(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 972 677 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
24.09.2008 Bulletin 2008/39

(21) Application number: **07706583.7**

(22) Date of filing: **11.01.2007**

(51) Int Cl.:
C10G 65/12 *(2006.01)* ***C10G 45/60*** *(2006.01)*
C10G 45/62 *(2006.01)* ***C10G 47/16*** *(2006.01)*
C10G 47/18 *(2006.01)*

(86) International application number:
PCT/JP2007/050236

(87) International publication number:
WO 2007/080920 (19.07.2007 Gazette 2007/29)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR

(30) Priority: **13.01.2006 JP 2006006252**

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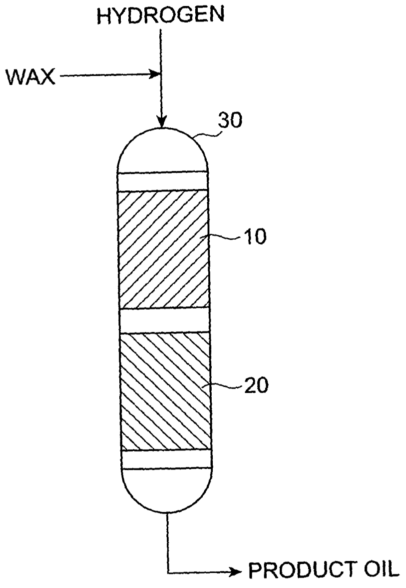
(54) METHOD OF HYDROTREATING WAX AND PROCESSES FOR PRODUCING FUEL BASE AND LUBRICATING OIL BASE

(57) The wax hydrotreating process of the present invention is **characterized by** hydrotreating the wax by bringing the wax, under a hydrogen atmosphere and at a liquid space velocity of 0.4 to 4.0 h^{-1}, into contact with a first catalyst 10 containing an ultrastable Y zeolite and an amorphous solid acid and thereafter into contact with a second catalyst 20 that contains a solid acid and substantially does not contain ultrastable Y zeolite.

Fig.1



Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a wax hydrotreating process and to a process for manufacturing fuel base material and lubricant base material.

Background Art

[0002] There have been rising expectations in the last few years for low-aromatic hydrocarbon, low-sulfur liquid fuels as environmentally-friendly clean liquid fuels. One method for producing such clean liquid fuels is Fischer-Tropsch (FT) synthesis using a hydrogen and carbon monoxide feed. The FT synthesis can also produce wax (FT wax) at the same time as the production of a paraffin-rich, sulfur-free liquid fuel base material. This FT wax can be converted into a middle distillate fraction by hydrocracking, while the uncracked wax fraction can be converted into a middle distillate fraction by recycle or can be converted into a high-quality lubricant base material by removal of the normal-paraffin by MEK dewaxing.

[0003] A high yield is desirable when a middle distillate fraction is produced by the hydrocracking of FT wax; moreover, when this middle distillate fraction is to be used as a fuel base material, a low normal-paraffin content and conversely a high isoparaffin content are desired for the middle distillate fraction. When, for example, a middle distillate fraction is used for diesel fuel, a high normal-paraffin content causes a deterioration in the low-temperature fluidity and, in the worst case, limits use as a commercial product.

[0004] When a lubricant base material is to be obtained from the uncracked fraction, a lower normal-paraffin content in the uncracked wax fraction is preferred in order to raise the yield of the lubricant base material and improve the operating efficiency in MEK dewaxing.

[0005] Technology for producing a fuel base material by wax hydrocracking has also been investigated to date; for example, hydrocracking methods that employ an FT wax feedstock are described in Patent References 1 to 3 given below.

[Patent document 1] WO 2004/028688
[Patent document 2] Japanese Patent Application Laid-open No. 2004-255241
[Patent document 3] Japanese Patent Application Laid-open No. 2004-255242

Disclosure of the Invention

Problems to be Solved by the Invention

[0006] However, it is quite difficult with the wax hydrocracking methods described in Patent References 1 to 3 to produce good yields of a middle distillate fraction with a satisfactorily reduced normal-paraffin content while simultaneously reducing the normal-paraffin content in the uncracked wax fraction. In addition, there has been almost no research done with regard to a hydrotreating process that would simultaneously yield such a middle distillate fraction having a low normal-paraffin content and an uncracked wax fraction having a low normal-paraffin content. The reason for this is thought to be due to hydrocracking, whose objective is the middle distillate fraction, having different optimal reaction conditions from hydroisomerization, whose objective is the lubricant base material. That is, in order to raise the yield of the middle distillate fraction, mild reaction conditions are preferred in order to inhibit lightening of the produced middle distillate fraction; however, isomerization of the uncracked wax fraction under such reaction conditions proceeds with difficulty, making it quite difficult to lower the normal-paraffin content. On the other hand, the use of severe reaction conditions in order to convert the normal-paraffin in the uncracked wax fraction to isoparaffin at good efficiencies facilitates overcracking of the produced middle distillate fraction, resulting in a reduced yield of the middle distillate fraction.

[0007] In view of the preceding, a wax hydrotreating process is desired that would be able, under constant reaction conditions, to simultaneously produce a middle distillate fraction having a low normal-paraffin content and an uncracked wax fraction having a low normal-paraffin content.

[0008] The present invention was pursued considering the problems described above for the prior art and takes as an object the introduction of a wax hydrotreating process that hydrotreats wax under constant reaction conditions and that is able to produce good yields of a middle distillate fraction that has a satisfactorily reduced normal-paraffin content while simultaneously producing an uncracked wax fraction that has a satisfactorily reduced normal-paraffin content. An additional object of the present invention is to provide a process for manufacturing fuel base material and lubricant base material.

Means for Solving the Problems

[0009] In order to achieve the objects cited above, the present inventor provides a wax hydrotreating process, characterized by hydrotreating the wax by bringing the wax, under a hydrogen atmosphere and at a liquid space velocity of 0.4 to 4.0 h^{-1}, into contact with a first catalyst containing an ultrastable Y zeolite and an amorphous solid acid and thereafter into contact with a second catalyst that contains a solid acid and substantially does not contain ultrastable Y zeolite.

[0010] The concept of the second catalyst substantially not containing ultrastable Y zeolite herein denotes either no content of ultrastable Y zeolite or, if ultrastable Y zeolite is present, that the content thereof is at a level that does not influence hydrotreating of the wax. More specifically, the ultrastable Y zeolite content in the second catalyst is preferably no more than 0.02 mass%, more preferably no more than 0.005 mass%, and most preferably is 0.

[0011] This wax hydrotreating process is able to first carry out a satisfactory cracking of the wax by bringing the wax into contact with the above-described first catalyst and then, by bringing the wax into contact with the above-described second catalyst, is able to bring about a satisfactory isomerization of the uncracked wax while controlling overcracking of the wax. Moreover, the wax hydrotreating process of the present invention can carry out this hydrotreating with the first catalyst and second catalyst under constant reaction conditions and is able to produce good yields of a middle distillate fraction that has a satisfactorily reduced normal-paraffin content while simultaneously producing an uncracked wax fraction that has a satisfactorily reduced normal-paraffin content.

[0012] In addition, the wax hydrotreating process of the present invention is preferably characterized by disposing the first catalyst within a fixed bed reaction column in an upstream position and disposing the second catalyst therein in a downstream position and carrying out the wax hydrotreating within the fixed bed reaction column. This wax hydrotreating process enables hydrotreating of the wax to be efficiently carried out in a single fixed bed reaction column with contact between the wax and the first catalyst and second catalyst being brought about under constant reaction conditions, and is able to produce good yields of a middle distillate fraction that has a satisfactorily reduced normal-paraffin content while simultaneously producing an uncracked wax fraction that has a satisfactorily reduced normal-paraffin content. Moreover, equipment costs can be kept down since the treatment is carried out in a single fixed bed reaction column.

[0013] The first catalyst and/or the second catalyst in the wax hydrotreating process of the present invention is preferably a catalyst comprising palladium and/or platinum supported on a catalyst support that is a constituent of the catalyst. The use of such a catalyst enables an even better reduction in the normal-paraffin content of the middle distillate fraction and/or uncracked wax produced by wax hydrotreating.

[0014] The average particle size of the ultrastable Y zeolite in the first catalyst is preferably no greater than 1.0 μm in the wax hydrotreating process of the present invention. This enables an even better reduction in the normal-paraffin content of the middle distillate fraction obtained by wax hydrotreating.

[0015] The ultrastable Y zeolite content in the first catalyst in the wax hydrotreating process of the present invention is preferably no more than 4.0 mass% based on the total mass of the first catalyst. This enables an even better reduction in the normal-paraffin content of the middle distillate fraction obtained by wax hydrotreating.

[0016] The amorphous solid acid in the first catalyst in the wax hydrotreating process of the present invention preferably contains at least one selected from the group consisting of silica-alumina, alumina-boria, and silica-zirconia. This enables an even better reduction in the normal-paraffin content of the middle distillate fraction obtained by wax hydrotreating.

[0017] The solid acid in the second catalyst in the wax hydrotreating process of the present invention preferably contains at least one selected from the group consisting of silica-alumina, alumina-boria, silica-zirconia, and silicoaluminophosphate. This enables an even better reduction in the normal-paraffin content of the uncracked wax obtained by wax hydrotreating.

[0018] Wax hydrotreating is preferably carried out in the wax hydrotreating process of the present invention under conditions of a reaction temperature of 270 to 360°C and a pressure of 2 to 5 MPa. Carrying out wax hydrotreating under these conditions provides an even better reduction in the normal-paraffin content of the resulting middle distillate fraction and uncracked wax. Additional improvements in the yield of the middle distillate fraction can also be obtained.

[0019] In addition, the present inventor provides a process for manufacturing fuel base material and lubricant base material, comprising: a first step in which a wax is hydrotreated by bringing the wax, under a hydrogen atmosphere and at a liquid space velocity of 0.4 to 4.0 h^{-1}, into contact with a first catalyst containing an ultrastable Y zeolite and an amorphous solid acid and thereafter into contact with a second catalyst that contains solid acid and substantially does not contain ultrastable Y zeolite; and a second step in which a middle distillate fraction and solid wax are obtained from the treated material obtained in the first step. This production method makes it possible to produce an uncracked wax fraction that has a satisfactorily reduced normal-paraffin content while simultaneously producing good yields of a middle distillate fraction that has a satisfactorily reduced normal-paraffin content.

Effect of the Invention

[0020] The present invention provides a wax hydrotreating process that carries out the hydrotreating of wax under constant reaction conditions and that can produce good yields of a middle distillate fraction that has a satisfactorily reduced normal-paraffin content while simultaneously producing an uncracked wax fraction that has a satisfactorily reduced normal-paraffin content. The present invention additionally provides a process for manufacturing fuel base material and lubricant base material.

Brief Description of the Drawings

[0021]

Fig. 1 is a schematic drawing that describes a suitable embodiment of the wax hydrotreating process of the present invention using a fixed bed reaction column.

Fig. 2 is a schematic drawing that describes another suitable embodiment of the wax hydrotreating process of the present invention using a fixed bed reaction column.

Explanation of Symbols

[0022] 10: first catalyst, 20: second catalyst, 30: fixed bed reaction column.

Best Mode for Carrying Out the Invention

[0023] The present invention is described in detail hereinbelow with reference to suitable embodiments thereof.

[0024] The wax hydrotreating process of the present invention is characterized by hydrotreating the wax by bringing the wax, under a hydrogen atmosphere and at a liquid space velocity of 0.4 to 4.0 h^{-1}, into contact with a first catalyst containing an ultrastable Y zeolite and an amorphous solid acid and thereafter into contact with a second catalyst that contains a solid acid and substantially does not contain ultrastable Y zeolite.

[0025] Wax hydrotreating according to the present invention can be carried out, for example, using a catalyst-packed fixed bed reaction column (a fixed bed reaction apparatus). In this connection, Figure 1 is a schematic drawing that describes a suitable embodiment of the wax hydrotreating process of the present invention using a fixed bed reaction column. As shown in Figure 1, wherein wax hydrotreating is carried out using a fixed bed reaction column 30, a first catalyst 10 is disposed within this reaction column 30 on the upstream side considered with respect to the introduction of the wax feedstock, while a second catalyst 20 is disposed downstream from the first catalyst 10. The wax is hydrotreated by sequential contact, under a hydrogen atmosphere, with the first catalyst 10 and then the second catalyst 20, thereby yielding a product oil. This first catalyst 10 and second catalyst 20 may be disposed within the reaction column 30 in contact with each other or may be disposed leaving a prescribed gap therebetween.

[0026] A known wax, e.g., a petroleum-based wax or a synthetic wax, can be used as the wax feedstock without particular limitation; however, the use is preferred of a synthetic wax or petroleum-based wax that contains at least 70 mass% normal-paraffin having at least 16 carbons and preferably at least 20 carbons. The petroleum-based wax can be exemplified by slack wax and microwax. The synthetic wax can be exemplified by the so-called Fischer-Tropsch (FT) waxes produced by the Fischer-Tropsch (FT) synthesis.

[0027] The first catalyst 10 contains at least an ultrastable Y zeolite (in some cases referred to below as USY zeolite) and an amorphous solid acid. For example, the use is preferred of a first catalyst 10 comprising USY zeolite and amorphous solid acid molded into pellet form using a binder.

[0028] The silica/alumina molar ratio in the USY zeolite is preferably 20 to 96, more preferably 25 to 60, and even more preferably 30 to 45. The yield of the middle distillate fraction tends to decline when the silica/alumina molar ratio is below 20, while at above 96 the reaction temperature rises and the catalyst life is therefore shortened and in addition the yield of the middle distillate fraction also tends to decline.

[0029] The upper limit on the average particle size of the USY zeolite is preferably 1.0 μm and more preferably is 0.5 μm. The lower limit on the average particle size of the USY zeolite is preferably 0.05 μm. The yield of the middle distillate fraction tends to decline when the average particle size exceeds 1.0 μm.

[0030] The content of the USY zeolite in the first catalyst 10 is a critical parameter from the standpoint of obtaining the effects of the present invention. The upper limit on this content is preferably 10 mass% and more preferably 4 mass%, in each case with respect to the total mass of the first catalyst 10. The lower content limit preferably is 0.1 mass% with respect to the total mass of the first catalyst 10. The yield of the middle distillate fraction tends to decline when the content exceeds 10 mass%, while the reaction temperature rises and the aromatics tend to increase at below 0.1 mass%.

[0031] The amorphous solid acid used in the first catalyst 10 can be exemplified by silica-alumina, alumina-boria, silica-zirconia, silica-magnesia, and silica-titania, and one or more selections from thereamong can be used. The use is preferred of one or more selections from among silica-alumina, alumina-boria, and silica-zirconia. The content of the amorphous solid acid in the first catalyst 10 is preferably 3 to 80 mass% and more preferably 7 to 60 mass%, in each case with respect to the total mass of the first catalyst 10.

[0032] The binder used in the first catalyst 10 can be, for example, silica, alumina, and so forth, wherein the use of alumina is preferred. The binder content in the first catalyst 10 is preferably 20 to 90 mass% and more preferably is 30 to 80 mass%, in each case with respect to the total mass of the first catalyst 10.

[0033] The first catalyst 10 preferably has a metal from group VIII of the Periodic Table, and specifically nickel, rhodium, palladium, iridium, platinum, and so forth, supported on a catalyst support that is a constituent thereof. This catalyst support constituent of the first catalyst 10 comprises, for example, the USY zeolite and amorphous solid acid as described above molded into pellet form using a binder. Among the group VIII metals, the use of palladium and/or platinum is preferred, while the use of platinum by itself or the combination of palladium and platinum at a palladium/platinum molar ratio no greater than 0.15 is more preferred. The amount of group VIII metal supported in the first catalyst 10 is preferably 0.05 to 2.0 mass% and more preferably 0.2 to 1.2 mass%, in each case with respect to the total mass of the first catalyst 10.

[0034] The second catalyst 20 contains at least a solid acid but substantially does not contain USY zeolite. That is, the second catalyst 20 is substantially composed of only a solid acid and material other than USY zeolite. For example, a solid acid molded into pellet form using a binder is preferably used as this second catalyst 20.

[0035] The solid acid used in the second catalyst 20 can be exemplified by silica-alumina, alumina-boria, silica-zirconia, silica-magnesia, silica-titania, and silicoaluminophosphate, and one or more selections from thereamong can be used. The use is preferred of one or more selections from among silica-alumina, alumina-boria, silica-zirconia, and silicoaluminophosphate. This silicoaluminophosphate is exemplified by SAPO-5, SAPO-11, SAPO-34, and so forth. An amorphous solid acid is preferably used for the solid acid in the second catalyst 20. The content of the solid acid in the second catalyst 20 is preferably 30 to 90 mass% and more preferably 40 to 80 mass%, in each case with respect to the total mass of the second catalyst 20.

[0036] The same binders as used for the first catalyst 10 described hereinabove can be used as the binder in the second catalyst 20. The content of the binder in the second catalyst 20 is preferably 10 to 70 mass% and more preferably 20 to 60 mass%, in each case with respect to the total mass of the second catalyst 20.

[0037] The second catalyst 20 preferably has a metal from group VIII of the Periodic Table, and specifically nickel, rhodium, palladium, iridium, platinum, and so forth, supported on a catalyst support that is a constituent thereof. This catalyst support constituent of the second catalyst 20 comprises, for example, the solid acid as described above molded into pellet form using a binder. Among the group VIII metals, the use of palladium and/or platinum is preferred, while the use of platinum by itself or the combination of palladium and platinum at a palladium/platinum molar ratio no greater than 0.15 is more preferred. The amount of group VIII metal supported in the second catalyst 20 is preferably 0.05 to 2.0 mass% and more preferably 0.1 to 0.8 mass%, in each case with respect to the total mass of the second catalyst 20.

[0038] The packing ratio between the first catalyst 10 and the second catalyst 20 in the fixed bed reaction column 30 is not particularly limited, but there is preferably 30 to 100 volume parts and more preferably 40 to 85 volume parts of the second catalyst 20 per 100 volume parts of the first catalyst 10. The normal-paraffin content in the uncracked wax tends to become large when the packing ratio for the second catalyst 20 is less than 30 volume parts, while the yield of the middle distillate fraction tends to decline at more than 100 volume parts.

[0039] The reaction conditions during execution of wax hydrotreating in the fixed bed reaction column 30 are preferably selected as appropriate as a function of the type of wax feedstock, the type of first catalyst, the type of second catalyst, and so forth. In general, the reaction temperature is preferably 270 to 360°C and more preferably is 280 to 340°C. While a satisfactory yield of liquid hydrocarbon comprising the middle distillate fraction can be obtained at a reaction temperature below 270°C, as compared to reaction temperatures in the range given above, it tends to be problematic to obtain a satisfactory reduction in the normal-paraffin content in the solid wax comprising the uncracked wax at reaction temperatures below 270°C. On the other hand, while a satisfactory reduction in the normal-paraffin in the uncracked wax can be obtained at a reaction temperature in excess of 340°C, as compared to reaction temperatures in the range given above, the yield of the middle distillate fraction tends to decline at reaction temperatures in excess of 340°C. Reaction temperatures in excess of 360°C are particularly undesirable from the standpoint of obtaining a clean fuel base material since, as compared to reaction temperatures in the range given above, the production of aromatic compounds is facilitated at reaction temperatures in excess of 360°C.

[0040] The liquid space velocity (LHSV) of the wax feedstock relative to the catalyst as a whole in the fixed bed reaction column 30 must be 0.4 to 4.0 h^{-1} and is preferably brought to 0.5 to 2.5 h^{-1}. A large normal-paraffin content in the uncracked wax occurs when this liquid space velocity is below 0.4 h^{-1}, while the yield of the middle distillate fraction declines at above 4.0 h^{-1}.

[0041] The pressure during the reaction, in order to influence the cracking activity, is preferably 1.5 to 7 MPa and more preferably is 2 to 5 MPa. The normal-paraffin content in the uncracked wax tends to become large when the pressure is less than 1.5 MPa, while the yield of the middle distillate fraction tends to decline at above 7 MPa.

[0042] The hydrogen/oil ratio is not particularly limited, but generally is preferably 200 to 2000 NL/L. The isoparaffin content in the uncracked wax tends to become small due to a hydrogen deficiency when the hydrogen/oil ratio is less than 200 NL/L, while the economics deteriorate due to increased equipment costs at above 2000 NL/L.

[0043] Hydrocracking and hydroisomerization, which have different reaction patterns, can be simultaneously carried out more efficiently and under the same conditions by carrying out wax hydrotreating by contacting the wax with the first and second catalysts in a fixed bed reaction column under the reaction conditions described above; this makes it possible to obtain higher yields of a middle distillate fraction, for example, kerosene and gas oil, that has an even better reduction in normal-paraffin content, while at the same time also making it possible to achieve an even better reduction in the normal-paraffin content in the uncracked wax.

[0044] Suitable embodiments of the present invention have been described in the preceding, but the present invention is not limited to the embodiments provided above. For example, while the preceding embodiments are described with the use of a single fixed bed reaction column 30, the wax hydrotreating process of the present invention can also use two or more reaction columns, as shown in Figure 2. In this case, the first catalyst 10 and the second catalyst 20 can be packed in different reaction columns 30. In an embodiment preferred for its ability to carry out wax hydrotreating efficiently and to keep equipment costs down, the first catalyst 10 and the second catalyst 20 are preferably packed as layers within a single reaction column, as shown in Figure 1, or as necessary in two or more serially connected reaction columns.

[0045] The wax hydrotreating process of the present invention can efficiently produce liquid hydrocarbon in the form of a middle distillate fraction with a boiling point of 140 to 360°C and solid wax in the form of the uncracked wax with a boiling point of 360°C or greater, in both cases with a satisfactorily reduced normal-paraffin content.

Examples

[0046] The present invention is more specifically described hereinbelow based on examples and comparative examples; however, the present invention is not limited by the examples that follow.

(Example 1)

[0047] FT wax (number of carbons: 21 to 82, normal-paraffin content: 96 mass%) was prepared as the feedstock. A catalyst support was obtained by mixing USY zeolite, alumina-boria (alumina/boria molar ratio: 5.7), and alumina binder at a mass ratio of 5 : 55 : 40; molding into cylinders with a diameter of 1.6 mm and a length of 2 to 3 mm; and calcining for 1 hour at 500°C. The USY zeolite used had a silica/alumina molar ratio therein of 40 and an average particle size of 0.9 μm. The resulting catalyst support was impregnated with an aqueous solution of dichlorotetraammine platinum(II) followed by drying for 3 hours at 120°C and then calcining for 1 hour at 500°C to obtain a first catalyst in which 0.6 mass% platinum, with respect to the total mass of the catalyst, was supported on the support. Silica-alumina (alumina content: 14 mol%) and alumina binder were also mixed at a mass ratio of 80 : 20 followed by molding into cylinders with a diameter of 1.6 mm and a length of 2 to 3 mm and then calcining for 1 hour at 500°C to give a catalyst support. The resulting catalyst support was impregnated with an aqueous solution of dichlorotetraammine platinum(II) followed by drying for 3 hours at 120°C and then calcining for 1 hour at 500°C to obtain a second catalyst in which 0.6 mass% platinum, with respect to the total mass of the catalyst, was supported on the support.

[0048] 140 mL of the first catalyst and 60 mL of the second catalyst were packed as layers in a fixed bed reaction column, and prior to reaction the metal (platinum) was reduced for 4 hours at 345°C in a hydrogen stream. This was followed by hydrotreating of the feedstock under conditions of a liquid space velocity of 2.5 h^{-1} for the feedstock with respect to the entire first and second catalysts, a reaction pressure of 4 MPa, and a hydrogen/oil ratio of 520 NL/L, with the reaction temperature set to 280°C in order to bring the fraction with a boiling point no greater than 360°C (the cracking product) to 80 mass% with respect to the feedstock. The product oil obtained in this manner was submitted to gas chromatographic analysis and the proportion (yield) of the middle distillate fraction with a boiling point from 140 to 360°C in the cracking product and the normal-paraffin content in this middle distillate fraction were determined. With regard to the uncracked wax with a boiling point of 360°C or greater, the normal-paraffin content in this uncracked wax was also determined at the same time. The results are shown in Table 1.

(Example 2)

[0049] Feedstock hydrotreating was carried out as in Example 1, with the exception that 0.02 mass% palladium and 0.6 mass% platinum were supported on the first and second catalysts rather than 0.6 mass% platinum; this was achieved using an aqueous solution of dichlorotetraammine palladium and an aqueous solution of dichlorotetraammine platinum (II). In this case, the reaction temperature that brought the fraction with a boiling point no greater than 360°C (the cracking product) to 80 mass% with respect to the feedstock was 279°C. The yield of the middle distillate fraction, the normal-paraffin content in the middle distillate fraction, and the normal-paraffin content in the uncracked wax are shown in Table 1.

(Example 3)

[0050] Feedstock hydrotreating was carried out as in Example 1, but in this example using USY zeolite (silica/alumina molar ratio: 40) with an average particle size of 0.42 μm for the first catalyst in place of the USY zeolite with an average particle size of 0.9 μm. In this case, the reaction temperature that brought the fraction with a boiling point no greater than 360°C (the cracking product) to 80 mass% with respect to the feedstock was 277°C. The yield of the middle distillate fraction, the normal-paraffin content in the middle distillate fraction, and the normal-paraffin content in the uncracked wax are shown in Table 1.

(Example 4)

[0051] Feedstock hydrotreating was carried out as in Example 1, but in this example changing the USY zeolite, alumina-boria, alumina binder mass ratio for the first catalyst to 3 : 55 : 42. In this case, the reaction temperature that brought the fraction with a boiling point no greater than 360°C (the cracking product) to 80 mass% with respect to the feedstock was 298°C. The yield of the middle distillate fraction, the normal-paraffin content in the middle distillate fraction, and the normal-paraffin content in the uncracked wax are shown in Table 1.

(Example 5)

[0052] Feedstock hydrotreating was carried out as in Example 1, but in this example using silica-zirconia (zirconia content: 45 mol%) in place of the silica-alumina in the second catalyst. In this case, the reaction temperature that brought the fraction with a boiling point no greater than 360°C (the cracking product) to 80 mass% with respect to the feedstock was 278°C. The yield of the middle distillate fraction, the normal-paraffin content in the middle distillate fraction, and the normal-paraffin content in the uncracked wax are shown in Table 1.

(Comparative Example 1)

[0053] Feedstock hydrotreating was carried out as in Example 1, but without using the second catalyst and bringing the amount of the first catalyst packed in the fixed bed reaction column to 200 mL. In this case, the reaction temperature that brought the fraction with a boiling point no greater than 360°C (the cracking product) to 80 mass% with respect to the feedstock was 279°C. The yield of the middle distillate fraction, the normal-paraffin content in the middle distillate fraction, and the normal-paraffm content in the uncracked wax are shown in Table 1.

(Comparative Example 2)

[0054] Feedstock hydrotreating was carried out as in Example 1, but without using the first catalyst and bringing the amount of the second catalyst packed in the fixed bed reaction column to 200 mL. In this case, the reaction temperature that brought the fraction with a boiling point no greater than 360°C (the cracking product) to 80 mass% with respect to the feedstock was 279°C. The yield of the middle distillate fraction, the normal-paraffin content in the middle distillate fraction, and the normal-paraffin content in the uncracked wax are shown in Table 1.

(Comparative Example 3)

[0055] Feedstock hydrotreating was carried out as in Example 1, but changing the liquid space velocity to 4.5 h^{-1}. In this case, the reaction temperature that brought the fraction with a boiling point no greater than 360°C (the cracking product) to 80 mass% with respect to the feedstock was 373°C. The yield of the middle distillate fraction, the normal-paraffin content in the middle distillate fraction, and the normal-paraffin content in the uncracked wax are shown in Table 1.

(Comparative Example 4)

[0056] Feedstock hydrotreating was carried out as in Example 1, but changing the liquid space velocity of 0.35 h^{-1}. In this case, the reaction temperature that brought the fraction with a boiling point no greater than 360°C (the cracking product) to 80 mass% with respect to the feedstock was 243°C. The yield of the middle distillate fraction, the normal-paraffin content in the middle distillate fraction, and the normal-paraffin content in the uncracked wax are shown in Table 1.

[0057]

[Table 1]

	yield of the middle distillate fraction (mass%)	normal-paraffin content in the middle distillate fraction (mass%)	normal-paraffin content in the uncracked wax (mass%)
Example 1	60.7	11.6	11.4
Example 2	61.1	10.9	11.2
Example 3	61.4	10.8	9.9
Example 4	61.5	10.8	9.8
Example 5	61.1	10.3	9.4
Comparative Example 1	57.9	16.9	21.4
Comparative Example 2	54.1	11.5	11.1
Comparative Example 3	46.1	10.8	9.3
Comparative Example 4	58.2	11.8	37.5

[0058] As is clear from the results shown in Table 1, it was confirmed that the wax hydrotreating process of the present invention (Examples 1 to 5), as compared to the hydrotreating processes in Comparative Examples 1 to 4, was able to hydrotreat wax under constant reaction conditions with the production of good yields of a middle distillate fraction having a satisfactorily reduced normal-paraffin content, while at the same producing an uncracked wax fraction that had a satisfactorily reduced normal-paraffin content.

Industrial Applicability

[0059] As described above, the present invention provides a wax hydrotreating process that can hydrotreat wax under constant reaction conditions with the production of good yields of a middle distillate fraction having a satisfactorily reduced normal-paraffin content, while at the same producing an uncracked wax fraction that has a satisfactorily reduced normal-paraffin content. In addition, the present invention can provide a process for manufacturing fuel base material and lubricant base material.

Claims

1. A wax hydrotreating process, **characterized by** hydrotreating the wax by bringing the wax, under a hydrogen atmosphere and at a liquid space velocity of 0.4 to 4.0 h^{-1}, into contact with a first catalyst containing an ultrastable Y zeolite and an amorphous solid acid and thereafter into contact with a second catalyst that contains a solid acid and substantially does not contain ultrastable Y zeolite.

2. The wax hydrotreating process according to claim 1, **characterized in that** the first catalyst is disposed in an upstream position in a fixed bed reaction column and the second catalyst is disposed in a downstream position therein, and the wax is hydrotreated in the fixed bed reaction column.

3. The wax hydrotreating process according to claim 1 or 2, **characterized in that** the first catalyst and/or the second catalyst comprise palladium and/or platinum supported on a catalyst support that is a constituent of the catalyst.

4. The wax hydrotreating process according to any of claims 1 to 3, **characterized in that** the average particle size of the ultrastable Y zeolite in the first catalyst is no greater than 1.0 μm.

5. The wax hydrotreating process according to any of claims 1 to 4, **characterized in that** the content of the ultrastable Y zeolite in the first catalyst is no more than 4.0 mass% with respect to the total mass of the first catalyst.

6. The wax hydrotreating process according to any of claims 1 to 5, **characterized in that** the amorphous solid acid of the first catalyst contains at least one selected from the group consisting of silica-alumina, alumina-boria, and silica-zirconia.

7. The wax hydrotreating process according to any of claims 1 to 6, **characterized in that** the solid acid of the second catalyst contains at least one selected from the group consisting of silica-alumina, aluminaboria, silica-zirconia, and silicoaluminophosphate.

8. The wax hydrotreating process according to any of claims 1 to 7, **characterized in that** the wax hydrotreating is carried out under conditions of a reaction temperature of 270 to 360°C and a pressure of 2 to 5 MPa.

9. A process for manufacturing fuel base material and lubricant base material, comprising:

a first step in which a wax is hydrotreated by bringing the wax, under a hydrogen atmosphere and at a liquid space velocity of 0.4 to 4.0 h^{-1}, into contact with a first catalyst containing an ultrastable Y zeolite and an amorphous solid acid and thereafter into contact with a second catalyst that contains solid acid and substantially does not contain ultrastable Y zeolite; and
a second step in which a middle distillate fraction and solid wax are obtained from the treated material obtained in the first step.

Fig.1

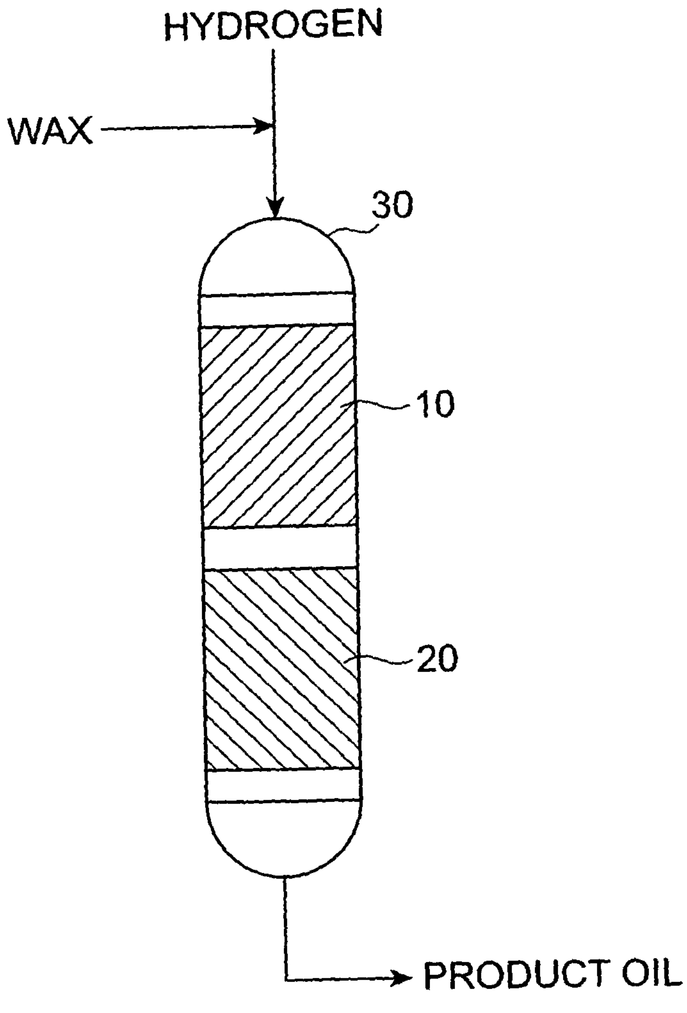
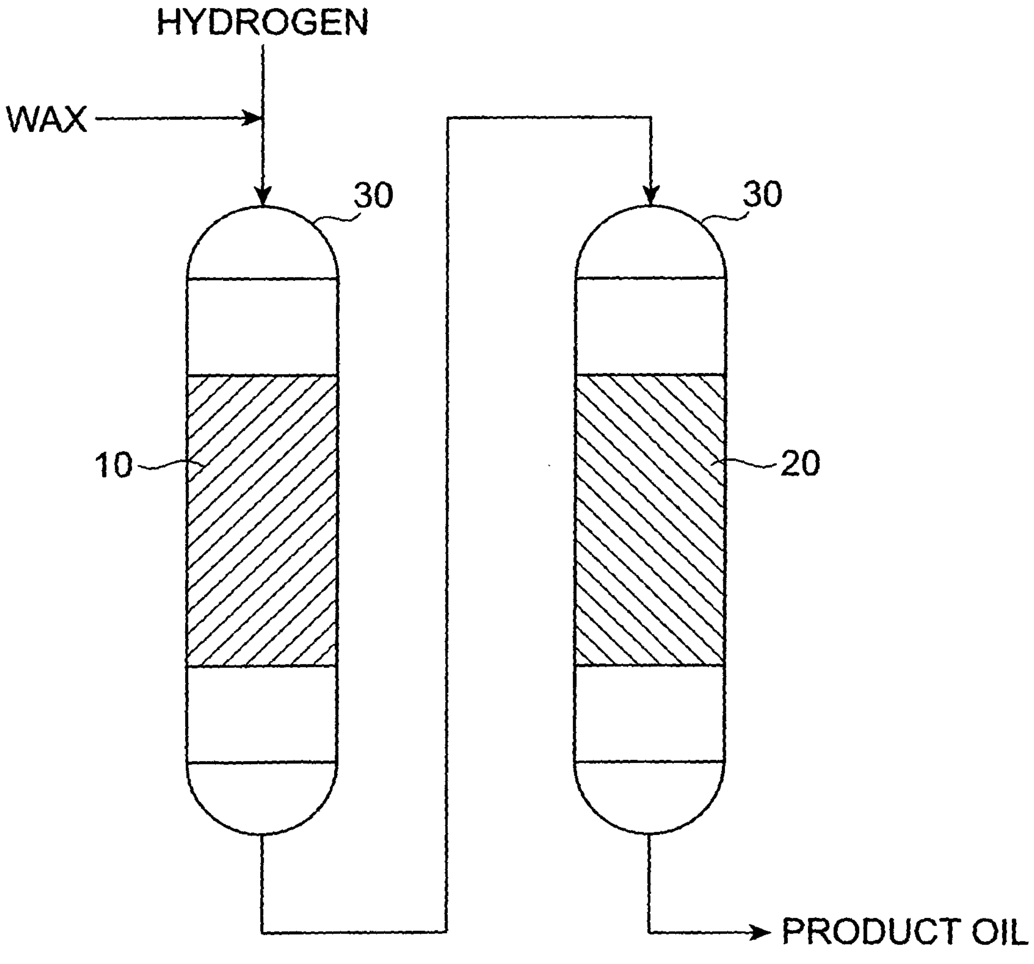


Fig.2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/050236

A. CLASSIFICATION OF SUBJECT MATTER
C10G65/12(2006.01)i, *C10G45/60*(2006.01)i, *C10G45/62*(2006.01)i, *C10G47/16*(2006.01)i, *C10G47/18*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G1/00-75/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2004/028688 A1 (Nippon Oil Corp.), 08 April, 2004 (08.04.04), Claims; page 3, line 5 to page 5, line 7; examples 1 to 5 & AU 2003266527 A & EP 1547683 A1 & US 2005/0145541 A1 & JP 2004-539467 A	1-9
Y	US 2004/0256287 A1 (S.J.Miller et al.), 23 December, 2004 (23.12.04), Claims; Par. Nos. [0042], [0043], [0045], [0049] to [0051], [0056], [0062] & WO 2004/113475 A2 & NL 1026461 C2 & GB 2420790 A & BR 200411606 A & AU 2004250190 A	1-9

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search 27 March, 2007 (27.03.07)	Date of mailing of the international search report 10 April, 2007 (10.04.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/050236

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2004-526035 A (Chevron U.S.A. Inc.), 26 August, 2004 (26.08.04), Claims & US 2002/0144930 A1 & GB 2377454 A & AU 200229338 A & NL 1020308 C & WO 2002/081599 A1 & ZA 200202597 A & GB 2377454 B & US 6589415 B2 & AU 2002257060 A & BR 200208327 A & AU 784632 B	1-9
A	JP 2005-320379 A (Nippon Oil Corp.), 17 November, 2005 (17.11.05), Claims; Par. Nos. [0016] to [0025] (Family: none)	1-9
A	JP 2004-285155 A (Japan Energy Corp.), 14 October, 2004 (14.10.04), Claims (Family: none)	1-9
A	JP 4-226594 A (Mobil Oil Corp.), 17 August, 1992 (17.08.92), Full text & EP 464547 A1 & AU 9179110 A & CA 2045106 A & AU 640490 B & EP 464547 B1 & ES 2116272 T3 & JP 3068245 B2 & CA 2045106 C	1-9

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/050236

Claim 1 pertains to a method of hydrotreating a wax which includes the step of "bringing the wax into contact with a first catalyst comprising ultrastable zeolite Y and an amorphous solid acid under the conditions of a liquid hourly space velocity of 0.4-4.0 h^{-1}."

In that step, any conditions other than liquid hourly space velocity, such as temperature and pressure, are included as far as the liquid hourly space velocity is 0.4-4.0 h^{-1}, and all catalysts which comprise ultrastable zeolite Y and an amorphous solid acid are involved.

However, the step which is disclosed in the meaning of Article 5 of the PCT is limited to ones in which the conditions include liquid hourly space velocities in that range and temperatures and pressures in specific ranges. Furthermore, the catalyst is limited to one which comprises ultrastable zeolite Y, an amorphous solid acid, and a specific metal deposited.

That the performance of a catalyst is not governed only by liquid hourly space velocity but is influenced by various conditions including temperature and pressure and depends also on an ingredient deposited on the catalyst is a matter of technical common sense. Consequently, claim 1 is considered to lack a support by the description in the meaning of Article 6 of the PCT.

The same applies to claim 9 and claims 2-8, in which claim 1 is cited.

Therefore, a search was made for that step in claims 1-9 on the assumption that the step is one specified in the description, i.e., the step which employs the catalyst having a metal deposited thereon shown in claim 3 and in which contacting is conducted at the temperature and pressure shown in claim 8.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2004028688 A **[0005]**
- JP 2004 A **[0005]**
- JP 2004255242 A **[0005]**