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(54) # HIGHLY PARAFFINIC, MODERATELY AROMATIC DISTILLATE FUEL BLEND STOCKS PREPARED BY LOW PRESSURE HYDROPROCESSING OF FISCHER-TROPSCH PRODUCTS

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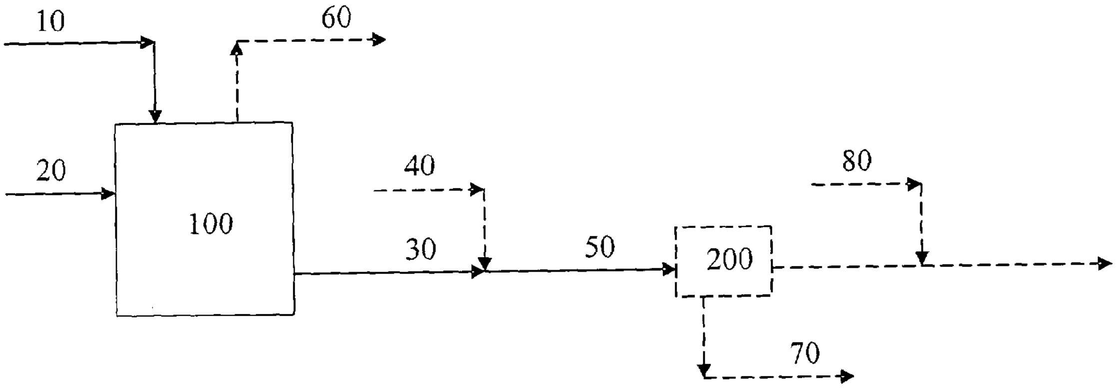
(57) **ABSTRACT**

The invention relates to a distillate fuel comprising a highly paraffinic, moderately aromatic distillate fuel blend stock. The highly paraffinic, moderately aromatic distillate fuel blend stock exhibits excellent combustion properties in diesel and jet engines as a result of the high paraffin content. In addition, the highly paraffinic, moderately aromatic distillate fuel blend stock exhibits improved seal-swell characteristics as a result of the moderate aromatic content. The blend stock is preferably prepared from a Fischer-Tropsch derived product that is hydroprocessed under conditions during which a moderate amount of aromatics are formed.



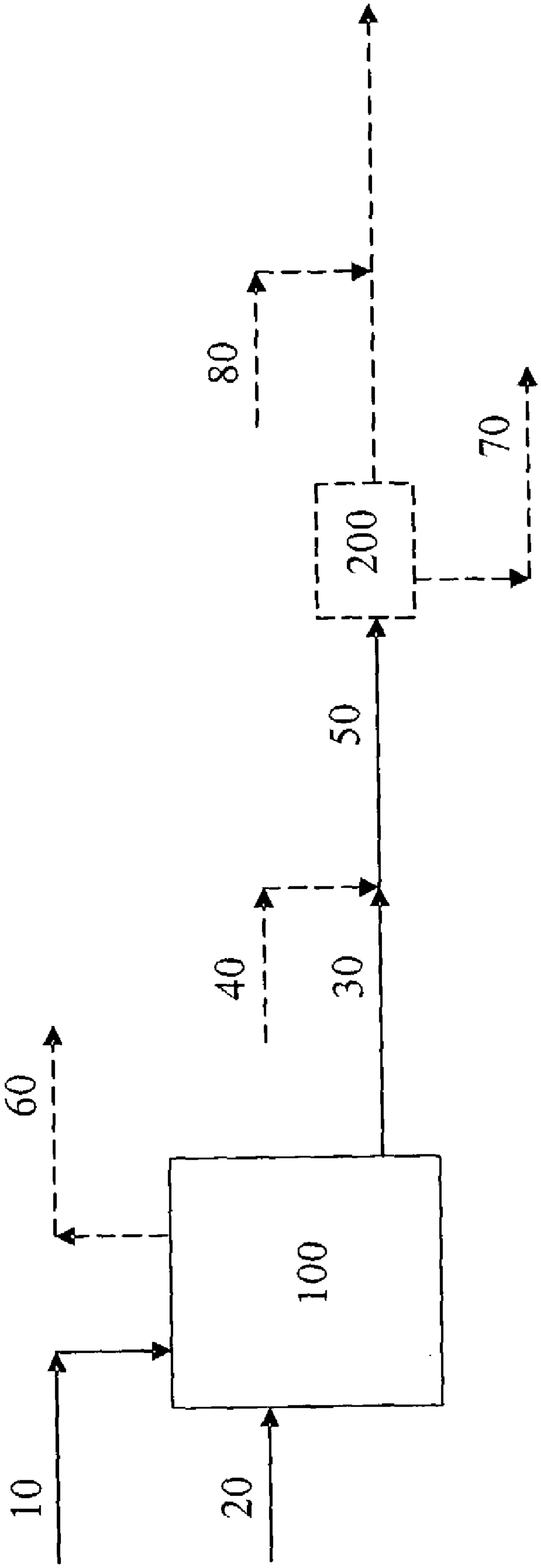
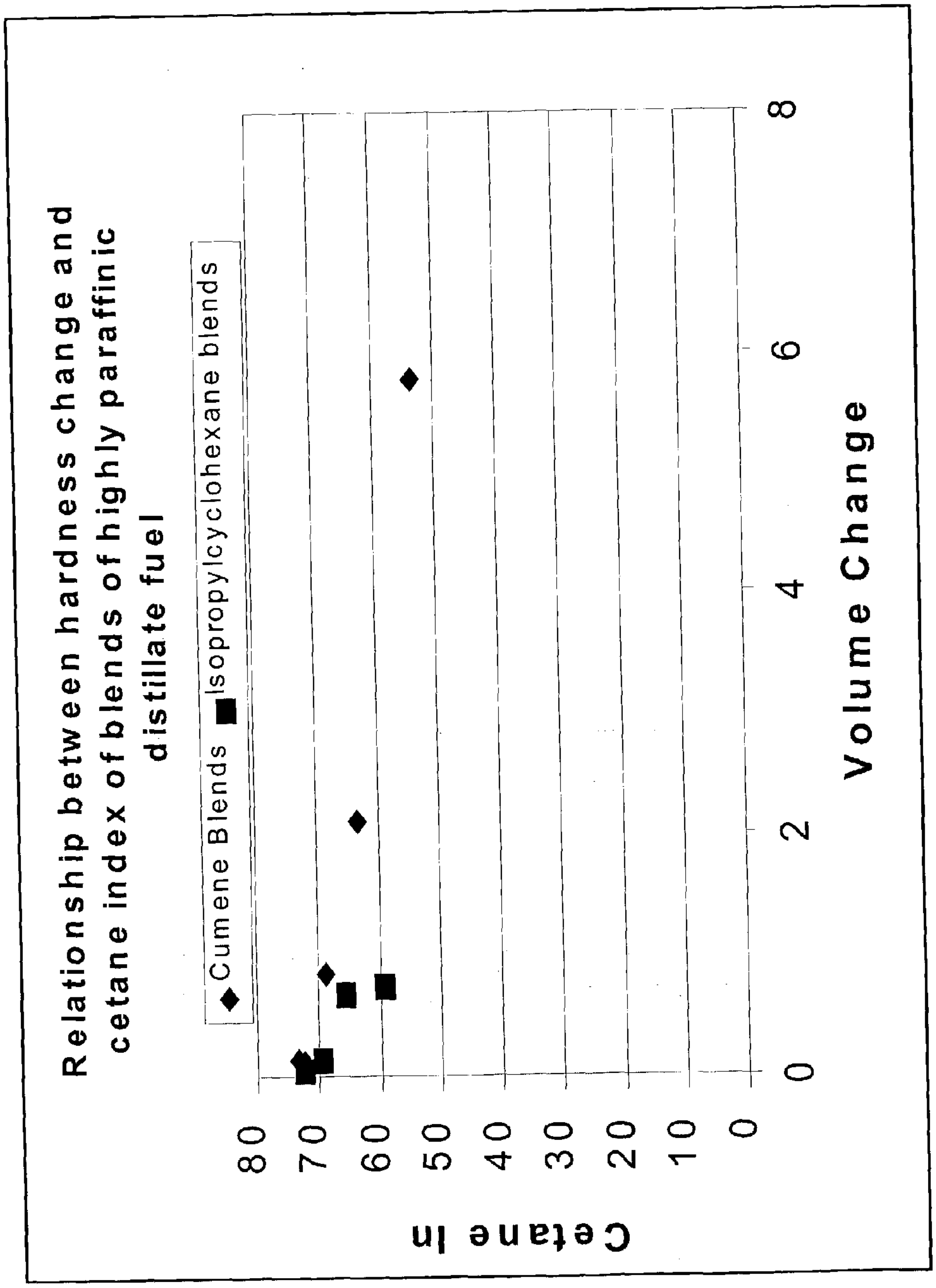


Figure 1

Figure 2


Relationship between hardness change and cetane index of blends of highly paraffinic distillate fuel
Cumene Blends
Isopropylcyclohexane blends
Cetane In
80
70
60
50
40
30
20
10
0
0
2
4
6
8
Volume Change

HIGHLY PARAFFINIC, MODERATELY AROMATIC DISTILLATE FUEL BLEND STOCKS PREPARED BY LOW PRESSURE HYDROPROCESSING OF FISCHER-TROPSCH PRODUCTS

RELATED APPLICATIONS

[0001] The present application is a continuation-in-part of U.S. application Ser. No. 09/999,667, "Distillate Fuel Blends from Fischer Tropsch Products with Improved Seal Swell Properties," filed Oct. 19, 2001, the contents of which are hereby incorporated by reference. The present application is also related to U.S. Patent Application No. ______ (Docket No. 005950-830) entitled "Stable, Moderately Unsaturated Distillate Fuel Blend Stock Prepared by Low Pressure Hydroprocessing of Fischer Tropsch Products," filed herewith.

FIELD OF THE INVENTION

[0002] The invention is directed to distillate fuels comprising a Fischer Tropsch distillate fuel blend stock, which have improved seal swell properties.

BACKGROUND OF THE INVENTION

[0003] Distillate fuel derived from the Fischer-Tropsch process is highly paraffinic and has excellent burning properties and very low sulfur. This makes Fischer-Tropsch products ideally suited for fuel use where environmental concerns are important. However, due to their highly paraffinic nature, Fischer-Tropsch distillate fuels have problems with poor seal swell properties.

[0004] The impact of lowering the aromatic content of distillate fuels used as diesel fuel or jet fuel on seal swell in diesel and jet engines is known, and became important when California switched from conventional diesel fuel to Low Aromatics Diesel Fuel (LAD). LAD does not contain zero aromatics, but must contain less than 10%. Literature references related to the problems encountered with lowering the aromatic content of distillate fuels include: Transport Topics, National Newspaper of the Trucking Industry, Alexandria, Va., "Fuel Pump Leaks Tied to Low Sulfur," Oct. 11, 1993; Oil Express, "EPA's diesel rules leading to shortages, fleet problems, price hikes," Oct. 11, 1993, p 4; Marin Independent Journal, "Motorists in Marin angry over fuel change," Nov. 11, 1993, p A1; San Jose Mercury News, "Mechanics finger new diesel fuel," Dec. 3, 1993; and San Francisco Chronicle, "Problems With New Diesel Fuel, Clean Air, Angry California Drivers," Dec. 23, 1993.

[0005] The problem of poor seal swell may be monitored by measuring the swelling of gaskets. The swelling of gaskets can be monitored by the use of known tests. For example, a description of test methodology is presented in SAE Paper No. 942018, "Effect of Automotive Gas Oil Composition on Elastomer Behavior," October 1994, which describes seal swell and hardness changes which were measured in test procedures, based as closely as possible, on a British Standard (BS) method BS 903 Part A 16 [British Standard Institute, 'Methods for testing vulcanized rubber,' Part A 16:1987—Determination of the effect of liquids], which is broadly similar to American Society for Testing and Materials (ASTM) procedures D471 [Test Method for Rubber Property—Effect of Liquids] and D2240 [Test Method for Rubber Property—Durometer Hardness]." (See FIG. 12). The paper examines volume swelling of five types of elastomers: hydrogenated nitrile, low nitrile, medium nitrile and low nitrile rubbers, and fluorocarbon elastomer.

[0006] A summary of work carried out to assess problems associated with California low sulfur/low aromatics fuels is presented in the California Governor's "Diesel Fuel Task Force Final Report," dated Mar. 29, 1996. The report notes results of measurements carried out on O-rings before and after immersion in fuels: volume and weight change by ASTM D471 [Test Method for Rubber Property—Effect of Liquids], hardness by ASTM D1415 [Test Method for Rubber Property—International Hardness], and modulus of elasticity, ultimate tensile strength and elongation by ASTM D1414 [Test Methods for Rubber O-Rings].

[0007] Since the transition from conventional distillate fuels to low aromatic fuels created problems with seal swell, greater seal swell problems associated with the transition to a highly paraffinic distillate fuel component made from a Fischer-Tropsch process are expected. The greater seal swell problems associated with Fischer-Tropsch distillate fuel components may limit the use of Fischer-Tropsch distillate fuel.

[0008] One additional problem associated with highly paraffinic distillate fuels is that hydroprocessing of these fuels consumes hydrogen. Hydrogen can be expensive to produce and store if necessary. Therefore, it would be desirable to reduce or eliminate the need for this hydrogen.

[0009] Accordingly, there is a need in the art for distillate fuels and distillate fuel blend stocks with acceptable seal swell properties. Finally, there is a need in the art for distillate fuels and distillate fuel blend stocks with satisfactory properties, which can be obtained from Fischer-Tropsch process products. This invention provides such distillate fuels and blend stocks and the processes for their manufacture.

SUMMARY OF THE INVENTION

[0010] The present invention relates to a distillate fuel comprising a Fischer Tropsch distillate fuel blend stock. The Fischer Tropsch distillate fuel blend stock comprises aromatics in an amount between 2 and 20 weight % and paraffins in an amount 80 weight % or greater. The Fischer Tropsch distillate fuel blend stock has a cetane index of greater than 60 and exhibits a volume change as measured by ASTM D471 of at least 0.25% using a Buta N nitrite O-Ring at 23+/−2° C. for 70 hours.

[0011] In another embodiment, the present invention relates to a Fischer-Tropsch diesel fuel blend stock. The Fischer-Tropsch diesel fuel blend stock comprises aromatics in an amount between 5 and 10 weight %, paraffins in an amount 90 weight % or greater, and sulfur in an amount less than 1 ppm. The aromatics comprise less than 20 weight % polynuclear aromatics and preferably less than 10 weight % polynuclear aromatics. Characteristics of the Fischer Tropsch diesel fuel blend stock include a cetane index greater than 60, a percent reflectance according to ASTM D6468 at 150° C. in excess of 65% when measured at 90 minutes, and a volume change as measured by ASTM D471 of at least 0.5% using a Buta N nitrite O-Ring at 23+/−2° C. for 70 hours.

[0012] In yet another embodiment, the present invention relates to a Fischer Tropsch jet fuel blend stock. The Fischer

Tropsch jet fuel blend stock comprises aromatics in an amount between 5 and 10 weight %, paraffins in an amount 90 weight % or greater, and sulfur in an amount less than 1 ppm. The aromatics comprise less than 20 weight % polynuclear aromatics and preferably less than 10 weight % polynuclear aromatics. Characteristics of the Fischer Tropsch jet fuel blend stock include a smoke point of 30 mm or greater, a passing rating in ASTM D324 1 (JFTOT Procedure) at 260° C. for 2.5 hours, and a volume change as measured by ASTM D471 of at least 0.5% using a Buta N nitrile O-Ring at 23+/−2° C. for 70 hours.

[0013] In a further embodiment, the present invention relates to a process for preparing a highly paraffinic, moderately aromatic distillate fuel blend stock. The process comprises converting syngas to a Fischer Tropsch derived feedstock by a Fischer Tropsch process, and hydroprocessing the Fischer-Tropsch derived feedstock. A highly paraffinic, moderately aromatic distillate fuel blend stock that contains between 2 and 20 weight % aromatics and 80 weight % or greater paraffins is recovered. Hydroprocessing conditions include a temperature of 525-775° F., a pressure of less than 1000 psig, and a liquid hourly space velocity of greater than 0.25 hr^{-1}.

[0014] In yet a further embodiment, the present invention relates to a process for preparing a highly paraffinic, moderately aromatic distillate fuel blend stock comprising converting syngas to a Fischer Tropsch derived feedstock by a Fischer Tropsch process, and hydroprocessing the Fischer-Tropsch derived feedstock to produce a distillate fuel blend stock. To the distillate fuel blend stock is added an aromatic blend stock to produce a highly paraffinic, moderately aromatic distillate fuel blend stock containing between 2 and 20 weight % aromatics and 80 weight % or greater paraffins.

[0015] In another embodiment, the present invention relates to a distillate fuel comprising a Fischer Tropsch distillate fuel blend stock. The Fischer Tropsch distillate fuel blend stock is made by a process comprising converting syngas to a Fischer Tropsch derived feedstock by a Fischer Tropsch process; hydroprocessing the Fischer-Tropsch derived feedstock at a temperature of 525-775° F., a pressure of less than 1000 psig, and a liquid hourly space velocity of greater than 0.25 hr^{-1}; and recovering a Fischer Tropsch distillate fuel blend stock. The Fischer Tropsch distillate fuel blend stock, which is recovered, comprises between 2 and 20 weight % aromatics and 80 weight % or greater paraffins.

[0016] In a further embodiment, the present invention relates to a method of operating a diesel engine comprising using a Fischer Tropsch diesel fuel blend stock as a diesel fuel wherein the Fischer Tropsch diesel fuel blend stock comprises aromatics in an amount between 5 and 10 weight %, paraffins in an amount 90 weight % or greater, and sulfur in an amount less than 1 ppm. The aromatics comprise less than 20 weight % polynuclear aromatics and preferably less than 10 weight % polynuclear aromatics. Characteristics of the Fischer Tropsch diesel fuel blend stock include a cetane index greater than 60, a percent reflectance according to ASTM D6468 at 150° C. in excess of 65% when measured at 90 minutes, and a volume change as measured by ASTM D471 of at least 0.5% using a Buta N nitrile O-Ring at 23+/−2° C. for 70 hours.

[0017] In yet another embodiment, the present invention relates to a method of operating a jet engine comprising using a Fischer Tropsch jet fuel blend stock as a jet fuel wherein the Fischer Tropsch jet fuel blend stock comprises aromatics in an amount between 5 and 10 weight %, paraffins in an amount 90 weight % or greater, and sulfur in an amount less than 1 ppm. The aromatics comprise less than 20 weight % polynuclear aromatics and preferably less than 10 weight % polynuclear aromatics. Characteristics of the Fischer Tropsch jet fuel blend stock include a smoke point of 30 mm or greater, a passing rating in ASTM D3241 (JFTOT Procedure) at 260° C. for 2.5 hours, and a volume change as measured by ASTM D471 of at least 0.5% using a Buta N nitrile O-Ring at 23+/−2° C. for 70 hours.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. **1** is a schematic flow diagram of one embodiment of the invention.

[0019] FIG. **2** is a graphical representation of the relationship between volume change and cetane index of blends of highly paraffinic distillate fuel blend stock and alkylaromatics or alkylcycloparaffins as described in the examples.

DETAILED DESCRIPTION OF THE INVENTION

[0020] According to the present invention, it has been found that highly paraffinic, moderately aromatic distillate fuel blend stocks have improved seal swell properties. The distillate fuel blend stocks can be prepared from a process including a Fischer Tropsch synthesis and hydroprocessing under conditions in which a moderate amount of aromatics are formed. The highly paraffinic, moderately aromatic Fischer Tropsch distillate fuel blend stocks can be mixed with other blend stocks to provide a distillate fuel or can be used neat directly in an engine as a fuel in the absence of other blend stocks with only the optional addition of minor amounts of additives.

[0021] For purposes of the present invention, the following definitions will be used herein:

[0022] The term “aromatics” means an unsaturated, cyclic and planar hydrocarbon with an uninterrupted cloud of electrons containing an odd number of pairs of π electrons.

[0023] A “distillate fuel blend stock” is a material that is mixed with other distillate fuel blend stocks to provide a distillate fuel, in particular a diesel or jet fuel, as herein defined. The blend stock itself does not necessarily meet specifications for the respective fuel, but preferably the resulting combination of blend stocks does. Jet fuel blend stocks are combined with other jet fuel blend stocks, and optionally additives, to provide jet fuel. Similarly, diesel fuel blend stocks are combined with other diesel fuel blend stocks, and optionally additives, to provide diesel fuel.

[0024] An “aromatic blend stock” is a blend stock comprising aromatics in an amount greater than or equal to 50 weight %, preferably greater than or equal to 75 weight %, and most preferably greater than or equal to 90 weight %. If a pure aromatic product is used as an aromatic blend stock, analysis of the aromatic content is not necessary. If the aromatic blend stock comprises aromatics and other hydrocarbons, a modified version of ASTM D6550 (Standard Test Method for the Determination of the Olefin Content of Gasolines by Supercritical Fluid Chromatography (SFC)) can be used to determine the aromatics. An aromatic blend stock may be blended with a Fischer Tropsch distillate fuel blend stock to increase the aromatic content of the Fischer Tropsch distillate fuel blend stock. Examples of aromatic blend stocks include commercially available pure aromatics (for example, benzene, alkylbenzenes, and the like); aromatics obtained from conventional petroleum products; aromatics obtained from reforming of reformable Fischer-Tropsch products; and the like.

[0025] ASTM D471 covers the required procedures to evaluate the comparative ability of rubber and rubber-like compositions to withstand the effect of liquids. It is designed for testing specimens of vulcanized rubber cut from standard sheets, specimens cut from fabric coated with vulcanized rubber, or finished articles of commerce. ASTM D471 provides procedures for exposing test specimens to the influence of liquids under definite conditions of temperature and time. The resulting deterioration is determined by measuring the changes in mass, volume, and dimension, before and after immersion in the test liquid. The test is particularly used for certain rubber articles, such as seals, gaskets, hoses, diaphragms, and sleeves which may be exposed to oils, greases, fuels, and other fluids during service. One of skill in the art could readily evaluate a distillate fuel using ASTM D471 to determine the volume change of a seal or gasket. It is to be understood that while stated that the fuels of the present invention exhibit a volume change as measured by ASTM D471, it is actually the rubber or rubber-like composition being tested that exhibits the volume change and not the fuels themselves.

[0026] A Buna N O-ring is a seal made from nitrile elastomer and is suitable for use in ASTM D471. Other suitable nitrile O-rings for use in ASTM D471 can be obtained from a number of sources, such as American United (compound C-70) and Parker Seals. Parker Seals provides three types of O-rings: standard nitrite, type N674; fuel-resistant nitrite (high-acrylic acrylonitrile), type N497; and fluorocarbon, type V747. Of these, the standard nitrile O-ring is the only one suitable for ASTM D471 as it is similar to the O-rings in common use in current diesel engines. The fuel-resistant and fluorocarbon O-rings are not representative of gaskets in wide commercial use.

[0027] The Cetane Index was determined by ASTM D4737-96a (2001) Standard Test Method for Calculated Cetane Index by Four Variable Equation.

[0028] Conventional petroleum products comprise products derived from petroleum crude.

[0029] A "petroleum blend stock" is a blend stock that comprises conventional petroleum products. Petroleum blend stocks may be comprised of the vapor overhead streams from distilling petroleum crude or refined products and the residual fuels that are the non-vaporizable remaining portion.

[0030] Derived from a Fischer-Tropsch process means that the feedstock, blend stock, or product in question originates from or is produced at some stage by a Fischer-Tropsch process.

[0031] A "Fischer Tropsch distillate fuel blend stock" is a blend stock that originates or is produced at some stage by a Fischer Tropsch process. A Fischer Tropsch distillate fuel blend stock can be mixed with other distillate fuel blend stocks to provide a distillate fuel, in particular a diesel or jet fuel. The blend stock itself does not necessarily meet specifications for the respective fuel, but the resulting combination of blend stocks does. Fischer Tropsch distillate fuel blend stocks include Fischer Tropsch diesel fuel blend stocks and Fischer Tropsch jet fuel blend stocks. As stated above, the Fischer Tropsch distillate fuel blend stocks can be mixed with other blend stocks to provide a distillate fuel, or the Fischer-Tropsch distillate fuel blend stocks can be used neat directly in an engine as a fuel in the absence of other blend stocks with only the optional addition of minor amounts of additives.

[0032] A distillate fuel is a material containing hydrocarbons with boiling points between approximately 60° F. to 1100° F. Within the broad category of distillate fuels are specific fuels including naphtha, jet fuel, diesel fuel, kerosene, aviation gas, fuel oil, and blends thereof.

[0033] A diesel fuel is a material suitable for use in diesel engines. Preferably, a diesel fuel conforms to at least one of the following specifications:

[0034] ASTM D975—"Standard Specification for Diesel Fuel Oils"

[0035] European Grade CEN 90

[0036] Japanese Fuel Standards JIS K 2204

[0037] The United States National Conference on Weights and Measures (NCWM) 1997 guidelines for premium diesel fuel

[0038] The United States Engine Manufacturers Association recommended guidelines for premium diesel fuel (FQP-1A)

A diesel fuel may be comprised of a combination of blend stocks or a single blend stock in the absence of other blend stocks with only the optional addition of minor amounts of additives.

[0039] A jet fuel is a material suitable for use in turbine engines in aircraft or other uses. Preferably, a jet fuel conforms to at least one of the following specifications:

[0040] ASTM D1655,

[0041] DEF STAN 91-91/3 (DERD 2494), TURBINE FUEL, AVIATION,

[0042] KEROSENE TYPE, JET A-1, NATO CODE: F-35,

[0043] International Air Transportation Association (IATA) Guidance Materials for Aviation, 4th edition, March 2000

A jet fuel may be comprised of a combination of blend stocks or a single blend stock in the absence of other blend stocks with only the optional addition of minor amounts of additives.

[0044] A Fischer Tropsch diesel fuel blend stock is a blend stock suitable for use in a diesel engine. The Fischer Tropsch diesel fuel blend stock may be mixed with other blend stocks to provide a diesel fuel or may be used in the absence of other blend stocks with only the optional addition of minor amounts of additives.

[0045] A Fischer Tropsch jet fuel blend stock is a blend stock suitable for use in turbine engines in aircraft or other uses. The Fischer Tropsch jet fuel blend stock may be mixed with other blend stocks to provide a jet fuel or may be used in the absence of other blend stocks with only the optional addition of minor amounts of additives.

[0046] A highly paraffinic, moderately aromatic distillate fuel blend stock is a distillate fuel blend stock that contains more than 70 weight % paraffins, preferably 80 weight % or greater paraffins, and most preferably 90 weight % or greater paraffins and 2 to 20 weight % aromatics, preferably 2 to 15 weight % aromatics, and most preferably 5 to 10 weight % aromatics. Preferably, the highly paraffinic, moderately aromatic distillate fuel blend stock is a Fischer Tropsch distillate fuel blend stock.

[0047] A "Fischer-Tropsch derived feedstock" or "Fischer Tropsch feedstock" is a feedstock that originates from or is produced at some stage by a Fischer Tropsch process. In the processes of the present invention, a Fischer-Tropsch derived feedstock may be blended with a petroleum blend stock during processing to provide a blended stream.

[0048] A reformable Fischer-Tropsch product is a product derived from a Fischer-Tropsch process that can be reformed to aromatics. A reformable light fraction typically boils below about 400° F., and preferably a reformable light fraction contains hydrocarbons boiling above n-pentane and below 400° F. More preferably the boiling range of the reformable light fraction is such that, after reforming, single ring aromatics, which boil above n-pentane (97° C.) and below n-decane (346° C.), are produced. Most preferably, the boiling range is such that after reforming, the reformed products are benzene; to produce benzene as the reformed product, the reformable Fischer Tropsch product's boiling range is above n-hexane and below n-decane.

[0049] Syngas is a mixture that includes both hydrogen and carbon monoxide. In addition to these species, water, carbon dioxide, unconverted light hydrocarbon feedstock and various impurities may also be present.

[0050] The aromatics content of the highly paraffinic, moderately aromatic blend stocks of the present invention is between 2 and 20 weight %, preferably between 2 and 15 weight %, and most preferably between 5 and 10 weight %. This aromatics content improves seal swell properties as measured by ASTM D1414. The test methods of ASTM D1414 include a test for volume percent change, as measured by ASTM D471 using a Buta N nitrile O-Ring at 23+/−2° C. for 70 hours. The volume percent change is in excess of 0.25%, preferably in excess of 0.5%, and most preferably in excess of 2%. The aromatics of the blend stock of the present invention are predominantly mono-aromatics (alkylbenzenes), with minimal amounts of polynuclear aromatics. Preferably, the aromatics comprise less than 25 weight % polynuclear aromatics, more preferably less than 20 weight % polynuclear aromatics, and most preferably less than 10 weight % polynuclear aromatics.

[0051] A modified version of ASTM D6550 (Standard Test Method for the Determination of the Olefin Content of Gasolines by Supercritical Fluid Chromatography (SFC) was used to determine the group types in the feedstocks and products. The modified method uses a 3-point calibration standard to quantify the total amount of saturates, aromatics, oxygenates (polars) and olefins. Calibration standard solutions were prepared using the following compounds: undecane, toluene, n-octanol and dodecene. External standard method was used for quantification and the detection limit for aromatics and oxygenates is 0.1% wt and for olefins is 1.0% wt. ASTM D6550 describes the instrument conditions.

[0052] A small aliquot of the sample was injected onto a set of two chromatographic columns connected in series and transported using supercritical carbon dioxide as the mobile phase. The first column was packed with high surface area silica particles. The second column contained high surface area silica particles loaded with silver ions.

[0053] Two switching valves were used to direct the different classes of components through the chromatographic system to the detector. In a forward-flow mode, saturates (normal and branched alkanes and cyclic alkanes) were passed through both columns to the detector, while olefins were trapped on the silver-loaded column and the aromatics and oxygenates are retained on the silica column. Aromatic compounds and oxygenates were subsequently eluted from the silica column to the detector in a back flush mode. Finally, the olefins were back flushed from the silver-loaded column to the detector.

[0054] A flame ionization detector (FID) was used for quantification. Calibration was based on the area of the chromatographic signal of saturates, aromatics, oxygenates and olefins, relative to standard reference materials, which contain a known mass % of total saturates, aromatics, oxygenates and olefins as corrected for density. The total mass collected was 100%+/−3%, and was normalized to 100% for convenience.

[0055] The Polynuclear Aromatic (PNA) content of the products was determined by ASTM D5186-99 Standard Test Method for Determination of Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography.

[0056] The paraffin content of the product was determined by the Supercritical Fluid Chromatography (SFC) analysis, using the following algorithm. The SFC analysis provides determinations of aromatics, olefins, oxygenates and saturates. Saturates in this analysis are a combination of paraffins and naphthenes (i.e. cycloparaffins). Thus,

$$\text{Paraffins}=\text{Saturates(SFC)}-\text{Naphthenes}$$

However, naphthenes were not found to be present in significant amounts (less than 10% of the saturates) in the products of the present invention. Thus, saturates from the SFC analysis typically can be taken as a good and proper measurement of the paraffin content of the products of the invention.

[0057] To verify that naphthenes are not present in significant amounts, the naphthene content was determined independently using GC-MS. GC-MS reports olefins and cycloparaffins as a combined sum because they have the same ratio of hydrogen to carbon in their structures and the technique cannot distinguish them. If GC-MS reports the combined sum of the olefins and cycloparaffins as being insignificant, then the naphthenes can be concluded to be present only in insignificant amounts. However, if GC-MS reports the sum as being significant, the portion of naphthenes can be determined by subtracting the olefin content (as determined by SFC) from the combined GC-MS sum to provide the naphthenes.

$$\text{Naphthenes}=(\text{Sum of Naphthenes and Olefins by GC-MS})-(\text{Olefins by SFC})$$

The naphthenes can then be subtracted from the saturates content (as determined by SFC) to provide a good and proper measurement of the paraffin content according to the first equation. If the naphthene content determined in this way is less than zero, it is reported as zero, and zero is used in the calculation of paraffins. Thus, in this case the paraffins are equal to the SFC saturates.

[0058] In the GC-MS test, deuterium labeled standards were used to quantify alkanes, olefins, alcohols, and acids. Selected deuterium labeled compounds were added to the sample of interest as internal standards. The mixture of sample and standards were treated with trimethylsilyl (TMS) reagent to form the TMS derivatives, followed by GCMS analysis. The mass spectrometer is a Hewlett-Packard bench top mass spectrometer interfaced to a HP GC with a 60 meter non-polar column. The normal alkanes and the branched alkanes were all quantified using deuterium labeled normal alkanes. Olefins, alcohols, and acids were all quantified using the corresponding deuterium labeled compounds.

[0059] The paraffin content of the highly paraffinic, moderately aromatic blend stocks of the present invention is at least 70 weight %, preferably 80 weight % or greater, and most preferably 90 weight % or greater. Due to their high content of paraffins, the highly paraffinic, moderately aromatic distillate fuel blend stocks of the present invention have excellent combustion properties. Characteristic combustion properties of the blend stocks of the present invention include smoke points in excess of 25 mm, preferably in excess of 30 mm, and cetane indexes in excess of 60, preferably in excess of 65. The paraffins consist of a mixture of normal and iso-paraffins with the ratio of iso/normal paraffins being between 0.3 and 10. Higher proportions of iso-paraffins are preferred when the blend stock is intended for use in cold climates (Jet A1 or diesel for arctic use).

[0060] Fuels comprising the highly paraffinic, moderately aromatic blend stocks of the present invention preferably conform to at least one specification for either diesel or jet fuel. The fuels may be comprised of a combination of blend stocks or the highly paraffinic, moderately aromatic blend stock in the absence of other blend stocks with only the optional addition of minor amounts of additives. The highly paraffinic, moderately aromatic blend stocks, and fuels comprising this blend stock, exhibit at least acceptable, and most often excellent, stability. For example, the percent reflectance of diesel fuels comprising the highly paraffinic, moderately aromatic blend stocks, as measured by ASTM D6468 at 150° C., will be in excess of 65% when measured at 90 minutes. Jet fuels comprising the highly paraffinic, moderately aromatic blend stocks have a passing rating in ASTM D3241 (JFTOT Procedure) at 260° C. for 2.5 hours. A passing rating corresponds to a tube rating of less than 3 (Code 3) and a pressure drop across a filter of less than 25 mm Hg.

[0061] The blend stocks of the present invention, and fuels comprising the blend stocks, typically have low sulfur (<1 ppm) and preferably low nitrogen content (<1 ppm). Therefore, environmental emissions of oxides of heteroatoms are minimized. Accordingly, the blend stocks and fuels comprising the blend stocks are desirable as environmentally friendly.

Fischer-Tropsch

[0062] The blend stocks of the present invention can be prepared from Fischer-Tropsch products, hydroprocessed under conditions in which a moderate amount of aromatics are formed. Preferably, the blend stocks of the present invention are prepared at least partially from Fischer-Tropsch products.

[0063] In Fischer-Tropsch chemistry, syngas is converted to liquid hydrocarbons by contact with a Fischer-Tropsch catalyst under reactive conditions. Typically, methane and optionally heavier hydrocarbons (ethane and heavier) can be sent through a conventional syngas generator to provide synthesis gas. Generally, synthesis gas contains hydrogen and carbon monoxide, and may include minor amounts of carbon dioxide and/or water. The presence of sulfur, nitrogen, halogen, selenium, phosphorus and arsenic contaminants in the syngas is undesirable. For this reason and depending on the quality of the syngas, it is preferred to remove sulfur and other contaminants from the feed before performing the Fischer-Tropsch chemistry. Means for removing these contaminants are well known to those of skill in the art. For example, ZnO guardbeds are preferred for removing sulfur impurities. Means for removing other contaminants are well known to those of skill in the art. It also may be desirable to purify the syngas prior to the Fischer-Tropsch reactor to remove carbon dioxide produced during the syngas reaction and any additional sulfur compounds not already removed. This can be accomplished, for example, by contacting the syngas with a mildly alkaline solution (e.g., aqueous potassium carbonate) in a packed column.

[0064] In the Fischer-Tropsch process, liquid and gaseous hydrocarbons are formed by contacting a synthesis gas comprising a mixture of H_2 and CO with a Fischer-Tropsch catalyst under suitable temperature and pressure reactive conditions. In general, a Fischer-Tropsch reaction can be conducted at temperatures from about 300 to 700° F. (149 to 371° C.), preferably from about 400 to 550° F. (204 to 228° C.); pressures of from about 10 to 600 psia, (0.7 to 41 bars), preferably 30 to 300 psia, (2 to 21 bars) and catalyst space velocities of from about 100 to about 10,000 cc/g/hr, preferably 300 to 3,000 cc/g/hr.

[0065] Fischer Tropsch processes can be categorized as either a high temperature Fischer Tropsch process or a low temperature Fischer Tropsch process. The process conditions and the predominate products from the two processes are different.

[0066] A high temperature Fischer Tropsch process is generally carried out at temperatures above 250° C., preferably at or above 350° C. High temperature Fischer Tropsch processes provide primarily lower molecular weight olefinic products generally within the C_3 to C_8 range, preferably propylene to pentenes. High temperature Fischer Tropsch products can also contain significant amounts of aromatics. The high temperature Fischer Tropsch products may be subjected to processes to saturate the aromatics, including reforming processes. The olefinic products from the high temperature Fischer Tropsch process are typically further processed by oligomerization and hydrogenation steps to produce a highly branched iso-paraffinic product. The products from the high temperature Fischer Tropsch process can be processed so that they meet specifications for gasoline. The products from high temperature Fischer Tropsch processes typically have cetane indexes of about 55 since the products are highly branched. An example of a high temperature Fischer Tropsch process is the Synthol process used by SASOL, as described in "High Yield High Quality Diesel from Fischer Tropsch Process, Dry, M.E., Chem. S.A., February 1984.

[0067] Jet fuels have also been produced by high temperature Fischer Tropsch processes, olefin oligomerization, and hydrogenation. A high temperature Fischer Tropsch process for making jet fuels is described in "Qualification of SASOL Semi-Synthetic Jet A-1 as Commercial Jet Fuel," SwRI-8531, November 1997. The jet fuels made by a high temperature Fischer Tropsch process, as described in the reference, contain no aromatics or unsaturates. The thermal stability, or JFTOT, breakpoint for blends of high temperature Fischer Tropsch derived jet with conventional petroleum-derived is presented in the literature as in excess of 300° C. Therefore the thermal stability, or JFTOT, breakpoint for such semi-synthetic blends is significantly above the specification requirement of 260° C. See "Qualification of SASOL Semi-synthetic Jet A-1 as Commercial Jet Fuel", Moses, Stavinoha, and Roets, South West Research Institute Publication SwRI-8531, November 1997.

[0068] Researchers working with high temperature Fischer Tropsch products and blends of high temperature Fischer Tropsch products and petroleum-derived products have not noted problems with stability.

[0069] A low temperature Fischer Tropsch process operates at temperatures below 250° C. and produces a heavier product. The heavier product of a low temperature Fischer Tropsch process commonly contains predominantly wax. The products from the low temperature Fischer Tropsch process are typically hydrotreated so that they will have acceptable peroxide stability, as shown by U.S. Pat. No. 6,180,842. Accordingly, the products from low temperature Fischer Tropsch processes are typically refined by hydroprocessing operations such as hydrotreating and hydrocracking to provide stable fuels meeting the desired specification. The products from low temperature Fischer Tropsch processes are predominantly linear, and even after hydrocracking, these products contain fewer branches than products made from a high temperature Fischer Tropsch process. Fewer branches in the products of low temperature Fischer Tropsch processes provide higher cetane indexes for these products in comparison to the products from the high temperature processes, which have increased branching. The low temperature Fischer Tropsch products typically have cetane indexes of greater than 60, and preferably greater than 70.

[0070] The Fischer Tropsch process, for making the distillate fuel blend stocks according to the present invention, is a low temperature Fischer Process. Examples of conditions for performing low temperature Fischer-Tropsch type reactions are well known to those of skill in the art.

[0071] The products may range from C_1 to C_{200+} with a majority in the C_5-C_{100+} range. The reaction can be conducted in a variety of reactor types for example, fixed bed reactors containing one or more catalyst beds, slurry reactors, fluidized bed reactors, or a combination of different type reactors. Such reaction processes and reactors are well known and documented in the literature. Slurry Fischer-Tropsch processes, which is a preferred process in the practice of the invention, utilize superior heat (and mass) transfer characteristics for the strongly exothermic synthesis reaction and are able to produce relatively high molecular weight, paraffinic hydrocarbons when using a cobalt catalyst. In a slurry process, a syngas comprising a mixture of H_2 and CO is bubbled up as a third phase through a slurry in a reactor which comprises a particulate Fischer-Tropsch type hydrocarbon synthesis catalyst dispersed and suspended in a slurry liquid comprising hydrocarbon products of the synthesis reaction which are liquid at the reaction conditions. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5.

[0072] Suitable Fischer-Tropsch catalysts comprise one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru and Re. Additionally, a suitable catalyst may contain a promoter. Thus, a preferred Fischer-Tropsch catalyst comprises effective amounts of cobalt and one or more of Re, Ru, Pt, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. In general, the amount of cobalt present in the catalyst is between about 1 and about 50 weight percent of the total catalyst composition. The catalysts can also contain basic oxide promoters such as ThO_2, La_2O_3, MgO, and TiO_2, promoters such as ZrO_2, noble metals (Pt, Pd, Ru, Rh, Os, Ir), coinage metals (Cu, Ag, Au), and other transition metals such as Fe, Mn, Ni, and Re. Support materials including alumina, silica, magnesia and titania or mixtures thereof may be used. Preferred supports for cobalt containing catalysts comprise titania. Useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be found, for example, in U.S. Pat. No. 4,568,663.

[0073] Certain catalysts are known to provide chain growth probabilities that are relatively low to moderate, and the reaction products include a relatively high proportion of low molecular (C_{2-8}) weight olefins and a relatively low proportion of high molecular weight (C_{30+}) waxes. Certain other catalysts are known to provide relatively high chain growth probabilities, and the reaction products include a relatively low proportion of low molecular (C_{2-8}) weight olefins and a relatively high proportion of high molecular weight (C_{30+}) waxes. Such catalysts are well known to those of skill in the art and can be readily obtained and/or prepared.

[0074] The products from low temperature Fischer-Tropsch reactions generally include a light reaction product and a waxy reaction product. The waxy reaction product (i.e. the wax fraction) includes hydrocarbons boiling above about 600° F. (e.g., vacuum gas oil through heavy paraffins), largely in the C_{20+} range, with decreasing amounts down to C_{10}. Both the light reaction product and the waxy product are substantially paraffinic. The waxy product generally comprises greater than 70 weight % normal paraffins, and often 80 weight % or greater normal paraffins.

Hydroprocessing

[0075] Hydroprocessing, in general, is well known to those of skill in the art and includes such processes as hydrotreating, hydrocracking, hydrogenation, catalytic dewaxing, or combinations of these processes. Preferably, the hydroprocessing operation of the present invention achieves several purposes in one or several reactors, most preferably a single reactor. Among the purposes of the hydroprocessing of the present invention are reducing, or preferably completely removing, heteroatoms such as nitrogen and sulfur. Further, the hydroprocessing may reduce, or completely remove, olefins. Moreover, the hydroprocessing may increase the ratio of iso/normal paraffins in the distillate product. Additionally, the hydroprocessing may increase the production of distillate product by converting heavy species. Finally unlike conventional hydroprocessing, the hydroprocessing of this invention creates a moderate amount of aromatics.

[0076] Hydroprocessing under conditions to create aromatics may reduce or eliminate net hydrogen consumption in the hydroprocessing process. While the addition of hydrogen is necessary to begin the hydroprocessing process, if the aromatics formation is high enough, the amount of hydrogen produced in the process can exceed the amount of hydrogen initially added to the process. Accordingly, there may be a net hydrogen production from the hydroprocessing of the present invention, i.e. the net hydrogen consumption is less than zero.

[0077] Produced hydrogen can be used for a variety of purposes in a Gas-To-Liquid (GTL) facility. Among these purposes are hydrotreatment of Fischer-Tropsch streams to reduce or eliminate olefins and/or heteroatoms. Further, produced hydrogen may be reacted with CO_2 produced in the GTL process or recovered from a CO_2—containing gas source to reduce CO_2. The product from the CO_2—H_2 reaction can be CO or a Fischer-Tropsch product and the reaction can be conducted in the syngas generator. Produced hydrogen may also be used in fuel production as a fuel component that does not form CO_2 emissions. The produced fuel can be used to generate process heat, produce electrical energy, and/or distill/purify water.

[0078] Typical temperatures for the hydroprocessing of Fischer-Tropsch products to generate aromatics are 525-775° F., preferably 575-725° F. Typical pressures for this operation are less than 1000 psig, preferably less than 600 psig, and most preferably between 200 and 500 psig. Typical liquid hourly space velocities (LHSV) for this operation are greater than 0.25 hr^{-1}, preferably between 0.5 and 1.5 hr^{-1}. Typical hydroprocessing catalysts for this operation include catalysts for hydroprocessing operations (described below) or catalysts for hydroisomerization dewaxing, preferably combinations of catalysts for hydroprocessing operations and hydroisomerization dewaxing are used as this combination is less expensive and also permits a concurrent reduction in the product pour point.

[0079] A conventional hydroprocessing catalyst may be used for generating aromatics. Hydroprocessing catalysts which are particularly suited for generating aromatics are bifunctional catalysts, which contain both a hydrogenation function and an acidic function. The aromatics-forming hydroprocessing catalyst is contrasted, for example, from a conventional hydrotreating catalyst by the presence of the acidic function, since hydrotreating catalysts typically include a non-acidic support such as alumina.

[0080] The acidic function is preferably based on a mixture of at least two metal oxides of different valences. The preferred mixture of metal oxides includes SiO_2 and Al_2O_3; or Al_2O_3, SiO_2, and P_2O_5. The mixture of metal oxides may be prepared in such a way as to provide a high dispersion of at least a portion of the metal oxides between themselves, for example dispersion of the SiO_2 and Al_2O_3 on an atomic scale rather than separate phases of SiO_2 and Al_2O_3. The presence of separate phases of SiO_2 and Al_2O_3 can be determined by an XRD examination. If all of the oxides are present as separate phases, the performance of the catalyst will be diminished. Examples of the acidic function composed of mixed metal oxides are zeolites, crystalline SAPO's, and co-precipitated SiO_2—Al_2O_3.

[0081] In contrast, conventional reforming technology which coverts naphtha to light aromatics (C_6-C_{10}) typically uses a halogen (most commonly chloride) as an acidic function. While halogens can be used in hydroprocessing catalyst as an acidic function, especially fluoride as in the form of a fluorided alumina, halogens are not preferred because they will slowly be stripped from the catalyst and can lead to corrosion of the reactor vessel.

[0082] The hydrogenation function in an aromatics-forming hydroprocessing catalyst comprises a metal. Suitable hydrogenation metals include Group VI metals such as Mo and/or W and Group VIII metals such as Ni or Co. These are present on the catalyst in sulfided form. Preferably, the hydrogenation metal is a noble metal, more preferably selected from the group consisting of Pt, Pd and mixtures thereof. These may be sulfided, but using them in the non-sulfided form is preferred.

[0083] Catalysts useful in hydroprocessing operations are well known in the art. Suitable catalysts include noble metals from Group VIIIA (according to the 1975 rules of the International Union of Pure and Applied Chemistry), such as platinum or palladium on an alumina or siliceous matrix, and Group VIIIA and Group VIB, such as nickel-molybdenum, cobalt-molybdenum, nickel-tungsten, or nickel-tin on an alumina or siliceous matrix. The non-noble metal (such as nickel-molybdenum) hydrogenation metals are usually present in the final catalyst composition as oxides, or more preferably or possibly, as sulfides when such compounds are readily formed from the particular metal involved. Preferred non-noble metal catalyst compositions contain in excess of about 5 weight percent, preferably about 5 to about 40 weight percent molybdenum and/or tungsten, and at least about 0.5, and generally about 1 to about 15 weight percent of nickel and/or cobalt determined as the corresponding oxides. The noble metal (such as platinum) catalyst may contain in excess of 0.01 percent metal, preferably between 0.1 and 1.0 percent metal. Combinations of noble metals may also be used, such as mixtures of platinum and palladium.

[0084] The matrix components include some that have acidic catalytic activity. Ones that have activity include amorphous silica-alumina or may be a zeolitic or non-zeolitic crystalline molecular sieve. Examples of suitable matrix molecular sieves include zeolite Y, zeolite X and the so called ultra stable zeolite Y and high structural silica:alumina ratio zeolite Y. Suitable matrix materials may also include synthetic or natural substances as well as inorganic materials such as clay, silica and/or metal oxides such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia zirconia. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays, which can be composited with the catalyst, include those of the montmorillonite and kaolin families. These clays can be used in the raw state as originally mined or initially subjected to calumniation, acid treatment or chemical modification. More than one catalyst type may be used in the reactor.

[0085] As stated above, hydroprocessing, in general, is well know to those of skill in the art and includes such processes as hydrotreating, hydrocracking, hydrogenation, catalytic dewaxing, or combinations of these processes. The hydroprocessing of the present invention upgrades the Fischer Tropsch derived feedstock by performing an operation selected from the group consisting of reducing the content of sulfur, nitrogen, and oxygen in the feedstock; reducing the content of olefins in the feedstock; increasing the ratio of iso/normal paraffins in the product to between 0.3 and 10; increasing the production of distillate fuel product by converting heavy species in the feedstock; and combinations thereof.

[0086] Typical hydrotreating conditions vary over a wide range. Typical pressures for this operation are less than 1000 psig, preferably less than 600 psig, and most preferably between 200 and 500 psig. Typical liquid hourly space velocities (LHSV) for this operation are greater than 0.25 hr^{-1}, preferably between 0.5 and 2.0 hr^{-1}. Hydrogen recirculation rates are typically greater than 50 standard cubic feet per barrel of oil (SCF/Bbl), and are preferably between 1000 and 5000 SCF/Bbl. Temperatures range from about 300° F. to about 750° F., preferably ranging from 450° F. to 600° F.

[0087] Hydrocracking may be conducted according to conventional methods known to those of skill in the art. Typically, hydrocracking is a process of breaking larger carbon molecules into smaller ones. It may be effected by contacting the particular fraction or combination of fractions, with hydrogen in the presence of a suitable hydrocracking catalyst at temperatures in the range of from about 600 to 900° F. (316 to 482° C.), preferably 650 to 850° F. (343 to 454° C.), and pressures in the range of from about 200 to 4000 psia (13 to 272 atm), preferably 500 to 3000 psia (34 to 204 atm) using space velocities based on the hydrocarbon feedstock of about 0.1 to 10 hr^{-1}, preferably 0.25 to 5 hr^{-1}. Generally, hydrocracking is utilized to reduce the size of the hydrocarbon molecules, hydrogenate olefin bonds, hydrogenate aromatics and remove traces of heteroatoms. Suitable catalysts for hydrocracking operations are known in the art and include sulfided catalysts. Sulfided catalyst may comprise amorphous silica-alumina, alumina, tungsten and nickel.

[0088] The conditions of hydrogenation are well known in the industry and include temperatures above ambient and pressures greater than atmospheric. Preferable conditions for hydrogenation include a temperature between 300 and 800° F., most preferably between 400 and 600° F., a pressure between 50 and 2000 psig, most preferably between 100 and 500 psig, a liquid hourly space velocity (LHSV) between 0.2 and 10 hr^{-1}, most preferably between 1.0 and 3.0 hr^{-1}, and a gas rate between 500 and 10,000 SCFB, most preferably between 1000 and 5000 SCFB.

[0089] The catalysts used for hydrogenation are those typically used in hydrotreating, but non-sulfided catalysts containing Pt and/or Pd are preferred, and it is preferred to disperse the Pt and/or Pd on a support, such as alumina, silica, silica-alumina, or carbon. The preferred support is silica-alumina.

[0090] Catalytic dewaxing consists of two main classes—conventional hydrodewaxing and hydroisomerization dewaxing; hydroisomerization dewaxing can be further subdivided into partial and complete hydroisomerization dewaxing. All classes involve passing a mixture of a waxy hydrocarbon stream and hydrogen over a catalyst that contains an acidic component to convert the normal and slightly branched iso-paraffins in the feed to other non-waxy species and thereby generate a lube base stock product with an acceptable pour point (below about +10° F. or −12° C.). Typical conditions for all classes involve temperatures from about 400 to 800° F., pressures from about 200 to 3000 psig, and space velocities from about 0.2 to 5 hr^{-1}. The method selected for dewaxing a feed typically depends on the product quality, and the wax content of the feed, with Conventional Hydrodewaxing generally preferred for low wax content feeds. The method for dewaxing can be effected by the choice of the catalyst. The general subject is reviewed by Avilino Sequeira, in *Lubricant Base Stock and Wax Processing*, Marcel Dekker, Inc pages 194-223.

[0091] The determination of the class of dewaxing catalyst among conventional hydrodewaxing, partial hydroisomerization dewaxing and complete hydroisomerization dewaxing can be made by using the n-hexadecane isomerization test as describe by Santilli et al. in U.S. Pat. No. 5,282,958. When measured at 96% n-hexadecane conversion under conditions described by Santilli et al., conventional hydrodewaxing catalysts will exhibit a selectivity to isomerized hexadecanes of less than 10%, hydroisomerization dewaxing catalysts will exhibit a selectivity to isomerized hexadecanes of greater than or equal to 10%, partial hydroisomerization dewaxing catalysts will exhibit a selectivity to isomerized hexadecanes of greater than 10% to less than 40%, and complete hydroisomerization dewaxing catalysts will exhibit a selectivity to isomerized hexadecanes of greater than or equal to 40%, preferably greater than 60%, and most preferably greater than 80%.

[0092] Conventional hydrodewaxing is defined for purposes of this document as a catalytic dewaxing process that uses a conventional hydrodewaxing catalyst. In conventional hydrodewaxing, the pour point is lowered by selectively cracking the wax molecules, mostly to smaller paraffins boiling between propane and about octane. Since this technique converts the wax to less valuable by-products, it is useful primarily for dewaxing oils that do not contain a large amount of wax. Waxy oils of this type are frequently found in petroleum distillate from moderately waxy crudes (Arabian, North Slope, etc). Catalysts that are useful for conventional hydrodewaxing are typically 12-ring zeolites and 10-ring zeolites. Zeolites of this class include ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, and Mordenite. Conventional hydrodewaxing catalysts favor cracking in comparison to other method of conversion of paraffins. This is demonstrated by use of the n-hexadecane isomerization test by Santilli et al., in which conventional hydrodewaxing catalysts exhibit a selectivity to isomerized hexadecane products of less than 10%. In addition to the zeolites, metals may be added to the catalyst, primarily to reduce fouling. Representative process conditions, yields, and product properties for conventional hydrodewaxing are described, for example, in U.S. Pat. No. 4,176,050 to Chen et al., U.S. Pat. No. 4,181,598 to Gillespie et al., U.S. Pat. No. 4,222,855 to Pelrine et al., U.S. Pat. No. 4,229,282 to Peters et al., and U.S. Pat. No. 4,211,635 to Chen. These patents are incorporated herein by reference for all purposes. Process conditions are further described and exemplified by Sequeira in the section titled "The Mobil Lube Dewaxing Process," pages 198-204 and references therein, J. D. Hargrove, G. J. Elkes, and A. H. Richardson, Oil and Gas J., p. 103, Jan. 15, 1979.

[0093] Hydroisomerization dewaxing is defined for purposes of this document as a catalytic dewaxing process that uses a hydroisomerization dewaxing catalyst. Hydroisomerization dewaxing converts at least a portion of the wax to non-waxy iso-paraffins by isomerization, while at the same time minimizing the conversion by cracking. When conventional hydrodewaxing and hydroisomerization dewaxing are compared on the same feed, the conversion of wax to non-waxy iso-paraffins during hydroisomerization dewaxing gives benefits of reducing the yield of less valuable by-products, increasing the yield of lube oil, and generating an oil with higher VI and greater oxidation and thermal stability. Hydroisomerization dewaxing uses a dual-functional catalyst consisting of an acidic component and a metal component. Both components are required to conduct the isomerization reaction. Typical metal components are platinum or palladium, with platinum most commonly used. The choice and the amount of metal in the catalyst is sufficient to achieve greater than 10% isomerized hexadecane products in the test described by Santilli et al. When the selectivity for hexadecane isomers following Santilli's test exceed 40%, the catalyst is a complete hydroisomerization dewaxing catalyst. Since hydroisomerization dewaxing converts wax to iso-paraffins which boil in the lube base stock range, it is useful for dewaxing oils that contain a large amount of wax. Waxy oils of this type are obtained from slack waxes from solvent dewaxing processes, and distillates from highly waxy crudes (Minas, Altamont, etc.) and products from the Fischer-Tropsch process.

[0094] Partial hydroisomerization dewaxing is defined for purposes of this document as a catalytic dewaxing process that uses a partial hydroisomerization dewaxing catalyst. In partial hydroisomerization dewaxing a portion of the wax is isomerized to iso-paraffins using catalysts that can isomerize paraffins selectively, but only if the conversion of wax is kept to relatively low values (typically below 70%). At higher conversions, wax conversion by cracking becomes significant, and yield losses of lube base stock becomes uneconomical. The acidic catalyst components useful for partial hydroisomerization dewaxing include amorphous silica aluminas, fluorided alumina, and 12-ring zeolites (such as Beta, Y zeolite, L zeolite). Because the wax conversion is incomplete, partial hydroisomerization dewaxing must be supplemented with an additional dewaxing technique, typically solvent dewaxing. The wax recovered from a solvent dewaxing operation following a partial hydroisomerization dewaxing can be recycled to the partial hydroisomerization dewaxing step.

[0095] Representative process conditions, yields, and product properties for partial hydroisomerization dewaxing are described, for example, in U.S. Pat. No. 5,049,536 to Belussi et al., and U.S. Pat. No. 4,943,672 to Hamner et al. These patents are incorporated herein by reference for all purposes. Process conditions are further described and exemplified in, EP 0 582 347 to Perego et al., EP 0 668 342 to Eilers et al., PCT WO 96/26993 by Apelian et al., and PCT WO 96/13563 by Apelian et al.

[0096] Complete hydroisomerization dewaxing is defined for purposes of this document as a catalytic dewaxing process that uses a complete hydroisomerization dewaxing catalyst. In complete hydroisomerization dewaxing, complete hydroisomerization dewaxing catalysts are used which can achieve high conversion levels of wax while maintaining acceptable selectivities to isomerization. The acidic catalyst components useful for partial hydroisomerization dewaxing include 10-ring, 1-dimensional, molecular sieves (such as ZSM-23, SSZ-32, Theta-1, ZSM-22, SAPO-11, and SAPO-41). Since wax conversion can be complete, or at least very high, this process typically does not need to be combined with additional dewaxing processes to produce a lube base stock with an acceptable pour point. Representative process conditions, yields, and product properties for complete hydroisomerization dewaxing are described, for example, in U.S. Pat. No. 5,135,638 to Miller; U.S. Pat. No. 5,246,566 to Miller; U.S. Pat. No. 5,282,958 to Santilli et al.; U.S. Pat. No. 5,082,986 to Miller; and U.S. Pat. No. 5,723,716 to Brandes et al.; the contents of each of which is incorporated herein by reference in their entirety.

	Catalytic Dewaxing		
		Hydroisomerization Dewaxing	
	Conventional Hydrodewaxing	Partial Hydroisomerization Dewaxing	Complete Hydroisomerization Dewaxing
Temperature, ° F.		400–800	
Pressure, psig		200–3000	
LHSV, hr-1		0.2–5.0	
n-C16 selectivity to isomerized products at 96% conversion	<10	10–40	>40 >60 preferably, >80 most preferably
Typical Acidic Components	ZSM-5, ZSM-11, ZSM-22, ZSM-35, Mordenite	Silica Alumina, Fluorided alumina, Beta, Y, and L zeolites	ZSM-23, SSZ-32, Theta-1, ZSM-22, SAPO-11, and SAPO-41
Typical metal Components	Optional, often absent	Pt or Pd, preferably Pt	Pt or Pd, preferably Pt

Blending with Petroleum Blend Stocks

[0097] The distillate fuel according to the present invention may be comprised of a combination of blend stocks, or the distillate fuel may be comprised of Fischer Tropsch distillate fuel blend stock in the absence of other blend stocks with only the optional addition of minor amounts of additives. Accordingly, the distillate fuels may comprise a Fischer-Tropsch distillate fuel blend stock mixed with petroleum blend stock. In a mixture of blend stocks, preferably the distillate fuel comprises 1 to 95 weight % Fischer Tropsch blend stock and 5 to 99 weight % petroleum blend stock. More preferably, the distillate fuel comprises 5 to 75 weight % Fischer Tropsch blend stock and 25 to 95 weight % petroleum blend stock. Even more preferably, the distillate fuel comprises 10 to 50 weight % Fischer Tropsch blend stock and 90 to 50 weight % petroleum blend stock.

[0098] In addition, in the process to make a highly paraffinic, moderately aromatic blend stock, the Fischer Tropsch feedstock may be blended with a petroleum blend stock at any stage in the process so long as a highly paraffinic, moderately aromatic distillate fuel blend stock according to the present invention is provided. By way of example, a petroleum blend stock may be blended with a Fischer Tropsch derived feedstock prior to hydroprocessing, after hydroprocessing but prior to removing polynuclear aromatics, or after removal of polynuclear aromatics but prior to use as a distillate fuel. Preferably, the petroleum blend stock is blended with the Fischer Tropsch feedstock prior to hydroprocessing and the resulting blended stream is hydroprocessed. If the Fischer Tropsch feedstock is mixed with a petroleum blend stock, preferably, the resulting blend comprises 1 to 95 weight % Fischer Tropsch feedstock and 99 to 5 weight % petroleum blend stock. More preferably, the blend comprises 5 to 75 weight % Fischer Tropsch feedstock and 95 to 25 weight % petroleum blend stock. Even more preferably, the blend comprises 10 to 50 weight % Fischer Tropsch feedstock and 50 to 90 weight % petroleum blend stock.

Removal of Polynuclear Aromatics

[0099] To meet the desired low content of polynuclear aromatics in the highly paraffinic, moderately aromatic blend stock, the product stream from the hydroprocessing operation can be further treated to remove polynuclear aromatics. Options for selectively removing polynuclear aromatics from the product stream while leaving desired mono-aromatics, include selective hydrotreating and adsorption.

[0100] The most preferred operation for removing polynuclear aromatics from the product stream is selective hydrotreating. The reaction conditions for selective hydrotreating do not vary greatly from the reaction conditions for hydrotreating described above. Reaction conditions for selective hydrotreating include low temperatures (less than 750° F., preferably less than 700° F., most preferably less than 600° F.), high pressures (greater than 250 psig, preferably greater than 350 psig, most preferably greater than 500 psig), and short contact times (LHSV of less than 5 hr^{-1}, preferably less than 3 hr^{-1}, and most preferably less than 2 hr^{-1}). Preferred catalysts for this selective hydrotreating contain Pt, Pd, and combinations thereof. The selective hydrotreating will reduce the polynuclear aromatic content by at least 50 weight %, preferably at least 75 weight %, and most preferably at least 90 weight %, and the mono-aromatic content by less than 50 weight %, preferably less than 35 weight %, and most preferably less than 20 weight %.

[0101] The removal of polynuclear aromatics from the product stream can also be achieved by adsorption on an oxide support, preferably one that has moderate acidity (an acidic clay such as montmorillonite or attapulgite). The temperatures for adsorption should be less than 200° F., preferably less than 150° F. Polynuclear aromatics can also be extracted with a solvent, such as n-methyl pyrollidinone or furfural.

Addition of Additives

[0102] The distillate fuel and distillate fuel blend stock may include additives that are commonly used for diesel or jet fuels. A description of diesel fuel additives that may be used in the present invention is as described in the Chevron Corporation, *Technical Review Diesel Fuels*, pp. 55-64 (2000) and a description of jet fuel additives that may be used in the present invention is as described in Chevron Corporation, *Technical Review Aviation Fuels*, pp 27-30 (2000). In particular, these additives may include, but are not limited to, antioxidants (especially low sulfur antioxidants), lubricity additives, pour point depressants, and the like. The additives are added to the fuels and blend stocks in a minor amount, preferably less than 1 weight %.

[0103] In particular, if necessary, the stability of a distillate fuel comprising the highly paraffinic, moderately aromatic blend stock or the stability of the blend stock of the present invention can be improved by addition of an antioxidant. A good review of the general field of antioxidants for fuels is in Gasoline and Diesel Fuel Additives, Critical Reports on Applied Chemistry, Vol. 25, John Wiley and Sons Publisher, Edited by K. Owen, pages 4 to 11.

[0104] Examples of anti-oxidants useful in the present invention include, but are not limited to, phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butyl-phenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tertbutyl-4-methylphenol, 2,6-di-tertbutyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-butyl-dimethylamino-p-cresol, 2,6-di-tert-4-(N,N'-dimethyl-aminomethylphenol), and bis(3,5-di-tert-butyl-4-hydroxybenzyl). Diphenylamine-type oxidation inhibitors include, but are not limited to, alkylated diphenylamine, phenyl-alpha-naphthylamine, and alkylated-alpha-naphthylamine. Mixtures of compounds may also be used. Antioxidants are added at below 500 ppm, typically below 200 ppm, and most typically from 5 to 100 ppm.

[0105] U.S. Pat. No. 4,320,021 to Lange, for example, discloses amino phenols having at least one substantially saturated hydrocarbon-based substituent of at least 30 carbon atoms. The amino phenols of this patent are taught to impart useful and desirable properties to oil-based lubricants and normally liquid fuels. Similar amino phenols are disclosed in related U.S. Pat. No. 4,320,020 to Lange. Similarly, U.S. Pat. No. 3,149,933 to Ley et al. discloses hydrocarbon-substituted amino phenols as stabilizers for liquid fuels.

[0106] U.S. Pat. No. 4,386,939 to Lange, discloses nitrogen-containing compositions prepared by reacting an amino phenol with at least one 3- or 4-membered ring heterocyclic compound in which the hetero atom is a single oxygen, sulfur or nitrogen atom, such as ethylene oxide. The nitrogen-containing compositions of this patent are taught to be useful as additives for lubricants and fuels.

[0107] Nitro phenols have also been employed as fuel additives. For example, U.S. Pat. No. 4,347,148 to Davis, discloses nitro phenols containing at least one aliphatic substituent having at least about 40 carbon atoms. The nitro phenols of this patent are taught to be useful as detergents, dispersants, antioxidants and demulsifiers for lubricating oil and fuel compositions.

Illustrative Embodiment

[0108] FIG. **1** represents a process for preparing a highly paraffinic, moderately aromatic distillate fuel blend stock according to the present invention. With reference to FIG. **1**, a Low Temperature Fischer-Tropsch derived feedstock (**10**) is hydroprocessed in a hydroprocessing unit (**100**) to which hydrogen (**20**) is added. Hydroprocessing conditions include a temperature of 600-750° F., a pressure of less than 1000 psig, and a liquid hourly space velocity of greater than 0.25 hr^{-1}. Optionally, to the product (**30**) of the hydroprocessing may be added an aromatic blend stock (**40**), such as commercially available pure aromatics or aromatics obtained from reforming of reformable Fischer-Tropsch products, to provide a highly paraffinic, moderately aromatic distillate fuel blend stock (**50**) containing between 2 and 20 weight % aromatics. The hydroprocessing may produce hydrogen (**60**), which can be used in other processes such as hydrotreatment, CO_2 reduction, and fuel production. Optionally, the highly paraffinic, moderately aromatic distillate fuel blend stock (**50**) may be further treated to remove polynuclear aromatics (**70**) in a processing unit (**200**) and/or an antioxidant (**80**) may be added.

[0109] The following examples are given to illustrate the invention and should not be construed to limit the scope of the invention.

EXAMPLES

Example 1

Preparation of Diesel Fuel Samples

[0110] A Low Temperature Fischer-Tropsch product was generated by reacting synthesis gas over an iron-containing catalyst. The product was separated into a diesel boiling range blend stock (A) and a wax. The diesel blend stock (A) was hydrotreated to remove oxygenates and saturate olefins. The wax was hydrocracked over a sulfided catalyst consisting of amorphous silica-alumina, alumina, tungsten and nickel. A second diesel blend stock (B) was recovered from the effluent of the hydrocracker. The two diesel blend stocks were blended in the proportion of 82% B and 18% A by weight. Properties of the Fischer-Tropsch (FT) diesel fuel blend are shown in Table I.

TABLE I

Properties of Fischer-Tropsch Diesel Fuel Blend

TESTS	ASTM D975 SPECIFICATIONS	Fischer-Tropsch Diesel Blend
API GRAVITY, 60° F.	40(min.)	52.3
NITROGEN, NG/UL		0.69
CETANE INDEX ASTM D613		72.3
NORMAL/NON-NORMAL PARAFFINS WT. %		
NORMAL PARAFFINS		17.24
NON NORMAL PARAFFINS		82.76
DISTILLATION D86, ° F. IBP		333
10%	540(min.), 640(max.)	371
50%		478
90%		631
95%		653
EPT		670

Example 2

Preparation and Evaluation of Blends of Fischer Tropsch Diesel with Alkylaromatics and Alkylcycloparaffins

[0111] Blends of a light alkylaromatic (cumene) or alkylcycloparaffin (isopropylcyclohexane) with a Fischer Tropsch diesel fuel blend stock were prepared. The improvement in the seal swell and lubricity were determined along with the decline in cetane index. A preference for alkylaromatics or alkylcycloparaffins can be determined by finding which species gives the greatest improvement in seal swell with the least decline in cetane index. The cetane index in these experiments was determined from a D2887 distillation, converted to D86 equivalent, molecular weight and density at 20° C. This method provides an acceptable and reproducible measurement of the cetane index.

The seat swell test followed ASTM D471:

[0112] O-ring type: Buna N O-ring, size 2-214; vendor: McDowell & Co.

[0113] Test Temperature: ambient 23+/−2° C.

[0114] Test Duration: 70 hours

[0115] Test sample size: 100 ml

[0116] Number of o-rings per sample: three

[0117] Results to report: Volume change and hardness change

TABLE II

	Seal Swell Results			
Blend	Vol. Change	Hardness	Density @ 20° C.	Cetane Index
Neat Fischer-Tropsch diesel blend stock	0.14	−6.3	0.7662	73.4
FT Diesel blend stock + 1 wt % cumene	0.11	−4.9	0.7671	72.5
FT Diesel blend stock + 5 wt % cumene	0.84	−5.5	0.7702	68.7
FT Diesel blend stock + 10 wt % cumene	2.12	−6.4	0.7742	63.0

TABLE II-continued

Blend	Seal Swell Results Vol. Change	 Hardness	Density @ 20° C.	Cetane Index
FT Diesel blend stock + 20 wt % cumene	5.78	−5.6	0.7825	53.7
FT Diesel blend stock + 1 wt % isopropylcyclohexane	0.02	−3.6	0.7665	72.8
FT Diesel blend stock + 5 wt % isopropylcyclohexane	0.11	−2.4	0.7679	69.9
FT Diesel blend stock + 10 wt % isopropylcyclohexane	0.66	−4.5	0.7696	65.8
FT Diesel blend stock + 20 wt % isopropylcyclohexane	0.72	−5.5	0.7730	59.6

[0118] Conventional petroleum derived diesel fuels cause seals of this type to expand and over a long time harden. Highly paraffinic fuels, such as Fischer Tropsch, cause less of an expansion, and can in fact cause a contraction if the seal had been exposed to a conventional fuel previously. These results demonstrate that adding an alkylaromatic or alkylcycloparaffin to a Fischer Tropsch diesel blend stock causes the seal to swell in a fashion similar to conventional fuels. Thus blends of highly paraffinic distillate fuel blend stocks and alkylaromatics and/or alkylcycloparaffins should exhibit fewer problems with leaking seals in commercial use. During the short term of this test, adding alkylaromatic or alkylcycloparaffin caused no significant change in hardness.

[0119] A comparison of blending an alkylaromatic (cumene) to an alkylcycloparaffin (isopropylbenzene) is shown in FIG. **2**. Adding an alkylaromatic is preferable to adding an alkylcycloparaffin. A smaller amount of an alkylaromatic is needed to make a given change in volume, and addition of alkylaromatics causes a smaller impact on the cetane index.

Example 3

[0120] A light Fischer-Tropsch wax (Table III) was hydrocracked over a sulfided nickel-tungsten/silica-alumina catalyst LHSV 1 hr^{-1}, 1000 psig, 685° F., and 6.3 MSCF/bbl. At these conditions, conversion below 650° F. was 80.4 weight %. The liquid product was cut at about 350° F. and about 675° F. to give a diesel blend stock fraction. Yields and properties of the diesel blend stock are given in Table IV.

TABLE III

FEEDSTOCK INSPECTIONS OF LIGHT FT WAX

Gravity, API	42.5
Nitrogen, ppm	3.2
Sim. Dist., LV %, ° F.	
ST/5	728/771
10/30	789/811
50	839
70/90	858/885
95/EP	898/943

[0121]

TABLE IV

HYDROCRACKING OF LIGHT FT WAX OVER Ni—W—SIO_2—AL_2O_3 AT LHSV 1 hr^{-1}, 685° F., 1000 PSIG, AND 6.3 MSCF/BBL

Conversion <650° F., Weight %	80.4
Yield, Weight %	
C_1–C_2	0.03
C_3–C_4	5.06
C_5-180° F.	17.77
180–350° F.	20.85
350–650° F.	37.51
650° F.+	19.71
C_{5+}	95.49
350–675° F. Properties	
Weight % of Feed	52.9
Gravity, API	50.7
Viscosity, 40° C., cSt	2.631
Cloud Point, ° C.	−26
SFC Analysis, Wt %	
Aromatics	0.3
Olefins	0.8
Oxygenates	<0.1
Saturates	98.9
PNA Aromatics, weight %	Not Detected
Cetane Index	75.9
Refractive Index @ 20° C.	1.4342
Density, g/ml @ 20° C.	0.7745
Molecular Wt.	253
Carbon Types by ndM, weight % P/N/A	100/0/0
D2887 Dist., Wt %, ° F.	
ST/5	288/342
10/30	368/448
50	523
70/90	594/673
95/EP	697/743

[0122] The lower limit of detection of PNA by Supercritical Fluid Chromatography (SFC) was 0.5 weight %. Thus non-detected values are less than this amount. Operation at these conditions produced only 0.3 percent aromatics and retained 0.8 wt % olefins due to the high pressure conventional operation. The paraffin content of this sample was equivalent to the saturate content (98.9). The ndM analysis, which is suitable for non-olefin containing samples, indicated the absence of naphthenic carbon structures.

Example 4

[0123] The same feed as in Example 3 was hydrocracked over a sulfided 3/1 layered bed of the same catalyst as in Example 3 over a Pt/SAPO-11 catalyst bound with 15 weight % alumina. Conditions were the same as in Example 3, that is overall LHSV 1.0 hr^{-1}, 1000 psig, 685° F., and 6.3 MSCF/bbl H_2. Conversion below 650° F. was 74.6 weight %. The product was cut at about 350° F. and about 650° F. to give a diesel blend stock cut. Yields and diesel blend stock properties are given in Table V. As determined by ASTM D6468, the diesel blend stock was very stable. Aromatics in the diesel blend stock were 0.1 weight % and olefins were 0.3 wt % due to the conventional high pressure operation and use of Pt as a catalytic metal. The paraffin content was 99.6 since naphthenes are absent as determined by GC-MS, and supported by ndM analysis. The Cetane Index was very high (73.8) and the cloud point very low (−57° C.).

TABLE V

HYDROCRACKING OF LIGHT FT WAX OVER
3/1 NI-W-SIO_2-AL_2O_3/PT-SAPO-11
AT LHSV 1 hr^{-1}, 685° F., 1000 PSIG, AND 6.3 MSCF/BBL

Conversion <650° F., Weight %	74.6
Yield, Weight %	
C_1–C_2	0.08
C_3–C_4	5.16
C_5-180° F.	13.02
180–350° F.	15.70
350–650° F.	40.97
650° F.+	25.59
C_5+	95.36
350–650° F. Properties	
Weight % of Feed	43.1
Gravity, API	51.3
Viscosity, 40° C., cSt	2.206
Cloud Point, ° C.	−57
Olefins, Weight % (GC-MS)	Not Detected
PNA Aromatics, weight %	Not Detected
SFC Analysis, Wt %	
Aromatics	0.1
Olefins	0.3
Oxygenates	<0.1
Saturates	99.6
% Reflectance, ASTM D6468 @150° C.	
1.5 hr	99.7
3.0 hr	99.8
Cetane Index	73.8
Refractive Index @ 20° C.	1.4318
Density, g/ml @ 20° C.	0.7699
Molecular Wt.	239
Carbon types by ndM, weight % P/N/A	100/0/0
D2887 Dist., Wt %, ° F.	
ST/5	314/352
10/30	370/433
50	496
70/90	549/606
95/EP	629/676

Example 5

[0124] Example 4 was repeated, but at a total pressure in the reactor of 500 psig, and a reactor temperature of 680° F. Conversion below 650° F. was 63.5 weight %. The product was cut at about 350° F. and about 590° F. to give a diesel blend stock cut. Yields and diesel blend stock properties are given in Table VI. As determined by ASTM D6468, the diesel blend stock was very stable. Aromatics in the diesel blend stock were 2.3 weight %. The Cetane Index was still quite high (69.1) and the cloud point very low (−50° C.).

TABLE VI

HYDROCRACKING OF LIGHT FT WAX OVER
3/1 NI-W-SIO2-AL2O3/PT-SAPO-11
AT LHSV 1 hr^{-1}, 680° F., 500 PSIG, AND 6.3 MSCF/BBL

Conversion <650° F., Weight %	63.5
Yield, Weight %	
C_1–C_2	0.23
C_3–C_4	10.53
C_5-180° F.	13.98
180–350° F.	15.63
350–650° F.	23.72
650° F.+	36.75
C_5+	90.0
350–590° F. Properties	
Weight % of Feed	19.1
Gravity, API	51.1
Viscosity, 40° C., cSt	1.94
Cloud Point, ° C.	−50
PNA Aromatics, weight %	Not Detected
% Reflectance, ASTM D6468 @150° C.	
1.5 hr	99.7
3.0 hr	99.7
Cetane Index	69.1
Refractive Index @ 20° C.	1.4323
Density, g/ml @ 20° C.	0.7704
Molecular Wt.	224
D2887 Dist., Wt %, ° F.	
ST/5	316/350
10/30	366/415
50	468
70/90	519/572
95/EP	591/643

Eample 6

[0125] A 700-1000° F. hydrotreated FT wax (Table VII) was hydrocracked over the same layered bed catalyst system of Example 2. Conditions included an overall LHSV 1.0 hr^{-1}, reactor pressure of 300 psig, 680° F. for the top catalyst and 690° F. for the bottom catalyst, and 6.3 MSCF/bbl H_2. Conversion below 650° F. was 58.2 weight %. The product was cut at about 300° F. and about 650° F. to give a diesel blend stock cut. Yields and properties of this diesel blend stock are given in Table VII. As determined by ASTM D6468, the diesel blend stock was very stable. Aromatics in the diesel blend stock were 4.3 weight, olefins were 1.0 wt %, and oxygenates were 0.5 wt %. Paraffins are equal to the saturates (94.2%) because the GC-MS technique did not detect significant quantities of the sum of olefins and naphthenes. The Cetane Index was high (67.6) and the cloud point was −44° C.

TABLE VII

FEEDSTOCK INSPECTIONS OF
700–1000° F. HYDROTREATED FT WAX

Gravity, API	42.3
Sim. Dist., LV %, ° F.	
ST/5	691/804
10/30	824/884
50	919
70/90	940/974
95/EP	991/1031

[0126]

TABLE VIII

HYDROCRACKING OF 700–1000° F. HYDROTREATED FT WAX OVER 3/1 NI-W-SIO_2-AL_2O_3/PT-SAPO-11 AT LHSV 1 hr^{-1}, 680° F./690° F., 300 PSIG, AND 6.3 MSCF/BBL

Conversion <650° F., Weight %	58.2
Yield, Weight %	
C_1–C_2	0
C_3–C_4	4.78
C_5-180° F.	14.93
180–350° F.	15.53
350–650° F.	23.22
650° F.+	41.92
C_5+	95.7
350–650° F. Properties	
Weight % of Feed	31.1
Gravity, API	50.1
Viscosity, 40° C., cSt	2.027
Cloud Point, ° C.	−44
Naphthenes + Olefins, Weight % (GC-MS)	Not Detected
SFC Analysis, Wt %	
Aromatics	4.3
Olefins	1.0
Oxygenates	0.5
Saturates	94.2
PNA Aromatics, weight %	0.5
% Reflectance, ASTM D6468 @150° C.	
1.5 hr	99.2
3.0 hr	99.2
Cetane Index	67.6
Refractive Index @ 20° C.	1.4348
Density, g/ml @ 20° C.	0.7741
Molecular Wt.	196
D2887 Dist., Wt %, ° F.	
ST/5	266/300
10/30	325/396
50	472
70/90	561/645
95/EP	667/698

[0127] The diesel blend stock of example 6 exhibited excellent stability as measured by ASTM D6468 at 150° C. for 180 minutes, as did the diesel blend stocks of examples 4 and 5, with results in excess of 99%. The polynuclear aromatic content of the diesel blend stock of example 6 was less than 12 weight % of the total aromatics (4.3%).

[0128] The following are a series of Comparative Examples illustrating that untreated Fischer Tropsch products are unstable with respect to peroxide formation and that the conventional hydroprocessing operation yields a product with an extremely low amount of unsaturates which is stable with respect to peroxide formation.

Comparative Example 7

Preparation of a Fully Hydrogenated Diesel Blend Stock

[0129] A highly paraffinic diesel blend stock was prepared from three individual Low Temperature Fischer-Tropsch feedstocks.

TABLE IX

Properties of Fischer-Tropsch Feedstocks

Property	Feedstock 1	Feedstock 2	Feedstock 3
Wt % in blend	27.8	23.1	49.1
Gravity, °API	56.8	44.9	40.0
Sulfur, ppm	<1	<1	
Oxygen, ppm by Neut. Act.	1.58	0.65	
Chemical Types, Wt % by GC-MS			
Paraffins	38.4	62.6	85.3
Olefins	49.5	28.2	1.6
Alcohols	11.5	7.3	9.3
Other Species	0.5	3.9	3.8
Distillation by D-2887, ° F. by wt %			
0.5/5	80/199	73/449	521/626
10/30	209/298	483/551	666/758
50	364	625	840
70/90	417/485	691/791	926/1039
95/99.5	518/709	872/1074	1095/1184

[0130] The blend stock was prepared continuously by feeding the different feedstocks down-flow to a hydroprocessing reactor. The reactor was filled with a catalyst containing alumina, silica, nickel, and tungsten. The catalyst was sulfided prior to use. The per-pass conversion was maintained at approximately 80% below the recycle cut point of 665-710° F. by adjusting the catalyst temperature.

[0131] The product from the hydroprocessing reactor after separation and recycling of unreacted hydrogen was continuously distilled to provide a gaseous by-product, a light naphtha fraction, a diesel blend stock fraction, and an unconverted fraction. The unconverted fraction was recycled to the hydroprocessing reactor. The temperatures of the distillation column were adjusted to maintain the flash and cloud points at their target values of 58° C. and −18° C., respectively.

[0132] The feedstocks were blended for several hours of consistent operation at 1.4 LHSV to provide the representative Product A in the Table X.

TABLE X

Properties of Blended Distillate Fuel Blend Stock Product

	Sample ID	
	A	B
Gravity, °API	52.7	52.5
Nitrogen, ppm	0.24	0.25
Sulfur, ppm	<1	0.61
Water, ppm by Karl Fisher, ppm	21.5	
Pour Point, ° C.	−23	−23
Cloud Point, ° C.	−18	−18
Flash Point, ° C.	58	59
Autoignition Temperature, ° F.	475	410
Viscosity at 25° C., cSt	2.564	2.304
Viscosity at 40° C., cSt	1.981	1.784
Cetane Number	74	72.3
Aromatics by Supercritical Fluid Chromatography, wt %	<1	0.9
Neutralization No.	0	
Ash Oxide, Wt %	<0.001	
Ramsbottom Carbon Residue, wt %	0.02	

TABLE X-continued

Properties of Blended Distillate Fuel Blend Stock Product

Cu Strip Corrosion	1A			
Color, ASTM D1500	0		0.2	
GC-MS Analysis				
Paraffins, Wt %	100		81.64	
Paraffin i/n ratio	2.1		1.02	
Oxygen as oxygenates, ppm	<6		1226	
Olefins, Wt %	0		17.52	
Average Carbon Number	14.4		13.20	
Distillation by D-2887 by Wt %, ° F. and D-86 by Vol %, ° F.	D-2887	D-86	D-2887	D-86
0.5/5	255/300	329/356	256/298	334/360
10/20	326/368	366/393	329/367	366/—
30/40	406/449	419/449	400/429	413/—
50	487	480	463	466
60/70	523/562	510/539	500/537	—/519
80/90	600/637	567/597	574/605	—/572
95/99.5	659/705	615/630	626/663	587/604

[0133] Oxygen can be present in the sample in the form of organic oxygenates, measured by gas chromatography-mass spectrometry (GC-MS), dissolved or suspended water, measured by Karl Fischer, or dissolved O_2 from the air.

[0134] The oxygenate content was determined by GC-MS. Oxygenates in the sample were treated with tetraethoxysilane (TEOS) to increase the sensitivity of the technique. Oxygenates could not be detected Product A. The limit of detection of the technique was determined to be 6.5 ppm per oxygenate. With the molecular weight range of diesel fuel this is equivalent to 0.6 ppm oxygen as oxygenates. Given that there are roughly 10 oxygenate compounds in a typical sample just below this limit of detection, the maximum amount of oxygen as oxygenates in the sample is 6 ppm (0.0006 weight %).

[0135] Using data from O_2 solubility in pure compounds, it has been estimated that the solubility of O_2 from air in Product A is approximately 92 ppm (0.0092 weight %). There are no readily available methods for measuring dissolved O_2. The GC-MS analyses are shown in Table XI.

TABLE XI

GC-MS analysis of distillate fuel blend stock

Formula	N-alkane area %	Branched alkane area %	Total alkanes	i/n by Carbon No.
C_9H_{20}	2.96	0.00	2.96	—
$C_{10}H_{22}$	3.59	4.24	7.83	1.18
$C_{11}H_{24}$	3.80	4.65	8.45	1.22
$C_{12}H_{26}$	3.65	4.77	8.42	1.31
$C_{13}H_{28}$	3.41	5.34	8.75	1.57
$C_{14}H_{30}$	3.00	5.34	8.34	1.78
$C_{15}H_{32}$	2.61	5.56	8.17	2.13
$C_{16}H_{34}$	2.33	8.65	10.98	3.71
$C_{17}H_{36}$	1.99	5.74	7.72	2.89
$C_{18}H_{38}$	1.51	6.11	7.62	4.04
$C_{19}H_{40}$	1.60	5.98	7.58	3.73
$C_{20}H_{42}$	1.18	5.35	6.53	4.52
$C_{21}H_{44}$	0.58	3.82	4.41	6.54
$C_{22}H_{46}$	0.22	2.00	2.23	8.94

TABLE XI-continued

GC-MS analysis of distillate fuel blend stock

Percent Paraffins	100.00
Percent Olefins	0.00
Average Carbon Number	15.12
Boiling point of Avg. Carbon No. ° F.	521
Total sample paraffin i/n ratio	2.08

[0136] As noted above, oxygenates were not detected in Product A. Also, Product A contains less than 1 weight % aromatics. The lack of aromatics further increases the likelihood that Product A will rapidly oxidize.

Comparative Example 8

Preparation of an Olefinic Diesel Fuel Blend Stock

[0137] In this example, Feedstock 1 of the Fischer-Tropsch blend stock in Table IX was by-passed around the hydroprocessing unit and fed directly to the distillation column. The same catalysts and conditions used in Example 7, including an LHSV of 1.4, were used, and the conditions of the distillation column were adjusted to maintain flash and cloud points in the product as used in Example 7. The yield of diesel fuel blend stock was less, near 73%, due to requirement to reduce the end point of the diesel fuel blend stock to maintain cloud point.

[0138] Diesel fuel blend stock was blended from several hours of consistent operation to provide the representative Product B in the Table X. In contrast to the operation where all the Fischer-Tropsch streams were fed to the hydroprocessing unit, by-passing the light components resulted in lower yields of diesel fuel blend stock as a result of the lower diesel end point. The lower diesel end point was probably a result of the higher concentration of heavy n-paraffins in Product B. The GC-MS analysis of Product B are shown in Table XII.

TABLE XII

GC-MS analysis of Product B

Carbon No.	1-alkenes	n-alkanes	i-alkanes	alcohols	Sum	Paraffin i/n ratio
C_6	0.00	0.00	0.00	0.03	0.03	
C_7	0.00	0.00	0.00	0.21	0.21	
C_8	0.00	0.00	0.00	0.32	0.32	
C_9	2.49	2.49	2.13	0.21	7.32	0.86
C_{10}	3.55	3.20	4.62	0.12	11.49	1.44
C_{11}	3.91	3.91	4.97	0.03	12.82	1.27
C_{12}	3.55	4.26	4.62	0.09	12.52	1.08
C_{13}	2.35	4.36	4.69	0.00	11.39	1.08
C_{14}	1.68	4.69	4.02	0.00	10.39	0.86
C_{15}	0.00	4.36	6.03	0.00	10.39	1.38
C_{16}	0.00	4.36	4.02	0.00	8.38	0.92
C_{17}	0.00	4.36	3.35	0.00	7.71	0.77
C_{18}	0.00	3.02	1.68	0.00	4.69	0.56
C_{19}	0.00	1.34	1.01	0.00	2.35	0.75
Sums	17.52	40.32	41.14	1.02	100.00	

Percent Paraffins	81.46
Percent Olefins	17.52
Average Carbon Number	13.20
Oxygen as oxygenates, ppm	1226
Total sample paraffin i/n ratio	1.02

[0139] These results also show that when a portion of the Fischer-Tropsch stream by-passes the hydroprocessing reactor and is blended into the final blend stock product, significant quantities of olefins are included in the blend stock product. The olefins in the blend stock product are in fact ten times greater than the alcohols. The olefins and oxygenates create potential stability problems.

Example 9

Stability Measurements

[0140] Product B was tested according to ASTM D6468 at 150° C. for 180 minutes and found to have a stability of 99.3%, which indicates that it is extremely stable towards deposit formation in this test.

[0141] The Products were then tested for peroxide formation under accelerated formation according to methods as described in U.S. Pat. Nos. 6,162,956 and 6,180,842. The Products were tested according to a standard procedure for measuring the buildup of peroxides. First, a 4 oz. sample was placed in a brown bottle and aerated for 3 minutes. An aliquot of the sample was then tested according to ASTM D3703 for peroxides. The peroxide content of the samples was measured by use of procedures following ASTM D3703 with exception that the Freon solvent was replaced by isooctane. The sample was then capped and placed into a 60° C. oven for 1 week. After this time the peroxide number was repeated, and the sample was returned to the oven. The procedure continued each week until 4 weeks have elapsed and the final peroxide number is obtained. Table XIII contains peroxide formation tendencies.

TABLE XIII

Peroxide Formation Tendencies

	A	B
Initial Peroxide No.	1.3	8.2
Peroxide No. after 1 weeks at 60° C.	1.0	35
Peroxide No. after 2 weeks at 60° C.	1.5	156
Peroxide No. after 3 weeks at 60° C.	1.88	204
Peroxide No. after 4 weeks at 60° C.	<5	>5

[0142] An additional test of Product A was done at 70° C. The initial peroxide number and the peroxide number after 4 weeks are both less than 1 ppm. These results indicate that Product A has significantly better peroxide stability than Product B. These test results demonstrate the stability of fully hydrogenated low temperature Fischer Tropsch products and the very rapid peroxide forming tendencies of distillate fuel blend stocks containing unhydroprocessed Fischer Tropsch streams.

Example 10

Effect of Trace Olefins on Peroxide Stability

[0143] A further study was done to determine the effects of adding small amounts of olefinic condensate to the stable blend stock Product A of Table X. A 300-600° F. portion of the low temperature cold condensate, Feedstock 1 of Table IX, was obtained by distillation. The properties of the 300-600° F. portion of the cold condensate are as follows:

TABLE XIV

Properties of the 300–600° F. Portion of the Cold Condensate

Property	Value
API Gravity	65.3
Nitrogen, ppm	0.79
Sulfur, ppm	2.29
Bromine No.	48.2
imulated Distillation, D-2887	
S° F. by Wt %	
0.5/5%	296/302
10/30%	332/383
50%	393
70/90%	459/523
95/99.5%	551/654

[0144] A GC-MS analysis of the 300-600° F. portion of the cold condensate produced these results in weight %:

TABLE XV

GC-MS analysis of the 300–600° F. Portion of the Cold Condensate

Carbon No.	n-Alkenes	Alkanes	Alcohols	Sum
C_6	0.00	0.00	0.00	0.00
C_7	0.00	0.00	1.54	1.54
C_8	0.00	0.00	0.32	0.32
C_9	2.20	3.30	1.32	6.82
C_{10}	12.37	5.35	1.03	18.75
C_{11}	11.46	5.28	0.81	17.54
C_{12}	10.37	5.94	0.54	16.85
C_{13}	8.43	5.72	0.29	14.44
C_{14}	5.85	4.69	0.19	10.74
C_{15}	3.31	3.01	0.00	6.32
C_{16}	1.60	1.76	0.00	3.36
C_{17}	0.73	0.95	0.00	1.69
C_{18}	0.34	0.55	0.00	0.89
C_{19}	0.15	0.33	0.00	0.48
C_{20}	0.06	0.21	0.00	0.26
Sums	56.87	37.10	6.03	100.00

Percent Paraffins	37.10	Oxygen as oxygenates, ppm	6769
Percent Olefins	56.87	Oxygen as primary C_{12}–C_{24} alcohols, ppm	832
Average Carbon Number	12.03	Oxygen as primary C_7–C_{12} alcohols, ppm	6398
Standard Deviation	2.10		
Percent C_{12}–C_{24} Material	55.02		

Example 11

[0145] The 300-600° F. portion of the cold condensate was blended in varying amounts with the Stable Fuel Blend Stock A of Table X and the blends were evaluated for peroxide formation with the following results:

TABLE XVI

Peroxide Formation of Blends 1-5

Sample No.	Volume Cold Condensate, ml	Volume Stable Blend Stock, ml	Olefins in the Blend, Wt %	Peroxide Result vs Weeks of Storage at 60° C., ppm				
				0	1	2	3	4
1	0	100	0	<1	<1	<1	<1	<1
2	0.2	99.8	0.1	<1	<1	<1	1.1	1.0
3	0.5	99.5	0.3	<1	<1	1.6	5.3	6.7
4	1	99.0	0.6	1.2	2.5	7.7	20.0	37.0
5	2	98.0	1.13	1.1	5.6	23.2	53.0	58.0

[0146] These results show that the blend stock prepared by hydrotreating the entire portion, without direct blending of cold condensate, is stable with respect to formation of peroxide. Blend stocks can tolerate only up to 0.2 weight % cold condensate (0.012 wt % oxygenates as alcohols determined by GC-MS and about 0.1 wt % olefins) and still be considered stable. Blend stocks with more than 0.012 wt % oxygenates or 0.1% olefins did not exhibit satisfactory stability. As the oxygenate content was increased beyond 0.012 wt %, the peroxide stability of the blend stock rapidly declined.

[0147] While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made without departing from the spirit and scope thereof.

1. A distillate fuel comprising a Fischer-Tropsch distillate fuel blend stock, wherein the Fischer-Tropsch distillate fuel blend stock comprises:

a) aromatics in an amount between 2 and 20 weight %;

b) paraffins in an amount 80 weight % or greater;

c) a cetane index greater than 60; and

d) a volume change as measured by ASTM D471 of at least 0.25%, using a Buta N nitrile O-Ring at 23+/−2° C. for 70 hours.

2. A fuel according to claim 1, wherein approximately 100 weight % of the distillate fuel is Fischer-Tropsch distillate fuel blend stock.

3. A fuel according to claim 1, further comprising petroleum blend stock.

4. A fuel according to claim 3, wherein the fuel comprises 5 to 75 weight % Fischer-Tropsch distillate fuel blend stock and 95 to 25 weight % petroleum blend stock.

5. A fuel according to claim 1, wherein at least a portion of the aromatics originate from an aromatic blend stock.

6. A fuel according to claim 1, wherein the Fischer-Tropsch distillate fuel blend stock comprises aromatics in an amount between 2 and 15 weight %.

7. A fuel according to claim 1, wherein the Fischer-Tropsch distillate fuel blend stock comprises aromatics in an amount between 5 and 10 weight %.

8. A fuel according to claim 1, wherein the Fischer-Tropsch distillate fuel blend stock comprises a volume change as measured by ASTM D471 of at least 0.5%.

9. A fuel according to claim 1, wherein the Fischer-Tropsch distillate fuel blend stock comprises a volume change as measured by ASTM D471 of at least 2%.

10. A fuel according to claim 1, wherein the aromatics comprise less than 20 weight % polynuclear aromatics.

11. A fuel according to claim 1, wherein the distillate fuel further comprises sulfur in an amount less than 1 ppm.

12. A fuel according to claim 1, wherein the distillate fuel further comprises nitrogen in an amount less than 1 ppm.

13. A fuel according to claim 1, wherein the distillate fuel further comprises an antioxidant.

14. A fuel according to claim 1, wherein the distillate fuel conforms to at least one specification for either diesel fuel or jet fuel.

15. A fuel according to claim 14, wherein the distillate fuel conforms to at least one specification for a diesel fuel and has a cetane index greater than 65.

16. A fuel according to claim 15, wherein the fuel has a percent reflectance according to ASTM D6468 at 150° C. in excess of 65% when measured at 90 minutes.

17. A fuel according to claim 14, wherein the distillate fuel conforms to at least one specification for a jet fuel and has a passing rating in ASTM D3241 at 260° C. for 2.5 hours.

18. A Fischer-Tropsch diesel fuel blend stock comprising:

a) aromatics in an amount between 5 and 10 weight % wherein the aromatics comprise less than 20 weight % polynuclear aromatics;

b) paraffins in an amount 90 weight % or greater;

c) sulfur in an amount less than 1 ppm;

d) a cetane index greater than 60;

e) a percent reflectance according to ASTM D6468 at 150° C. in excess of 65% when measured at 90 minutes; and

f) a volume change as measured by ASTM D471 of at least 0.5% using a Buta N nitrile O-Ring at 23+/−2° C. for 70 hours.

19. A blend stock according to claim 18, wherein the blend stock has a cetane index of greater than 65.

20. A blend stock according to claim 18, wherein the blend stock has a cetane index of greater than 70.

21. A blend stock according to claim 18, wherein the aromatics comprise less that 10 weight % polynuclear aromatics.

22. A Fischer-Tropsch jet fuel blend stock comprising:

a) aromatics in an amount between 5 and 10 weight % wherein the aromatics comprise less than 20 weight % polynuclear aromatics;

b) paraffins in an amount 90 weight % or greater;

c) sulfur in an amount less than 1 ppm;

d) a smoke point of 30 mm or greater;

e) a passing rating in ASTM D3241 at 260° C. for 2.5 hours; and

f) a volume change as measured by ASTM D471 of at least 0.5% using a Buta N nitrile O-Ring at 23+/−2° C. for 70 hours.

23. A blend stock according to claim 22, wherein the blend stock has a passing rating in ASTM D3241 at 270° C. for 2.5 hours.

24. A blend stock according to claim 22, wherein the aromatics comprise less than 10 weight % polynuclear aromatics.

25-36. (canceled)

37. A distillate fuel comprising a Fischer-Tropsch distillate fuel blend stock, wherein the Fischer-Tropsch distillate fuel blend stock is made by a process comprising:

a) converting syngas to a Fischer-Tropsch derived feedstock by a Fischer-Tropsch process;

b) hydroprocessing the Fischer-Tropsch derived feedstock at a temperature of 525-775° F., a pressure of less than 1000 psig, and a liquid hourly space velocity of greater than 0.25 hr^{-1}; and

c) recovering a Fischer-Tropsch distillate fuel blend stock, wherein the Fischer-Tropsch distillate fuel blend stock comprises between 2 and 20 weight % aromatics and 80 weight % or greater paraffins.

38. A fuel according to claim 37, wherein the Fischer-Tropsch distillate fuel blend stock exhibits a volume change as measured by ASTM D471 of at least 0.5% using a Buta N nitrile O-Ring at 23+/−2° C. for 70 hours.

39. A fuel according to claim 38, wherein the distillate fuel conforms to at least one specification for a diesel fuel and has a cetane index greater than 60.

40. A fuel according to claim 38, wherein the distillate fuel conforms to at least one specification for a jet fuel and has a passing rating in ASTM D3241 at 260° C. for 2.5 hours.

41-45. (canceled)

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