A process for producing a premium Fischer-Tropsch diesel fuel which comprises (a) hydroprocessing a waxy Fischer-Tropsch feed to remove the oxygenates that are present in the feed; whereby a first Fischer-Tropsch intermediate product is produced with reduced olefins and oxygenates relative to the Fischer-Tropsch feed; (b) separating the first Fischer-Tropsch intermediate product in a separation zone into a heavy Fischer-Tropsch fraction and a light Fischer-Tropsch fraction under controlled separation conditions; (c) hydro-isomerizing the heavy Fischer-Tropsch fraction to improve the cold flow properties of the heavy Fischer-Tropsch fraction and recovering an isomerized heavy Fischer-Tropsch fraction; (d) mixing the isomerized heavy Fischer-Tropsch fraction with at least a portion of the light Fischer-Tropsch fraction of (b); and (e) recovering from the blend a Fischer-Tropsch derived diesel product meeting a target value for at least one pre-selected specification for diesel fuel.
PROCESS FOR PRODUCING PREMIUM FISCHER-TROPSCH DIESEL AND LUBE BASE OILS

FIELD OF THE INVENTION

[0001] The present invention relates to the production of a premium Fischer-Tropsch derived diesel product produced by the blending of a Fischer-Tropsch derived diesel fraction and a heavier isomerized Fischer-Tropsch derived base oil fraction to meet at least one pre-selected target property for the diesel product.

BACKGROUND OF THE INVENTION

[0002] Transportation fuels intended for use in diesel engines must conform to the current version of at least one of the following specifications:


[0004] European Grade CEN 90

[0005] Japanese Fuel Standards JIS K 2204

[0006] The United States National Conference on Weights and Measures (NCWM) 1997 guidelines for premium diesel fuel

[0007] The United States Engine Manufacturers Association recommended guideline for premium diesel fuel (FQP-1A)

[0008] These specifications set a number of minimum technical requirements for diesel, so establishing a minimum quality level below which the diesel fuel is not considered technically fit for the purpose. Fischer-Tropsch derived transportation fuels meeting the specifications for diesel fuels have certain advantageous properties which make it possible to prepare a premium diesel fuel having very low sulfur content and an excellent cetane number. However, due to the unique characteristics of Fischer-Tropsch derived syncrude additional processing operations must be carried out to produce a suitable diesel fuel. Since Fischer-Tropsch derived products generally contain a significant proportion of olefins, in order to improve the oxidation stability a hydrotreating operation, such as mild hydrotreating, is usually necessary to saturate the double bonds. In addition, in order to improve the cold flow properties of the fuel, the isoparaffin content usually must be increased by a dewaxing step. Unfortunately, in the large volumes characteristic of transportation fuels, the cost of the dewaxing step may make the Fischer-Tropsch derived diesel fuel uncompetitive with conventional petroleum derived diesel fuels.

[0009] Premium lubricating base oils may also be prepared from Fischer-Tropsch derived hydrocarbons, but due to the high proportion of linear paraffins in the product a dewaxing step is also required to improve the cold flow properties prior to sale. However, lubricating base oils generally are produced in smaller quantities than transportation fuels and have a higher commercial value, so the dewaxing operation is not commercially impractical.

[0010] The present invention is directed to an integrated process which is able to produce a premium Fischer-Tropsch derived diesel fuel in combination with a premium Fischer-Tropsch derived lubricating base oil. In the process of the invention, the properties of the base oil fraction recovered from the syncrude are carefully controlled to produce a product which after further processing may be blended back into the diesel fraction to produce a diesel fuel having the desired properties. The process of the invention is advantageous because it is possible to produce a premium diesel fuel without hydrosanimerizing the entire diesel product. This decrease in feed results in significant savings in capital costs due to the smaller vessel size required for the isomerization reactor. By significantly lowering the cost of processing the Fischer-Tropsch derived diesel fuel, it is possible to produce a premium product which is competitive in cost with conventional petroleum derived diesel fuel.

[0011] The Fischer-Tropsch syncrude fraction which is processed into diesel fuels usually will have a boiling range between about 150 degrees F. (about 65 degrees C.) and about 750 degrees F. (about 400 degrees C.), typically between about 400 degrees F. (about 205 degrees C.) and about 600 degrees F. (about 315 degrees C.). The majority of the hydrocarbons boiling in the range of diesel will contain between about 9 and about 19 carbon atoms in the molecule. Lubricating base oils are generally prepared from that portion of the Fischer Tropsch syncrude boiling above about 600 degrees F. (about 315 degrees C.) and containing at least 20 carbon atoms in the molecule. However, the initial boiling point of the base oil fraction may be higher, for example about 750 degrees F. (about 400 degrees C.). One skilled in the art will recognize that there is considerable overlap between the upper boiling point of diesel and the initial boiling point of the base oil fractions. The precise cut point selected will depend upon the properties desired in the final products. By carefully controlling the separation point between diesel and base oil, it is possible to tailor the properties of the two products, so that when a portion of the hydrosanimerized base oil is blended back into the diesel, the diesel product will meet the criteria of a premium diesel fuel without the necessity of isomerizing the entire diesel stream.

[0012] Naphtha which is also produced by the process of present invention has a boiling range below that of diesel but above that of the normally gaseous hydrocarbons, such as butane and propane. Accordingly, naphtha generally has a boiling range between ambient temperature and about 150 degrees F. (about 65 degrees C.), and the molecules boiling within this range will contain between about 5 and about 8 carbon atoms. The naphtha produced by this process will usually have a low octane rating due to the highly paraffinic nature of Fischer-Tropsch materials. Consequently, the naphtha produced by this process generally is not suitable for use as a transportation fuel without further processing. However, the naphtha produced may be used as feed to an ethylene cracker without additional processing. Hydrocarbons having less than 5 carbon atoms in the molecule are normally gaseous at ambient temperature and are included among the overhead gases and may be recycled upstream in the Fischer-Tropsch processing train before or after optionally recovering the LPG (C₃ and C₄) fraction.

[0013] Processing schemes similar to the process of the present invention have been proposed and been commercially practiced for conventional petroleum derived products. See, for example, U.S. Pat. Nos. 5,976,354; 5,980,729; 6,337,010 B1; and 6,432,297 B1. However, none of these processes were intended for the processing of Fischer-Tropsch derived materials and their purpose is quite
different. In addition, for most of these process schemes the primary product of concern is the lubricating base oil fraction. In the present process, while a lubricating base oil may be one of the products recovered, the primary product of interest is the diesel fuel product. Accordingly, the temperature conditions under which the separation between the diesel fraction and the base oil fraction is made is carefully controlled to assure that the portion of the isomerized base oil fraction which is blended back into the diesel fraction will produce a diesel product having the desired properties.

In addition, since most of these processes are concerned with processing petroleum derived feeds, the hydroprocessing operations to which the feed is subjected prior to separation of the diesel and base oil fractions is for a different purpose, typically involving a hydrotreating operation to remove sulfur and nitrogen (see U.S. Pat. No. 5,976,354) or a hydrocracking operation to reduce the average molecular weight of the feed (see U.S. Pat. No. 6,337,010 B1). In the present process, the hydroprocessing operation is primarily intended to saturate the olefins and to remove the oxygenates.

[0014] As used in this disclosure the words “comprised” or “comprising” are intended as an open-ended transition meaning the inclusion of the named elements, but not necessarily excluding other unnamed elements. The phrases “consists essentially of” or “consisting essentially of” are intended to mean the exclusion of other elements of any essential significance to the composition. The phrases “consisting of” or “consists of” are intended as a transition meaning the exclusion of all but the recited elements with the exception of only minor traces of impurities.

SUMMARY OF THE INVENTION

[0015] The present invention is directed to a process for producing a premium Fischer-Tropsch diesel fuel which comprises (a) treating a waxy Fischer-Tropsch feed recovered from a Fischer-Tropsch synthesis in a hydrosprocessing zone under hydrosprocessing conditions in the presence of a hydrosprocessing catalyst intended to saturate the olefins and to remove the oxygenates that are present in the feed, whereby a first Fischer-Tropsch intermediate product is produced with reduced olefins and oxygenates relative to the Fischer-Tropsch feed; (b) separating the first Fischer-Tropsch intermediate product in a separation zone into a heavy Fischer-Tropsch fraction and a light Fischer-Tropsch fraction under controlled separation conditions wherein the light Fischer-Tropsch fraction is characterized by an end boiling point falling within the boiling range of diesel, and the heavy Fischer-Tropsch fraction being characterized by a boiling range above that of the light Fischer-Tropsch fraction; (c) contacting the heavy Fischer-Tropsch fraction with a hydroisomerization catalyst in a hydroisomerization zone under hydroisomerization conditions selected to improve the cold flow properties of the heavy Fischer-Tropsch fraction and recovering an isomerized heavy Fischer-Tropsch fraction; (d) mixing the isomerized heavy Fischer-Tropsch fraction with at least a portion of the light Fischer-Tropsch fraction of (b); and (e) recovering from the blend a Fischer-Tropsch derived diesel product meeting a target value for at least one pre-selected specification for diesel fuel. The heavy Fischer-Tropsch fraction will generally have an initial boiling point within the lower end of the boiling range for lubricating base oil and the upper end of the boiling range for diesel, i.e., the initial boiling point will usually be between about 550 degrees F. (about 285 degrees C.) and about 750 degrees F. (about 400 degrees C.). However, in order to meet the target value for the selected specification or specifications for the diesel product, it may under certain circumstances be desirable to produce more of the heavy fraction by lowering the initial boiling point of the heavy fraction below 600 degrees F., perhaps as low as 450 degrees F. (about 230 degrees C.). In this instance, the amount of the heavy fraction that will be isomerized and blended back into the diesel will be significantly increased.

[0016] The hydrosprocessing conditions in the first step of the process used to saturate the olefins and remove the oxygenates present in the Fischer-Tropsch feed are preferably mild and usually are selected to minimize the cracking of the molecules. However, by varying the conversion rate of the hydrosprocessing operation, the amount of diesel or of lubricating base oil may be maximized. For example, by operating at a higher conversion, typically greater than about 20 percent conversion, the amount of diesel produced by the process may be increased, since a portion of the C20 plus molecules present in the feed will be cracked into products within the boiling range of transportation fuels. Similarly, by minimizing the amount of conversion in this step, generally less than 20 percent conversion, the amount of base oil produced will be maximized due to the very low cracking rate.

[0017] As used in this disclosure “conversion” of a hydrocarbon feedstock refers to the percent of the hydrocarbons recovered from the hydrosprocessing zone which have an initial boiling point above a given reference temperature following the conversion of the Fischer-Tropsch feed into products boiling below the reference temperature. See U.S. Pat. No. 6,224,747. For the purposes of this disclosure the reference temperature selected is usually about 650 degrees F. (340 degrees C.).

[0018] A portion of the isomerized heavy Fischer-Tropsch fraction produced is blended back with the diesel in order to meet the target value for one or more pre-selected specifications for diesel. One skilled in the art will recognize that the specification or specifications selected will depend on the nature of the operation and the market into which the diesel product is to be sold.

[0019] Generally, the diesel specification or specifications selected will include one or more of the cold filter plugging point, the cloud point, or the pour point. Each of these specifications may be readily controlled in the diesel product by the blending back a portion of the isomerized heavy Fischer-Tropsch fraction.

[0020] In most embodiments of the invention, the separation zone will include at least two separation zones, referred to herein as a first and a second separation zone. The first separation zone, which in most embodiments will comprise a hot high pressure separator, is used to separate the heavy Fischer-Tropsch fraction from the naphtha, diesel and gaseous hydrogen rich fraction and usually will be operated at a temperature which is about 50 degrees F. (28 degrees C.) below the temperature of the hydrosprocessing zone. The second separation zone, which in most embodiments will comprise a cold high pressure separator, is used to separate the overhead gases from the remaining hydrocarbons boiling in the range of transportation fuels. The operation of the separation zone is critical to the invention, since the sepa-
ration between the heavy and light Fischer-Tropsch fractions will determine how much of those hydrocarbons boiling in the diesel range will be isomerized along with the heavy fraction which is will be blended back as part of the final diesel product.

[0021] In order to facilitate the separation in the high pressure separator it is preferable that a stripping gas be used. Stripping gases, such as, for example, steam or hydrogen may be employed in the hot high pressure separator. Generally hydrogen is preferred as the stripping gas in the present scheme.

BRIEF DESCRIPTION OF THE DRAWING

[0022] The drawing is a diagram illustrating a process scheme which represents one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0023] The present invention may be more clearly understood by reference to the drawing which represents one embodiment of the process scheme. In the drawing the Fischer-Tropsch condensate feed 2 and the Fischer-Tropsch wax feed 4 are shown separately prior to entering the hydrotreating reactor 6 via a common conduit 8 where the feeds are also mixed with hydrogen from line 11 which is provided by make-up hydrogen entering by lines 9 and 10 and by recycle hydrogen from line 28. In the hydrotreating reactor 6 the olefins present in the feed are saturated and the oxygenates, mostly consisting of alcohols, are removed. The effluent from the hydrotreating reactor referred to in this disclosure as the first Fischer-Tropsch intermediate is carried via line 12 to the first separation zone 14 comprising a high pressure separator where the heavy Fischer-Tropsch fraction comprising primarily waxy material boiling in the base oil range, but also including at least some hydrocarbons boiling in the diesel range, are separated from a lower boiling Fischer-Tropsch fraction which includes hydrocarbons boiling both in the range of naphtha and diesel as well as overhead gaseous comprising hydrogen and C4 minus hydrocarbons. The hot high pressure separator is usually operated at a temperature that is at least 50 degrees F. (28 degrees C.) below the operating temperature of the hydrotreating reactor 6. The heavy Fischer-Tropsch fraction is collected in conduit 16 and carried to the hydrosomerization unit 18. Hydrogen for the isomerization step is added from make-up hydrogen via lines 9 and 19. Returning to the hot high pressure separator 14, the lower boiling hydrocarbons and overhead gaseous are collected by conduit 20 and carried to the second separation zone which comprises a cold high pressure separator 22. In the cold high pressure separator the hydrogen rich overhead gaseous are separated from those hydrocarbons boiling in the range of transportation fuels. The hydrogen rich overhead gases pass via line 24 to an optional recycle gas scrubber 26 in order to remove any hydrogen sulfide or ammonia present prior to being sent via line 28 to the recycle gas compressor 30 to be recycled by line 11 back to the hydrotreating reactor 6. The hydrocarbons comprising primarily those boiling within the range of naphtha and diesel are recovered by line 32 from the cold high pressure separator and sent to a low pressure separator 34.

[0024] Returning to the hydrosomerization unit 18, the heavy Fischer-Tropsch fraction which contains most of the Fischer-Tropsch wax is isomerized to increase the isoparaffin content of the fraction and improve its cold flow properties, such as the cold filter plugging point, the pour point, and the VI, as well as the cloud point. The isomerized heavy Fischer-Tropsch fraction is collected in line 36 and passed to the hydronforming reactor 38 where the oxidation stability is further improved. The isomerized and hydronformed heavy fraction is carried by line 40 to a high pressure separator 42 where the hydrogen rich overhead gases are collected and carried by line 44 back to the cold high pressure separator 22 to be recycled to the hydrotreating unit. The effluent from cold high pressure separator containing the heavy fraction is carried by line 46 to the low pressure separator 34 where the isomerized and hydronformed heavy fraction are mixed with the light fraction coming from the cold high pressure separator 22. The overhead gases comprising primarily C4 minus hydrocarbons are collected from the top of the low pressure separator by line 47 and carried to the top of a product stripper 48. The mixture of heavy and light Fischer-Tropsch fractions is collected in line 49 from the bottom of the low pressure separator and passed to the lower section of the product stripper 48 where additional C4 minus hydrocarbons are separated from the C4 plus hydrocarbons. The C4 minus hydrocarbons are collected from stripper by conduit 50. The product stream comprising C4 plus hydrocarbons are collected in line 52 and passed to the atmospheric distillation unit 54 where the naphtha 56 and diesel 58 are collected separately from any remaining C4 minus hydrocarbons in line 60. The heavy bottoms fraction is collected and sent via line 62 to the vacuum distillation unit 64 where the light base oil fraction 66, medium base oil fraction 68, and heavy base oil fraction 70 are shown being separately collected.

[0025] By controlling the operation of the hot high pressure separator 14, the non-waxy molecules are removed from the feed to the hydrosomerization unit 18 and prevented from contacting the isomerization catalyst. The light Fischer-Tropsch fraction comprising the majority of the diesel and substantially all of the naphtha fraction thus bypass the isomerization operation making the isomerization step much more efficient, since it handles a smaller volume of hydrocarbons than it might otherwise. Only that fraction containing the majority of the Fischer-Tropsch wax will enter the hydrosomerization zone. This separation step also is used to meet the specifications for the diesel fuel that is produced by the integrated process. By blending a portion of the isomerized and hydronformed heavy Fischer-Tropsch fraction with the diesel, the overall cold flow properties and cloud point of the diesel product is improved without the necessity of hydrosmerizing and hydronfinishing the entire diesel product. Most of the heavy fraction which is recovered with the diesel product from the atmospheric distillation column 54 will comprise a lighter base oil fraction, i.e., the base oil fraction which has an upper boiling point of less than 750 degrees F. (400 degrees C.). Thus by controlling the cut points in the hot high pressure separator and in the fractionation operation the amount of isomerized and hydronformed base oil blended into the diesel product may be controlled. In addition, the operation of the hydrosomerization unit may be controlled to optimize the conversion of the heavy fraction which also will contribute to the properties of the final diesel product recovered from the operation.

[0026] As already noted, the operation of the hydrosprocessing unit, shown in the drawing as the hydrotreating unit 6, may be varied to make more hydrocarbons boiling in the...
range of transportation fuels. By operating under more severe conditions to increase the conversion, the larger molecules may be cracked to yield more diesel.

[0027] As an integrated process, the process of the present invention also allows for the efficient recycling of the hydrogen rich C4 minus overhead gases to the hydroprocessing zone, the catalytic dewaxing zone, and the hydofinishing zone. It is generally advantageous to operate the hydoreprocessing reactor, catalytic dewaxing reactor, and hydofinishing reactor at substantially the same pressure, since such operation reduces the capital cost by saving on the need for additional pumps and compressors. However, hydrosisomerization generally has an optimal reaction pressure below that for hydorecracking, hydrotreating, and hydofinishing. Therefore, it may be advantageous under certain circumstances to operate the catalytic dewaxing unit at a lower pressure than the hydoreprocessing unit and the hydofinishing unit. See, for example, U.S. Pat. No. 6,337,010 B1.

[0028] Fischer-Tropsch Synthesis

[0029] In the Fischer-Tropsch synthesis process, liquid and gaseous hydrocarbons are formed by contacting a synthesis gas (syngas) comprising a mixture of hydrogen and carbon monoxide with a Fischer-Tropsch catalyst under suitable temperature and pressure reactive conditions. The Fischer-Tropsch reaction is typically conducted at temperatures of from about 300 degrees F. to about 700 degrees F. (about 150 degrees C. to about 370 degrees C.) preferably from about 400 degrees F. to about 550 degrees F. (about 205 degrees C. to about 230 degrees C.); pressures of from about 10 psia to about 600 psia (0.7 bars to 41 bars), preferably 50 psia to 300 psia (2 bars to 21 bars), and catalyst space velocities of from about 100 cc/g/hr. to about 10,000 cc/g/hr., preferably 300 cc/g/hr. to 3,000 cc/g/hr.

[0030] The products may range from C1 to C200 plus hydrocarbons with a majority, by weight, in the C7-C100, plus 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 for producing the feedstocks used for carrying out 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 hydrogen and carbon monoxide is bubbled up in the reactor as a third phase through a slurry 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 about 4, but is more typically within the range of from about 0.7 to about 2.75 and preferably from about 0.7 to about 2.5. A particularly preferred Fischer-Tropsch process is taught in EP 0609079, also completely incorporated herein by reference for all purposes.

[0031] Suitable Fischer-Tropsch catalysts comprise one or more Group VII catalytic metals such as Fe, Ni, Co, Ru and Re, with cobalt generally being one preferred embodiment. Additionally, a suitable catalyst may contain a promoter. Thus, in one embodiment, the Fischer-Tropsch catalyst will comprise 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 ThO2, La2O3, MgO, K2O and TiO2, promoters such as ZrO2, noble metals (Pt, Pd, Ru, Rh, Os, Ir), coinage metals (Cu, Ag, Au), and other transition metals such as Fe, Mn, Ni, and Re. Suitable support materials include alumina, silica, magnesia and titania or mixtures thereof. Preferred supports for cobalt containing catalysts comprise alumina or titania. Useful catalysts and their preparation are known and illustrated in U.S. Pat. No. 4,568,663, which is intended to be illustrative but non-limiting relative to catalyst selection.

[0032] The products from the Fischer-Tropsch process usually are collected separately as a waxy fraction which contains the majority of the Fischer-Tropsch wax, a condensate fraction which contains the hydrocarbons boiling in the range of transportation fuels, and a gaseous fraction containing unreacted hydrogen and carbon monoxide and C4 minus hydrocarbons. The waxy fraction is normally a solid at ambient temperature and represents the fraction which makes up the majority of the material that will be isomerized in the present process. The condensate fraction, in addition to containing most of the hydrocarbons boiling in the range of naphtha and diesel, also contains oxygenates, mostly in form of alcohols, which must be removed prior to further processing. All of the fractions contain a significant amount of olefins which must be saturated in the hydoreprocessing step.

[0033] Hydoreprocessing

[0034] Hydoreprocessing in the present invention refers to the step intended primarily for the purpose of removing any residual nitrogen, saturating the olefins, and removing oxygenates that may be present in the Fischer-Tropsch feed stock. By increasing the severity of the hydoreprocessing step, the amount of diesel recovered in the final product slate may be increased. For the purposes of this discussion, the term hydoreprocessing is intended to refer to either hydrotreating or hydrocracking. Hydrosisomerization and hydofinishing, while also a type of hydoreprocessing, will be treated separately because of their different functions in the process scheme.

[0035] Hydrotreating refers to a catalytic process, usually, carried out in the presence of free hydrogen, in which the primary purpose when used to process conventional petroleum derived feed stocks is the removal of various metal contaminants, such as arsenic; heteroatoms, such as sulfur and nitrogen; and aromatics from the feed stock. In the present process, the primary purpose is to saturate the olefins and remove the oxygenates in the feed stock prior to the catalytic dewaxing operation. Generally, in hydrotreating operations cracking of the hydrocarbon molecules, i.e., breaking the larger hydrocarbon molecules into smaller hydrocarbon molecules is minimized. For the purpose of this discussion the term hydrotreating refers to a hydoreprocessing operation in which the conversion is 20 percent or less.
Hydrocracking refers to a catalytic process, usually carried out in the presence of free hydrogen, in which the cracking of the larger hydrocarbon molecules is the primary purpose of the operation. In contrast to hyrdrotreating, the conversion rate for hydrocracking, for the purpose of this disclosure, shall be more than 20 percent. Hydrogenation of the olefins and removal of the oxygenates as well as denitration of the feedstock will also occur. In the present invention, cracking of the hydrocarbon molecules may be desirable. Norder et al. (1988) to increase the yield of diesel and minimize the amount of heavy Fischer-Tropsch fraction passing through the catalytic dewaxing operation.

Catalysts used in carrying out hyrdrotreating and hydrocracking operations are well known in the art. See for example U.S. Pat. Nos. 4,347,121 and 4,810,357, the contents of which are hereby incorporated by reference in their entirety, for general descriptions of hydrotreating, hydrocracking, and of typical catalysts used in each of the processes. 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 unsulfided Group VIIIA and Group VIIB, such as nickel-molybdenum or nickel-tin on an alumina or siliceous matrix. U.S. Pat. No. 3,852,207 describes a suitable noble metal catalyst and mild conditions. Other suitable catalysts are described, for example, in U.S. Pat. Nos. 4,157,294 and 5,904,513. The non-noble hydrogenation metals, such as nickel-molybdenum, 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. Catalysts containing noble metals, such as platinum, 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.

The hydrogenation components can be incorporated into the overall catalyst composition by any one of numerous procedures. The hydrogenation components can be added to matrix component by co-mulling, impregnation, or ion exchange and the Group VI components, i.e., molybdenum and tungsten can be combined with the refractory oxide by impregnation, co-mulling or co-precipitation. Although these components can be combined with the catalyst matrix as the sulfides, that is generally not preferred, as the sulfur compounds can interfere with the Fischer-Tropsch catalysts.

The matrix component can be of many types including 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 such as that described in U.S. Pat. Nos. 4,401,556; 4,820,402; and 5,059,567. Small crystal size zeolite Y, such as that described in U.S. Pat. No. 5,073,530 also can be used. Non-zeolitic molecular sieves which can be used include, for example, silicoaluminophosphates (SAPO), ferroaluminophosphate, titanium aluminophosphate and the various ELAPO molecular sieves described in U.S. Pat. No. 4,913,799 and the references cited therein. Details regarding the preparation of various non-zeolite molecular sieves can be found in U.S. Pat. Nos. 5,114,563 (SAPO) and 4,913,799 and the various references cited in U.S. Pat. No. 4,913,799. Mesoporous molecular sieves can also be used, for example the M41S family of materials as described in J. Am. Chem. Soc., 114:10834-10843(1992)), MCM-41; U.S. Pat. Nos. 5,246,689; 5,198,203; and 5,334,368; and MCM-48 (Kresge et al., Nature 359:710 (1992)). 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 compounded 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 calcination, acid treatment or chemical modification.

In performing the hydrocracking and/or hyrdrotreating operation, more than one catalyst type may be used in the reactor. The different catalyst types can be separated into layers or mixed.

Hydrocracking conditions have been well documented in the literature. In general, the overall LHSV is about 0.1 hr⁻¹ to about 15.0 hr⁻¹ (v/v), preferably from about 0.25 hr⁻¹ to about 2.5 hr⁻¹. The reaction pressure generally ranges from about 500 psig to about 3500 psig (about 10.4 MPa to about 24.2 MPa), preferably from about 1500 psig to about 5000 psig (about 3.5 MPa to about 34.5 MPa). Hydrogen consumption is typically from about 500 to about 2500 SCF per barrel of feed (89.1 to 445 m³H₂/m³ feed). Temperatures in the reactor will range from about 400 degrees F. to about 950 degrees F. (about 205 degrees C. to about 510 degrees C.), preferably ranging from about 650 degrees F. to about 850 degrees F. (about 340 degrees C. to about 455 degrees C.).

Typical hydrotreating conditions vary over a wide range. In general, the overall LHSV is about 0.5 to 5.0. The total pressure ranging from about 200 psig to about 2000 psig. Hydrogen recirculation rates are typically greater than 50 SCF/Bbl, and are preferably between 1000 and 5000 SCF/Bbl. Temperatures in the reactor will range from about 400 degrees F. to about 800 degrees F. (about 205 degrees C. to about 425 degrees C.).

Separation Zone

In the process of the present invention, the separation zone is used to separate those hydrocarbons boiling in the range of transportation fuels, i.e., in range of naphthas and diesel (referred to as the light Fischer-Tropsch fraction) from those hydrocarbons boiling in the base oil range (referred to as the heavy Fischer-Tropsch fraction) from the first Fischer-Tropsch intermediate product collected from the hydroprocessing operation. Generally, the cut-point for the separation between the heavy Fischer-Tropsch fraction and the light Fischer-Tropsch fraction will be within the temperature range.
range of between about 550 degrees F. and about 750 degrees F. (about 285 degrees C. to about 400 degrees C). Usually the cut-point will be about 600 degrees F. (315 degrees C.). However, due to the unique properties of Fischer-Tropsch derived products the cut-point may be as low as 450 degrees F. (about 230 degrees C.). The precise cut-point selected will depend upon how much of the base oil present in the first Fischer-Tropsch intermediate product is selected for isomerization. The selection of how much base oil to send to the catalytic dewaxing zone will depend upon the target value selected for the property or properties of the final diesel product. In general, the lower the cut-point between the heavy and light fractions, the more Fischer-Tropsch wax will be sent to the catalytic dewaxing zone. More wax isomerization will result in improved cold-flow properties in the diesel product. However, most of the Fischer-Tropsch wax is concentrated in the higher boiling fractions. Thus dropping the cut-point below a certain temperature yields decreasing benefits in the properties of the diesel product. In addition, the more heavy Fischer-Tropsch fraction sent to the catalytic dewaxing zone, the larger the reaction vessel must be to handle the increased volume of material which results in higher capital costs. Thus once skilled in the art will recognize that a balance must be achieved between the size of the catalytic dewaxing reactor and the properties of the final diesel product. The diesel product must meet the target values for the selected specification while at the same time minimizing the amount of material sent to the catalytic dewaxing unit.

The separation in the separation zone will usually take place at a temperature that is at least 50 degrees F. (30 degrees C.) below the operating temperature of the hydroprocessing reactor. This is necessary in the present scheme due to the nature of the Fischer-Tropsch feed. This aspect differs from the operation of similar schemes described in the prior art which are directed to the processing of conventional petroleum derived feed stocks. See U.S. Pat. Nos. 5,976,354 and 6,432,297. Although the configuration of the equipment used in the prior art schemes is similar to that used for the scheme described herein, the actual operation is quite different. In processing conventional petroleum feeds, the separator is operated at substantially the same temperature as the hydroprocessing operation. Since petroleum derived fractions which include diesel are not waxy, substantially all of the diesel is recovered along with the napthena and overhead gases in the prior art processes. Virtually none of the final diesel product has passed through the catalytic dewaxing unit in these schemes. In the present process, due to the waxy nature of the Fischer-Tropsch diesel, a significant amount of the material that will be included in the final diesel product is isomerized. Typically, between about 25 and about 75 volume percent of the final diesel product will have passed through the catalytic dewaxing unit. The actual amount of the final diesel product which has passed through the catalytic dewaxing unit will depend on the target value selected for the diesel specification.

Usually the separation zone will comprise at least two separation vessels. In the drawing, the separation zone comprises a hot high pressure separator and a cold high pressure separator. In this scheme the hot high pressure separator makes the initial separation between the heavy Fischer-Tropsch fraction and the light Fischer-Tropsch fraction. While this separation will take place at a relatively high temperature, it usually will still be at a temperature that is at least 50 degrees F. (30 degrees C.) lower than the temperature in the hydroprocessing reactor. In the cold high pressure separator, the overhead gases are separated from the hydrocarbons boiling in the range of those transportation fuels which will not pass through the catalytic dewaxing zone.

Catalytic Dewaxing and Hydroisomerization

Catalytic dewaxing consists of three main classes, conventional hydrodewaxing, complete hydroisomerization dewaxing, and partial hydroisomerization dewaxing. All three classes involve passing a mixture of a waxy hydrocarbon stream and hydrogen over a catalyst that contains an acidic component to reduce the normal and slightly branched iso-paraffins in the feed and increase the proportion of other non-waxy species. The method selected for dewaxing a feed typically depends on the product quality, and the wax content of the feed, with conventional hydrodewaxing often 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 Sequiera, in Lubricant Base Stock and Wax Processing, Marcel Dekker, Inc., pages 194-223. The determination between conventional hydrodewaxing, complete hydroisomerization dewaxing, and partial hydroisomerization dewaxing can be made by using the n-hexadecane isomerization test as described in U.S. Pat. No. 5,282,958. When measured at 96 percent, n-hexadecane conversion using conventional hydrodewaxing catalysts will exhibit a selectivity to isomerized hexadecanes of less than 10 percent, partial hydroisomerization dewaxing catalysts will exhibit a selectivity to isomerized hexadecanes of greater than 10 percent to less than 40 percent, and complete hydroisomerization dewaxing catalysts will exhibit a selectivity to isomerized hexadecanes of greater than or equal to 40 percent, preferably greater than 60 percent, and most preferably greater than 80 percent.

In conventional hydrodewaxing, the pour point is lowered by selectively cracking the wax molecules mostly to smaller paraffins using a conventional hydrodewaxing catalyst, such as, for example ZSM-5. Metals may be added to the catalyst, primarily to reduce fouling. In the present invention conventional hydrodewaxing may be used to increase the yield of diesel in the final product slate by cracking the Fischer-Tropsch wax molecules. In the present process, the isomerization of the paraffins also is used to improve the cold flow properties and cloud point of the diesel fraction. Typical conditions for hydroisomerization as used in the present process involve temperatures from about 400 degrees F to about 800 degrees F. (about 200 degrees C. to about 425 degrees C.), pressures from about 100 psig to 2000 psig, and space velocities from about 0.2 to 5 hr⁻¹.

Complete hydroisomerization dewaxing typically achieves high conversion levels of wax by isomerization to non-waxy iso-paraffins while at the same time minimizing the conversion by cracking. 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 lubricating oil base stock with an acceptable pour point. Complete hydroisomerization dewaxing uses a dual-functional catalyst consisting of an acidic component and an active metal component having hydrogenation activity. Both components are required to conduct the isomer-
ization reaction. The acidic component of the catalysts used in complete hydroisomerization preferably include an intermediate pore SAPO, such as SAPO-11, SAPO-31, and SAPO-41, with SAPO-11 being particularly preferred. Intermediate pore zeolites, such as ZSM-22, ZSM-23, SSZ-32, ZSM-35, and ZSM-48, also may be used in carrying out complete hydroisomerization dewaxing. Typical active metals include molybdenum, nickel, vanadium, cobalt, tungsten, zinc, platinum, and palladium. The metals platinum and palladium are especially preferred as the active metals, with platinum most commonly used.

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 50 percent). At higher conversions, wax conversion by cracking becomes significant, and yield losses of lubricating base stock becomes uneconomical. Like complete hydroisomerization dewaxing, the catalysts used in partial hydroisomerization dewaxing include both an acidic component and a hydrogenation component. The acidic catalyst components useful for partial hydroisomerization dewaxing include amorphous silica aluminas, fluorided aluminas, and 12-ring zeolites (such as Beta, Y zeolite, L zeolite). The hydrogenation component of the catalyst is the same as already discussed with complete hydroisomerization dewaxing. Because the wax conversion is incomplete, partial hydroisomerization dewaxing must be supplemented with an additional dewaxing technique, typically solvent dewaxing, complete hydroisomerization dewaxing, or conventional hydrodewaxing in order to produce a lubricating base stock with an acceptable pour point (below about +10 degrees F. or -12 degrees C).

In preparing those catalysts containing a non-zeolitic molecular sieve and having a hydrogenation component for use in the present invention, it is usually preferred that the metal be deposited on the catalyst using a non-aqueous method. Catalysts, particularly catalysts containing SAPO's, on which the metal has been deposited using the non-aqueous method, have shown greater selectivity and activity than those catalysts which have used an aqueous method to deposit the active metal. The non-aqueous deposition of active metals on non-zeolitic molecular sieves is taught in U.S. Pat. Nos. 5,939,349. In general, the process involves dissolving a compound of the active metal in a non-aqueous, non-reactive solvent and depositing it on the molecular sieve by ion exchange or impregnation.

Hydrofinishing

Hydrofinishing operations are intended to improve the UV stability and color of the products. It is believed this is accomplished by saturating the double bonds present in the hydrocarbon molecules, including those found in aromatics, especially polycyclic aromatics. As shown in the drawing, only the heavy Fischer-Tropsch fraction which has passed through the catalytic dewaxer is sent to a hydrofinisher. A general description of the hydrofinishing process may be found in U.S. Pat. Nos. 3,852,207 and 4,673,487. As used in this disclosure the term UV stability refers to the stability of the lubricating base oil or other products when exposed to ultraviolet light and oxygen. Instability is indicated when a visible precipitate forms or darker color develops upon exposure to ultraviolet light and air which results in a cloudiness or flocc in the product. It may also be desirable that the diesel product prepared by the process of the present invention be UV stabilized prior to marketing in which case this fraction may also be hydrofinished.

Typically, the total pressure in the hydrofinishing zone will be about 200 psig and about 3000 psig, with pressures in the range of about 500 psig and about 2000 psig being preferred. Temperature ranges in the hydrofinishing zone are usually in the range of from about 400 degrees F. (about 205 degrees C.) to about 650 degrees F. (about 345 degrees C.). The LHSV is usually within the range of from about 0.3 to about 5.0. Hydrogen is usually supplied to the hydrofinishing zone at a rate of from about 1000 to about 10,000 SCF per barrel of feed. Typically the hydrogen is fed at a rate of about 3000 SCF per barrel of feed.

Suitable hydrofinishing catalysts typically contain a Group VIII metal component together with an oxide support. Metals or compounds of the following metals are useful in hydrofinishing catalysts include nickel, ruthenium, rhodium, iridium, palladium, platinum, and osmium. Preferably the metal or metals will be platinum, palladium or mixtures of platinum and palladium. The refractory oxide support usually consists of alumina, silica, silica-alumina, silica-alumina-zirconia, and the like. The catalyst may optionally contain a zeolite component. Typical hydrofinishing catalysts are disclosed in U.S. Pat. Nos. 3,852,207; 4,157,294; and 4,673,487.

Diesel Product

In the present invention the final diesel product is prepared by blending a lower boiling fraction of the isomerized heavy fraction back into the diesel fraction recovered from the separation zone. As illustrated in the drawing the isomerized heavy fraction and the light fraction are blended together in the low pressure separator. The diesel product, including part of the isomerized heavy fraction, is shown in the drawing as being separated from the lighter naphtha, C₄ minus fraction, and base oil in the atmospheric fractionation unit. The various lube fractions may be further separated, if desired in a vacuum fractionation column.

In the present invention, the properties of diesel product may be controlled at several points in the process. The first control point and the most important are in the separation zone. As already noted, the separation zone controls how much of the waxy material which will be included in the diesel product will pass through the hydroisomerization operation. The second point of control resides in the hydroisomerization unit. By controlling the wax conversion, the cold flow properties of the diesel also may be adjusted. Finally, the properties of the diesel product may be controlled in the fractionation step. How much of the isomerized base oil fraction remains as part of the diesel product also will help determine what the final properties of the diesel product will be. One skilled in the art will recognize that there are other schemes than the one shown in the drawing to accomplish the overall process without departing from the spirit of the invention.

In the present invention the diesel fraction and isomerized base oil fraction are blended to achieve a target value for at least one diesel specification. The diesel specifications will usually be selected from one or more of the
cold filter plugging point, the cloud point, and the pour point. In the case of the cold filter plugging point, the target value will usually be a temperature of −10 degrees C. or less, preferably −20 degrees C. or less. The target value for cloud point will usually be a temperature of −8 degrees C. or less, preferably −18 degrees C. or less. The target value for pour point will typically be −15 degrees C. or less, preferably −25 degrees C. or less.

[0061] The cold filter plugging point ("CFPP") is a standard test used to determine the ease with which fuel moves under suction through a filter grade representative of field equipment. The determination is repeated periodically during steady cooling of the fuel sample, the lowest temperature at which the minimum acceptable level of filterability is still achieved being recorded as the "CFPP" temperature of the sample. The details of the CFPP test and cooling regime are specified in ASTM D-6571.

[0062] Pour point is the temperature at which a sample of the diesel fuel will begin to flow under carefully controlled conditions. In this disclosure, pour point, unless stated otherwise, is determined by the standard analytical method ASTM D-5950.

[0063] Fischer-Tropsch Derived Lubricating Base Oil

[0064] In addition, to producing a premium diesel product, the present invention may also be used to produce a premium Fischer-Tropsch derived lubricating base oil. Fischer-Tropsch derived base oils recovered from the process of this invention typically will contain very low sulfur and aromatics, have excellent oxidation stability, and excellent cold flow properties. Generally, the lubricating base oils recovered from the process will have a kinematic viscosity of at least 3 cSt at 100 degrees C., preferably at least 4 cSt; a pour point below 20 degrees C., preferably below −12 degrees C.; and a VI that is usually greater than 90, preferably greater than 100. The lower boiling base oils usually will be included in the final diesel blend, therefore, there is very little of the low viscosity material recovered from the vacuum distillation column.

What we claim is:

1. A process for producing a premium Fischer-Tropsch diesel fuel which comprises:

(a) treating a waxy Fischer-Tropsch feed recovered from a Fischer-Tropsch synthesis in a hydroprocessing zone under hydroprocessing conditions in the presence of a hydroprocessing catalyst intended to saturate the olefins and to remove the oxygenates that are present in the feed, whereby a first Fischer-Tropsch intermediate product is produced with reduced olefins and oxygenates relative to the Fischer-Tropsch feed;

(b) separating the first Fischer-Tropsch intermediate product in a separation zone into a heavy Fischer-Tropsch fraction and a light Fischer-Tropsch fraction under controlled separation conditions wherein the light Fischer-Tropsch fraction is characterized by an end boiling point falling within the boiling range of diesel, and the heavy Fischer-Tropsch fraction being characterized by a boiling range above that of the light Fischer-Tropsch fraction;

(c) contacting the heavy Fischer-Tropsch fraction with a hydroisomerization catalyst in a hydroisomerization zone under hydroisomerization conditions selected to improve the cold flow properties of the heavy Fischer-Tropsch fraction and recovering an isomerized heavy Fischer-Tropsch fraction;

(d) mixing the isomerized heavy Fischer-Tropsch fraction with at least a portion of the light Fischer-Tropsch fraction of (b), and

(e) recovering from the blend a Fischer-Tropsch derived diesel product meeting a target value for at least one pre-selected specification for diesel fuel.

2. The process of claim 1 wherein the conversion of the Fischer-Tropsch feed in the hydroprocessing zone is 20 percent or less.

3. The process of claim 2 wherein the hydroprocessing conditions include a hydrogen partial pressure of between about 200 psig to about 2000 psig, a temperature in the range of from about 400 degrees F. to about 800 degrees F., a LHSV of between about 0.5 and about 5.0.

4. The process of claim 2 wherein the hydroprocessing catalyst comprises at least one active metal selected from Group VIII of the Periodic Table of the Elements and at least one active metal selected from Group VI of the Periodic Table of the Elements, said active metals being present on a refractory support.

5. The process of claim 2 further including the intermediate step of hyrofinishing the isomerized heavy Fischer-Tropsch fraction of step (c) in a hydrofinishing zone under hydrofinishing conditions prior to blending the first portion of the isomerized heavy Fischer-Tropsch fraction with the light Fischer-Tropsch fraction.

6. The process of claim 5 wherein the hydrofinishing conditions include a pressure between about 500 psig and about 2000 psig, a temperature of between about 400 degrees F. and about 650 degrees F., a LHSV between about 0.3 and about 5.0.

7. The process of claim 5 wherein a second portion of the hyrofinished and isomerized heavy Fischer-Tropsch fraction is also recovered separately as a lubricating base oil.

8. The process of claim 5 wherein the pressure in the hydroprocessing zone and in the hydrofinishing zone are substantially the same.

9. The process of claim 8 wherein the hydroisomerization zone is operated at a lower pressure than the hydroprocessing zone and the hydrofinishing zone.

10. The process of claim 1 wherein the light Fischer-Tropsch fraction has an end point falling within the range between about 450 degrees F. and about 750 degrees F.

11. The process of claim 1 wherein the isomerization catalyst in the catalytic dewaxing zone is a hydroisomerization catalyst.

12. The process of claim 11 wherein the hydroprocessing catalyst contains a molecular sieve selected from the group consisting essentially of ZSM-22, ZSM-23, SSZ-32, ZSM-35, ZSM-48, SAPO-11, SAPO-31, and SAPO-41.

13. The process of claim 12 wherein the hydroisomerization catalyst contains an active metal selected from platinum, palladium, or a combination of platinum and palladium.

14. The process of claim 1 wherein the hydroisomerization conditions include a temperature of between about 400 degrees F. and about 800 degrees F., a pressure of from about 100 psig to about 2000 psig, and an liquid hourly space velocity of between about 0.2 hr⁻¹ and about 5 hr⁻¹.
15. The process of claim 1 wherein the pre-selected specification for diesel fuel to which the Fischer-Tropsch diesel product is blended is the cold filter plugging point.

16. The process of claim 15 wherein the target value for the cold filter plugging point is 0 degrees C. or less.

17. The process of claim 16 wherein the target value for the cold filter plugging point is −20 degrees C. or less.

18. The process of claim 1 wherein the pre-selected specification for diesel fuel to which the Fischer-Tropsch diesel product is blended is cloud point.

19. The process of claim 18 wherein the target value for the cloud point is about −5 degrees C. or less.

20. The process of claim 19 wherein the target value for the cloud point is about −18 degrees C. or less.

21. The process of claim 1 wherein the pre-selected specification for diesel fuel to which the Fischer-Tropsch diesel product is blended is pour point.

22. The process of claim 21 wherein the target value for the pour point is about −15 degrees C. or less.

23. The process of claim 1 in which the separation zone of step (b) is divided into at least a first intermediate separation zone and a second intermediate separation zone and wherein the separation of step (b) includes the additional steps of (i) separately recovering from the first intermediate separation zone the heavy Fischer-Tropsch fraction and a mixture containing the light Fischer-Tropsch fraction and a hydrogen-rich C₄ minus fraction; (ii) feeding the mixture containing the light Fischer-Tropsch fraction and the hydrogen-rich C₄ minus fraction to the second intermediate separation zone; and (iii) recovering separately from the second intermediate separation zone the light Fischer-Tropsch fraction and the hydrogen-rich C₄ minus fraction.

24. The process of claim 23 wherein the hydrogen-rich C₄ minus fraction is recycled to the hydproprocessing zone.

25. The process of claim 23 wherein the hydrogen-rich C₄ minus fraction is sent to the hydroisomerization zone.

26. The process of claim 23 wherein the hydrogen-rich C₄ minus fraction is sent to a hydrofinishing zone.

27. The process of claim 23 wherein a stripping gas is used in the first intermediate separation zone to assist in recovering the mixture containing the light Fischer-Tropsch fraction and the hydrogen-rich C₄ minus fraction.

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