrystalline materials, but whose regular arrangement and uniformity of size (e.g., having a pore size distribution within a single phase of, for instance, ±25% or less, usually ±15% or less, of the average pore size of that phase) can tend to resemble more those of crystalline framework materials such as zeolites. The term “hexagonal,” with reference to pores, should be under-

stood herein to encompass not only materials that exhibit mathematically perfect hexagonal symmetry within the limits of experimental measurement, but also those with significant observable deviations from that ideal state, so long as most channels in the material are surrounded by six nearest neighbor channels at roughly the same distance. Defects and imperfections can cause significant numbers of channels to violate this criterion to varying degrees, depending on the quality of the material's preparation. However, samples which exhibit as much as  $\pm 25\%$  random deviation from the average repeat distance between adjacent channels can still show recognizable XRD and/or neutron scattering order. Comparable variations can similarly be observed in the  $d_{100}$  values from electron/x-ray diffraction patterns.

**[0058]** The most regular preparations of support material suitable for upgrading catalysts according to the invention can show XRD patterns with a few distinct maxima in the extreme low (2-theta) angle region. The positions of such maxima (peaks) approximately fit the positions of certain  $hk0$  reflections from a hexagonal crystalline lattice. XRD spectra, however, may not always be a sufficient indicator of the presence of such order, as the degree of regularity in the microstructure and/or the extent of repetition of the structure within individual particles can affect the number and/or position of peaks observed. For instance, preparations with only one distinct peak in the low angle region of an XRD spectrum have been found to contain substantial amounts of mesoporous material. Thus, other techniques, such as transmission electron microscopy (TEM) and electron diffraction, can be used to elucidate details of the microstructure. In some embodiments, properly oriented specimens of mesoporous material can show a hexagonal arrangement of large channels, and the corresponding electron diffraction pattern can yield an approximately hexagonal arrangement of diffraction maxima. The  $d_{100}$  spacing of the electron diffraction patterns can be described as the distance between adjacent spots on the  $hk0$  projection of the hexagonal lattice and can be related to the repeat distance,  $a_0$ , between channels observed in electron micrographs through the formula  $d_{100} = a_0(3/2)^{1/2}$ . This  $d_{100}$  spacing observed in certain electron diffraction patterns can correspond to the d-spacing of an XRD low angle peak of mesoporous material.

**[0059]** In some embodiments, in its calcined form, the crystalline support material may be further characterized by an XRD spectrum with at least one peak at a position corresponding to at least about an 18 Å d-spacing ( $\leq 4.91^\circ 2\theta$ , for Cu—K $\alpha$  radiation), which can correspond to the  $d_{100}$  value of an electron diffraction pattern, and by an equilibrium benzene adsorption capacity of at least about 15 grams of benzene per 100 grams of material at about 50 torr (about 6.7 kPaa) and at about 25° C. (which equilibrium benzene adsorption capacity is measured on the basis of no pore blockage by incidental contaminants, such as water and/or inorganic amorphous materials such as silica, which can be removed by dehydration techniques, e.g., thermal treatment, and/or chemical techniques, e.g., acid/base treatments, such that any detrimental material can be removed, preferably without significant detrimental effect).

**[0060]** In an embodiment, a calcined, crystalline, non-layered material that can be used as a support material according to this invention can be characterized by an XRD spectrum with at least two peaks at positions corresponding to at least about a 10 Å d-spacing ( $\leq 8.84^\circ 2\theta$ , for Cu—K $\alpha$  radiation), at least one of which can be at a position corresponding to at

least about an 18 Å d-spacing ( $\leq 4.91^\circ 2\theta$ , for Cu—K $\alpha$  radiation), and none of which peaks can correspond to at least about a 1.0 Å d-spacing having a relative intensity greater than about 20% of the magnitude of the strongest XRD peak, for example having a relative intensity greater than about 10%. In this embodiment, at least one peak in the XRD spectrum can advantageously have a d-spacing that corresponds to the  $d_{100}$  value of the electron diffraction pattern of the material.

**[0061]** If an ammonium-containing form of catalytic support material is made, it can be converted to the hydrogen form, e.g., by thermal treatment (calcination), which can be performed at a temperature from about 400° C. to about 750° C. for a time from about 1 minute to about 20 hours, for example from about 1 hour to about 10 hours. While sub-atmospheric pressure can be employed for such thermal treatments, atmospheric pressure can be preferable in some embodiments, for reasons of convenience, in an environment comprising air, nitrogen, and/or ammonia, optionally with one or more other gases, as desired.

**[0062]** Where sulfur and other contaminants such as phosphorus are present only in relatively low concentrations in the feedstock (e.g., a sulfur content of about 50 wppm or less, such as about 30 wppm or less, about 20 wppm or less, or about 10 wppm or less, and a phosphorous content about 20 wppm or less, such as about 10 wppm or less or about 5 wppm or less), a combination of at least two noble metals can be preferred. Where at least two noble metals are used as hydrogenation components, a preferred example includes the combination of Pd and Pt. In addition to the synergistic benefit which a combination of platinum and palladium provides with respect to hydrogenation activity, the palladium metal can optionally also provide the catalyst composition with an added resistance to nitrogen poisoning.

**[0063]** The content of the hydrogenation component can vary according to catalytic activity. Thus, highly active (noble) metals may be used in relatively smaller amounts. However, increasing loading may nevertheless be desirable, e.g., to the extent that the catalyst has low cracking activity, to maintain a relatively high activity for smoke point upgrading, e.g., through hydrogenation, dearomatization, and/or aromatic saturation, which can improve product quality by increasing API density, increasing cetane index/number, or the like, or a combination thereof.

**[0064]** At least one noble metal can be disposed on the support material in a total noble metal concentration from about 0.01 wt % to about 10 wt %, based on the total weight of the catalyst, with individual noble metal concentrations being from about 0.01 wt % to about 5 wt %, from about 0.05 wt % to about 3 wt %, or from about 0.1 wt % to about 2 wt %. In embodiments where more than one noble metal is present, each individual noble metal can have a concentration from about 0.01 wt % to about 5 wt %, based on the total weight of the catalyst.

**[0065]** The hydrogenation component metal can be exchanged onto the support material, impregnated into it, physically admixed with it, or a combination thereof. If the metal is impregnated into or exchanged onto the support material, it can be accomplished in one embodiment by treating the support with a metal-containing ion, e.g., containing Pt and/or Pd. Suitable platinum ion forming compounds can include, but are not limited to, chloroplatinic acid, platinumous chloride, various compounds containing a platinum amine complex, and combinations thereof. The metal-containing



ion can additionally or alternately manifest in a cation or anion form. Non-limiting examples of such palladium and/or platinum compounds can include ammonia chlorides complexes (e.g.,  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$  and  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ ), anionic nitrate complexes, anionic vanadate complexes, and anionic metatungstate ions. Ionic forms of hydrogenation metals can be rather useful, as they may be exchanged onto the crystalline material or impregnated into it.

**[0066]** In various embodiments, in addition to a support material on which at least one noble metal can be disposed, the smoke point upgrading catalyst can contain a binder material. The binder material can, in many embodiments, comprise or be a refractory inorganic oxide, for example one or more of alumina, silica, silica-alumina, titania, zirconia, and magnesia, inter alia.

#### Smoke Point Upgrading Conditions

**[0067]** Smoke point upgrading of the feedstock/fuel into a premium feedstock can preferably be carried out at conditions including a relatively mild average reactor temperature, for example from about 100° C. to about 300° C., from about 125° C. to about 275° C. or from about 175° C. to about 225° C., Additionally or alternately, since the feedstock to be upgraded to increase smoke point can typically be relatively low in sulfur content, low to moderate pressures can be used, for example from about 50 psig (about 450 kPag) to about 2000 psig (about 17.8 MPag) or from about 300 psig (about 2.1 MPag) to about 1000 psig (about 6.9 MPag). Further additionally or alternately, smoke point upgrading can be effectively carried out at LHSV's from about 0.3 hr<sup>-1</sup> to about 10 hr<sup>-1</sup>, for example from about 1 hr to about 5 hr<sup>-1</sup>. Still further additionally or alternately, smoke point upgrading can be effectively carried out by applying a hydrogen-containing treat gas, for example at a hydrogen treat gas rate from about 34 Sm<sup>3</sup>/m<sup>3</sup> (about 200 scf/bbl) to about 1700 Sm<sup>3</sup>/m<sup>3</sup> (about 10000 scf/bbl) or from about 85 Sm<sup>3</sup>/m<sup>3</sup> (about 500 scf/bbl) to about 850 Sm<sup>3</sup>/m<sup>3</sup> (about 5000 scf/bbl).

#### Upgraded Product

**[0068]** The upgraded fuel product produced according to the inventive process can have a relatively high smoke point, for example at least 25 mm, which is believed to be indicative of premium quality jet fuels, such as Jet A and/or Jet A-1 aviation turbine fuels.

**[0069]** Additionally or alternately, the smoke point upgrading process can be carried out to produce and/or recover a kerosene type or a gasoline type jet fuel. For instance, a kerosene type jet fuel can be produced/recovered according to the inventive process so as to exhibit an ASTM D86 90% distillation point within the range from about 250° C. to about 290° C., for example from about 260° C. to about 280° C. Additionally or alternately in such an embodiment, a kerosene type jet fuel can be produced/recovered according to the inventive process so as to exhibit an ASTM D86 10% distillation point within the range from about 150° C. to about 200° C., for example from about 160° C. to about 180° C. In an alternate embodiment, a gasoline type jet fuel can be produced/recovered according to the inventive process so as to exhibit an ASTM D86 90% distillation point within the range from about 200° C. to about 240° C., for example from about 210° C. to about 230° C. Additionally or alternately in such an embodiment, a gasoline type jet fuel can be produced/recovered according to the inventive process so as to exhibit an

ASTM D86 10% distillation point within the range from about 110° C. to about 140° C. for example from about 120° C. to about 130° C.

#### Additional Embodiments

**[0070]** The present invention can additionally or alternately include one or more of the following embodiments.

**[0071]** Embodiment 1. A process for increasing smoke point of a fuel, comprising: providing a feedstock fuel having a smoke point from 18 mm to below 25 mm and a total aromatics content of  $A_r \geq 68 - 2.6S_m$ , wherein  $A_r$  is vol % total aromatics of the feedstock and  $S_m$  is the smoke point of the feedstock, provided that  $A_r$  is at least about 4 vol %; and contacting the feedstock fuel with a smoke point upgrading catalyst comprised of at least one noble metal hydrogenation component disposed on a support having an inorganic, porous crystalline phase material to provide a fuel product having a smoke point of at least 25 mm.

**[0072]** Embodiment 2. The process of embodiment 1, further comprising hydrocracking a mineral oil feedstock under conditions sufficient to provide the feedstock fuel.

**[0073]** Embodiment 3. The process of embodiment 1 or embodiment 2, wherein the feedstock fuel exhibits one or more of: an initial and final boiling point within the range from about 90° C., to about 360° C.; an ASTM D86 10% distillation point within the range from about 110° C. to about 190° C.; a total aromatics content of at least about 6 vol %; a total aromatics content of not greater than about 25 vol %; a smoke point of at least 19 mm; and a sulfur content of not greater than about 3000 wppm.

**[0074]** Embodiment 4. The process of any one of the previous embodiments, wherein the smoke point upgrading catalyst comprises a support material comprising an inorganic, porous crystalline phase material having pores with diameters of at least about 13 Å and exhibiting, after thermal treatment, an XRD spectrum having at least one peak corresponding to a d-spacing greater than about 18 Å with a relative intensity of about 100, and having an equilibrium benzene sorption capacity of at least about 15 grams of benzene per 100 grams of material at about 50 torr (about 6.7 kPa) and at about 25° C.

**[0075]** Embodiment 5. The process of any one of the previous embodiment, wherein the at least one noble metal is selected from the group consisting of Pd, Pt, Rh, Ru, Ir, and combinations thereof.

**[0076]** Embodiment 6. The process of any one of the previous embodiments, wherein crystalline phase material is a metasilicate or an aluminosilicate.

**[0077]** Embodiment 7. The process of any one of the previous embodiments, wherein the at least one noble metal is present on the catalyst in an amount from about 0.01 wt % to about 5 wt %, based on total catalyst weight.

**[0078]** Embodiment 8. The process of any one of the previous embodiments, wherein the at least one noble metal is bound by a refractory inorganic oxide selected from the group consisting of alumina, silica, silica-alumina, titania, zirconia, magnesia, and combinations thereof.

**[0079]** Embodiment 9. The process of any one of the previous embodiments, wherein the smoke point upgrading catalyst is a Pt/Pd-containing M41S catalyst or a Pt/Pd-containing MCM-41 catalyst.

#### EXAMPLES

##### Example 1

**[0080]** An ~11,500 barrel per day kerosene upgrading process was designed to upgrade a vacuum gas oil (VGO) hydro-

cracker kerosene feed to 25 mm smoke point jet fuel according to computer simulation. In this Example, two catalysts were compared: a Pt/Pd upgrading catalyst on a support having an inorganic, porous crystalline phase material according to the invention (e.g., a Pt/Pd-modified MCM-41) and a commercial Pt/Pd catalyst on alumina support. Table 1 shows the feed properties.

TABLE 1

Feed Rate, BPSD	11550
Feed Rate, m <sup>3</sup> /hr	76.5
API Gravity	43.8
Specific Gravity @ ~15° C.	0.807
Total Sulfur, wppm	<1
Total Nitrogen, wppm	<1
Smoke Point, mm	18
Freeze Point, ° C.	<-47
Flash Point D93, ° C.	51
Kinematic Visc @ ~40° C., cSt	1.5
Total Aromatics, vol %	25
Naphthenics, vol %	1.5
ASTM D86 distillation, ° C.	
IBP	170
5%	171
10%	171
30%	182
50%	192
70%	201
90%	210
95%	216
FBP	221

[0081] In order to control the temperature rise across the catalyst bed, e.g., due to the high heat release associated with the aromatic saturation reaction, some of the product was recycled back to the reactor. The recycle rate was set to be about 50 vol % of the feed rate. For this case, the total feed to the reactor was about 17250 barrels per day, as shown below in Table 2:

TABLE 2

	B/D	m <sup>3</sup> /hr
Raw Kerosene	11500	76.5
Product Recycle	5750	38.3
Total Feed	17250	115

[0082] A large number of catalyst beds could be used to control the heat release for each catalyst bed. However, this approach could be impractical, since bed length can be too short to give acceptable flow dynamics, and since it would require the use of a very large recycle compressor to provide the amount of quench gas needed to control the overall reactor temperature across the entire reactor.

[0083] The total catalyst volume used was 30 m<sup>3</sup>, divided into two catalyst beds for the both cases, where the first bed volume was about 10 m<sup>3</sup> and the second bed volume was about 20 m<sup>3</sup>.

[0084] The operating conditions were set to be as follows:

Product Recycle Rate, vol %	~50
Inlet Total Pressure, barg	~50
Make-Up H <sub>2</sub> Gas Rate, Sm <sup>3</sup> /m <sup>3</sup>	~71.7
Make-Up H <sub>2</sub> Purity, %	~98.2

-continued

Recycle Gas Rate, Sm <sup>3</sup> /m <sup>3</sup>	~350
Purge Gas Rate, Sm <sup>3</sup> /m <sup>3</sup>	~3

It should be noted that gas flow rates in these operating conditions are based on the total feed rate.

[0085] The comparison between the catalysts in this Example was made at the same reaction temperature. For commercial operation, the reaction temperature can be defined as WABT (weighted average bed temperature), which is defined as follows:

$$\text{WABT} = \text{Catalyst bed inlet temperature} + \frac{1}{2} \Delta T,$$

wherein  $\Delta T$  represents the temperature rise across the catalyst bed. As shown in Table 3, the operating conditions were simulated at the same WABT for each catalyst bed for the both catalysts.

TABLE 3

		Commercial Catalyst	Pt/Pd MCM-41 catalyst
Catalyst Recycle Rate on Feed	vol %	~50	~50
	Bed-1		
Temperature-Inlet	° C.	~214	~186
Temperature-Outlet	° C.	~238	~210
DT	° C.	~24	~24
WABT	° C.	~230	~202
	Bed-2		
Temperature-Inlet	° C.	~224	~196
Temperature-Outlet	° C.	~257	~234
DT	° C.	~33	~38
WABT	° C.	~246	~221
Cumulative WABT	° C.	~240	~215

[0086] As can be seen from Table 4 below, which shows fuel yields and product properties, the smoke point attained with the catalyst used according to this invention was substantially higher than the comparative commercial catalyst. Although total aromatics content of the catalyst used according to this invention was substantially lower than that of the comparative commercial catalyst, the naphthalenes content was a bit higher.

TABLE 4

		Commercial Catalyst	Pt/Pd MCM-41 Catalyst
Recycle Rate on Feed	vol %	~50	~50
API Gravity		~45.9	~46.6
Specific Gravity @ ~60° F.		~0.798	~0.794
Freeze Point	° C.	<-47	<-47
Smoke Point	mm	~24	~26
Total Aromatics content	vol %	~8.4	~3.8
Naphthalenes content	wt %	~0.003	~0.012

## Example 2

[0087] Unexpectedly, it has also been found that not all fuels in the jet fuel boiling point range can be upgraded to produce a smoke point greater than 25, as shown in Table 5 below.

TABLE 5

Sample #	Smoke Point mm	Aromatic Content vol %	Can Produce >25 mm Smoke Point Fuel? Yes or No
1	7	70.5	Yes
2	7	78.6	Yes
3	9	58.3	Yes
4	12.5	31.5	No
5	12.5	55.7	Yes
6	13	54.2	Yes
7	13	46	Yes
8	13	54.7	Yes
9	15	31.5	Yes
10	16	9.2	No
11	21	22.6	Yes
12	22	2.9	No
13	22	14.7	Yes
14	23	16.5	Yes
15	23	22.7	Yes
16	24	22.6	Yes
17	24	4	No

**[0088]** To produce at least a 25 mm smoke point fuel, the minimum aromatic content required can be a function of the original smoke point of the feed, e.g., as shown in FIG. 1. As shown in the FIG. 1, the feeds suitable for producing at least a 25 mm smoke point fuel should have an aromatic content as follows:  $A_r \geq 68 - 2.6S_m$ , wherein  $A_r$  is vol % aromatics of the feedstock and  $S_m$  is the smoke point of the feedstock.

**[0089]** The principles and modes of operation of this invention have been described above with reference to various exemplary and preferred embodiments. As understood by those of skill in the art, the overall invention, as defined by the claims, may encompass other preferred embodiments not specifically enumerated herein.

What is claimed is:

1. A process for increasing smoke point of a fuel, comprising:

providing a feedstock fuel having a smoke point from 18 mm to below 25 mm and a total aromatics content of  $A_r \geq 68 - 2.6S_m$ , wherein  $A_r$  is vol % total aromatics of the feedstock and  $S_m$  is the smoke point of the feedstock, provided that  $A_r$  is at least about 4 vol %; and

contacting the feedstock fuel with a smoke point upgrading catalyst comprised of at least one noble metal hydrogenation component disposed on a support having an inorganic, porous crystalline phase material to provide a fuel product having a smoke point of at least 25 mm.

2. The process of claim 1, wherein the feedstock fuel has an initial and final boiling point within the range from about 90° C. to about 360° C.

3. The process of claim 1, wherein the feedstock fuel has an ASTM D86 10% distillation point within the range from about 110° C. to about 190° C.

4. The process of claim 1, wherein the feedstock fuel has a total aromatics content of at least about 6 vol %.

5. The process of claim 4, wherein the feedstock fuel has a smoke point of at least 19 mm.

6. The process of claim 1, wherein the feedstock fuel has a total aromatics content of not greater than about 25 vol %.

7. The process of claim 1, wherein the feedstock fuel has a sulfur content of not greater than about 3000 wppm.

8. The process of claim 1, wherein the smoke point upgrading catalyst comprises a support material comprising an inorganic, porous crystalline phase material having pores with diameters of at least about 13 Å and exhibiting, after thermal treatment, an XRD spectrum having at least one peak corresponding to a d-spacing greater than about 18 Å with a relative intensity of about 100, and having an equilibrium benzene sorption capacity of at least about 15 grams of benzene per 100 grams of material at about 50 torr (about 6.7 kPa) and at about 25° C.

9. The process of claim 1, wherein the at least one noble metal is selected from the group consisting of Pd, Pt, Rh, Ru, Ir, and combinations thereof.

10. The process of claim 1, wherein crystalline phase material is a metallocsilicate or an aluminosilicate.

11. The process of claim 1, wherein the at least one noble metal is present on the catalyst in an amount from about 0.01 wt % to about 5 wt %, based on total catalyst weight.

12. The process of claim 1, wherein the at least one noble metal is bound by a refractory inorganic oxide selected from the group consisting of alumina, silica, silica-alumina, titania, zirconia, magnesia, and combinations thereof.

13. The process of claim 1, wherein the smoke point upgrading catalyst is a Pt/Pd-containing M41S catalyst or a Pt/Pd-containing MCM-41 catalyst.

14. A process for increasing smoke point of a fuel, comprising:

hydrocracking a mineral oil feedstock;

providing from the hydrocracked mineral oil feedstock a first fuel having a smoke point from 18 mm to below 25 mm and a total aromatics content of  $A_r \geq 68 - 2.6S_m$ , wherein  $A_r$  is vol % total aromatics of the feedstock and  $S_m$  is the smoke point of the feedstock, provided that  $A_r$  is at least 4 vol %; and

contacting the first fuel with a smoke point upgrading catalyst comprised of at least one noble metal hydrogenation component disposed on a support having an inorganic, porous crystalline phase material to provide a fuel product having a smoke point of at least 25 mm.

15. The process of claim 14, wherein the first fuel has an initial and final boiling point within the range from about 90° C. to about 360° C.,

16. The process of claim 14, wherein the first fuel has an ASTM D86 10% distillation point within the range from about 110° C. to about 190° C.

17. The process of claim 14, wherein the first fuel has a total aromatics content of at least about 6 vol %.

18. The process of claim 14, wherein the first fuel has a total aromatics content of not greater than about 25 vol %.

19. The process of claim 14, wherein the feedstock fuel has a sulfur content of not greater than about 3000 wppm.

20. The process of claim 14, wherein the smoke point upgrading catalyst is a Pt/Pd-containing M41S catalyst or a Pt/Pd-containing MCM-41 catalyst.

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