

Description

Title of Invention: METHOD AND MANUFACTURING APPARATUS FOR MANUFACTURING AVIATION FUEL FROM WASTE PLASTIC PYROLYSIS OIL

Technical Field

- [1] The present disclosure relates to a method and apparatus for producing aviation fuel by refining waste plastic pyrolysis oil.

Background Art

- [2] Waste plastics, which are produced using petroleum as a raw material, are not recyclable and are mostly disposed of as garbage. These wastes are difficult to degrade in nature, and cause many environmental problems such as large amounts of air pollution and hazardous substances generated during an incineration process, which has become a social problem.
- [3] The biggest problem with plastics is that it is almost non-biodegradable. Plastics take decades or more to degrade and disappear in the natural environment, and in this process, the plastics are converted into microplastics and cause a disastrous effect on the environment. Therefore, the importance of waste plastic treatment technologies has significantly increased. As one of the waste plastic treatment technologies, there is a method for pyrolyzing waste plastics to convert the waste plastics into oil so as to recycle the waste plastics.
- [4] However, waste plastic pyrolysis oil may not be immediately used as a high-value-added fuel such as gasoline or diesel oil because it has a higher content of impurities such as chlorine, nitrogen, and metals compared to fractions produced from crude oil, and therefore, waste plastic pyrolysis oil needs to go through a refinery process.
- [5] In addition, low-temperature properties of oil including waste plastic pyrolysis oil vary depending on a hydrocarbon structure, and for example, the low-temperature properties appear in the order of Aromatic > Naphthene > Branched hydrocarbon > Linear hydrocarbon. Waste plastic pyrolysis oil has low-temperature properties that are inferior to those of general crude oil having the same hydrocarbon distribution because it is mainly composed of linear hydrocarbons.
- [6] Unlike automobile fuel, aviation fuel used in flight should be used in a high altitude and low temperature environment of -4°C or lower, and therefore, low-temperature properties of oil act as a significantly important factor in determining fuel quality.
- [7] As a refinery process to improve the low-temperature properties of the waste plastic pyrolysis oil, a dewaxing process using a noble metal catalyst and a dewaxing process

using a strong acid site catalyst such as zeolite or clay have been performed. However, there is a limit to improving a freezing point, a pour point, and the like due to the deteriorated low-temperature properties of the waste plastic pyrolysis oil, and an excessive amount of impurities contained in the waste plastic pyrolysis oil cause deactivation of the catalyst, resulting in a significant decrease in reaction yield. As another method, it is possible to further improve the low-temperature properties of the pyrolysis oil by inducing dewaxing and hydrocracking at the same time through a reaction at a high temperature reaction condition of 450°C or higher. However, the reaction is performed under excessive conditions, which causes a decrease in yield of 50% or more.

- [8] That is, due to the deteriorated low-temperature properties of the waste plastic pyrolysis oil, it is difficult to produce aviation fuel that satisfies the aviation fuel standard JET A-1 or JP-8 with a high yield from the waste plastic pyrolysis oil.
- [9] Therefore, there is a demand for a method and apparatus for producing aviation fuel that may produce high-quality aviation fuel that satisfies the aviation fuel standard and has a minimized content of impurities with a high yield from waste plastic pyrolysis oil.

[10]

Disclosure of Invention

Technical Problem

- [11] An object of the present disclosure is to provide a method and apparatus for producing aviation fuel that may produce aviation fuel that satisfies a freezing point in accordance with the aviation fuel standard JET A-1 or JP-8 with a high yield through a refinery process of waste plastic pyrolysis oil.
- [12] Another object of the present disclosure is to provide a method and apparatus for producing aviation fuel that may produce high-quality aviation fuel having a minimized content of impurities through a refinery process of waste plastic pyrolysis oil.
- [13] Still another object of the present disclosure is to provide a method and apparatus for producing aviation fuel that may implement a stable operation for a long period of time by preventing deactivation of a catalyst due to impurities during a refinery process of waste plastic pyrolysis oil containing impurities including chlorine and nitrogen.

[14]

Solution to Problem

- [15] In one general aspect, a method for producing aviation fuel includes: a first step of subjecting waste plastic pyrolysis oil to an olefin migration reaction; a second step of subjecting a product obtained in the first step to an olefin branching reaction; a third step of hydrotreating a product obtained in the second step in the presence of a hy-

hydrotreating catalyst; and a fourth step of hydrocracking a product obtained in the third step in the presence of a hydrocracking catalyst.

- [16] In an embodiment, the first step may be performed in the presence of a weak acid site catalyst, and the second step may be performed in the presence of a catalyst of zeolite having a one-dimensional pore structure (1-D zeolite).
- [17] In an embodiment, the weak acid site catalyst may include a titanium oxide catalyst.
- [18] In an embodiment, a weight ratio of the weak acid site catalyst to the 1-D zeolite catalyst may be 60:40 to 90:10.
- [19] In an embodiment, the hydrotreating catalyst in the third step may be a catalyst in which an active metal including one or two or more selected from molybdenum, nickel, cobalt, and tungsten is supported on a support.
- [20] In an embodiment, the hydrocracking catalyst in the fourth step may be a catalyst in which an active metal including one or two or more selected from molybdenum, nickel, cobalt, and tungsten is supported on zeolite.
- [21] In an embodiment, the produced aviation fuel may have a freezing point of -45°C or lower and a yield of 75% or more.
- [22] In an embodiment, the produced aviation fuel may have a chlorine content of 10 ppm or less and a nitrogen content of 10 ppm or less.
- [23] In an embodiment, the first step and the second step may be performed at a reaction temperature of higher than 300°C .
- [24] In an embodiment, the first step and the second step may be performed under conditions of a reaction pressure of 5 to 70 bar and a gas/oil ratio (GOR) of 100 to 3,000 in an inert atmosphere.
- [25] In an embodiment, the third step may be performed under conditions of a reaction temperature of lower than 300°C , a reaction pressure of 100 bar or less, and a gas/oil ratio (GOR) of 100 to 3,000 in hydrogen gas.
- [26] In an embodiment, the fourth step may be performed under conditions of a reaction temperature of higher than 300°C , a reaction pressure of 100 bar or less, and a gas/oil ratio (GOR) of 100 to 3,000 in hydrogen gas.
- [27] In an embodiment, the method for producing aviation fuel may further include a fifth step of hydrofinishing a product obtained in the fourth step under conditions of a reaction temperature of higher than 300°C , a reaction pressure of 100 bar or less, and a gas/oil ratio (GOR) of 100 to 3,000 in the presence of a hydrofinishing catalyst.
- [28] In another general aspect, an apparatus for producing aviation fuel includes: a first reactor into which waste plastic pyrolysis oil is introduced and in which an olefin migration reaction and an olefin branching reaction are sequentially performed; a second reactor into which a reaction product and hydrogen gas are introduced from the first reactor and in which hydrotreating is performed in the presence of a hydrotreating

catalyst; and a third reactor into which a reaction product and hydrogen gas are introduced from the second reactor and in which hydrocracking is performed in the presence of a hydrocracking catalyst.

[29] In an embodiment, the first reactor may include a first zone filled with a weak acid site catalyst, and a second zone filled with a catalyst of zeolite having a one-dimensional pore structure (1-D zeolite), and the waste plastic pyrolysis oil may be refined by sequentially passing through the first zone and the second zone.

[30] In an embodiment, the first reactor to the third reactor may be fixed bed reactors.

[31] In an embodiment, the apparatus for producing aviation fuel may further include a fourth reactor into which a reaction product and hydrogen gas are introduced from the third reactor and in which hydrofinishing is performed in the presence of a hydrofinishing catalyst.

[32]

Advantageous Effects of Invention

[33] As set forth above, in the method for producing aviation fuel according to the present disclosure, it is possible to produce aviation fuel that satisfies a freezing point in accordance with the aviation fuel standard JET A-1 or JP-8 with a high yield from waste plastic pyrolysis oil.

[34] In the method for producing aviation fuel according to the present disclosure, it is possible to produce high-quality aviation fuel having a minimized content of impurities from waste plastic pyrolysis oil.

[35] In the method for producing aviation fuel according to the present disclosure, deactivation of a catalyst is prevented during a refinery process of waste plastic pyrolysis oil containing impurities including chlorine and nitrogen, such that a method and apparatus for producing aviation fuel that may implement a stable operation for a long period of time are provided.

[36]

Brief Description of Drawings

[37] FIG. 1 illustrates an apparatus for producing aviation fuel including a first reactor, a second reactor, and a third reactor according to an embodiment of the present disclosure.

[38] FIG. 2 illustrates an apparatus for producing aviation fuel further including a fourth reactor in the apparatus for producing aviation fuel of FIG. 1 according to an embodiment of the present disclosure.

[39]

Best Mode for Carrying out the Invention

[40] Unless otherwise defined, all the technical terms and scientific terms used in the

present specification have the same meanings as commonly understood by those skilled in the art to which the invention pertains.

- [41] Unless the context clearly indicates otherwise, the singular forms of the terms used in the present specification may be interpreted as including the plural forms.
- [42] A numerical range used in the present specification includes upper and lower limits and all values within these limits, increments logically derived from a form and span of a defined range, all double limited values, and all possible combinations of the upper and lower limits in the numerical range defined in different forms. Unless otherwise specifically defined in the present specification, values out of the numerical ranges that may occur due to experimental errors or rounded values also fall within the defined numerical ranges.
- [43] The expression "comprise(s)" described in the present specification is intended to be an open-ended transitional phrase having an equivalent meaning to "include(s)", "contain(s)", "have (has)", or "are (is) characterized by", and does not exclude elements, materials, or steps, all of which are not further recited herein.
- [44] Unless otherwise defined, a unit of "%" and a unit of "vol%" used in the present specification unless specifically mentioned refer to "wt%" and "vol%" at 1 atm and 25°C, respectively.
- [45] Unless otherwise defined, a unit of "ppm" used in the present specification unless specifically mentioned refers to "mass ppm".
- [46] A boiling point (bp) used in the present specification unless specifically mentioned refers to a boiling point at 1 atm and 25°C.
- [47] As described above, waste plastic pyrolysis oil has deteriorated low-temperature properties, such that it is difficult to produce high-quality aviation fuel having a low freezing point from the waste plastic pyrolysis oil. In addition, waste plastic pyrolysis oil contains an excessive amount of impurities including chlorine or nitrogen, such that it is difficult to use the waste plastic pyrolysis oil as it is.
- [48] Accordingly, the present disclosure provides a method for producing aviation fuel, the method including: a first step of subjecting waste plastic pyrolysis oil to an olefin migration reaction; a second step of subjecting a product obtained in the first step to an olefin branching reaction; a third step of hydrotreating a product obtained in the second step in the presence of a hydrotreating catalyst; and a fourth step of hydrocracking a product obtained in the third step in the presence of a hydrocracking catalyst.
- [49] Through a continuous refinery process including the first step to the fourth step, it is possible to produce high-quality aviation fuel that satisfies a freezing point in accordance with the aviation fuel standard JET A-1 or JP-8 and has a minimized content of impurities with a high yield from waste plastic pyrolysis oil.
- [50] Specifically, the waste plastics may be solid or liquid waste related to synthetic

polymer compounds such as waste synthetic resins, waste synthetic fibers, waste synthetic rubber, and waste vinyl, and a mixture of hydrocarbon oils produced by pyrolyzing the waste plastics may be waste plastic pyrolysis oil. The mixture of hydrocarbon oils may contain impurities such as a chlorine compound, a nitrogen compound, and a metal compound in addition to hydrocarbon oil, and may contain, for example, 300 ppm or more of nitrogen, 30 ppm or more of chlorine, 20 vol% or more of olefins, and 1 vol% or more of conjugated diolefins.

- [51] Most of the olefins contained in the waste plastic pyrolysis oil may have a linear hydrocarbon structure of an α -olefin. The waste plastic pyrolysis oil may be a mixture of various hydrocarbon oils, and the hydrocarbon oil may include, for example, H-naphtha (to C8, bp < 150°C): Kero (C9 to C17, bp 150 to 265°C), LGO (C18 to C20, bp 265 to 340°C), and VGO/AR (from C21, bp > 340°C). Specifically, the waste plastic pyrolysis oil may include 70 wt% or more of Kero (C9 to C17, bp 150 to 265°C) as main hydrocarbon oil.
- [52] Linear α -olefins contained in the waste plastic pyrolysis oil may be converted into linear internal olefins through the first step of subjecting the waste plastic pyrolysis oil to the olefin migration reaction, and internal olefins contained in the waste plastic pyrolysis oil may be branched through the second step of subjecting the product obtained in the first step to the olefin branching reaction.
- [53] In an embodiment, the first step may be performed in the presence of a weak acid site catalyst, and the second step may be performed in the presence of a catalyst of zeolite having a one-dimensional pore structure (1-D zeolite).
- [54] In the related art, a noble metal catalyst such as Pt or Pd has been used as a catalyst for converting linear α -olefins in various petroleum oils such as crude oil into linear internal olefins. However, since the noble metal catalyst is vulnerable to impurities, the catalyst is deactivated due to an excessive amount of nitrogen impurities contained in the waste plastic pyrolysis oil. Accordingly, it is possible to prevent deactivation of the catalyst and to effectively improve reaction efficiency using a weak acid site catalyst as a catalyst for the olefin migration reaction.
- [55] In an embodiment, the weak acid site catalyst may include a titanium oxide catalyst. Examples of the weak acid site catalyst include catalysts having a weak acid site, such as γ -Al₂O₃, Kaolin, TiO₂, and ZrO₂, and in consideration of a chain length distribution of the mixture of hydrocarbon oils included in the waste plastic pyrolysis oil and a conversion yield into linear internal olefins in the presence of impurities such as chlorine and nitrogen, a titanium oxide catalyst may be preferred among weak point site catalysts. In the case of the titanium oxide catalyst, deactivation of the catalyst is suppressed even in the presence of an excessive amount of impurities, such that an aviation fuel production process may be stably performed for a long period of time,

and a reaction yield may be improved.

- [56] The second step of subjecting the product obtained in the first step to the olefin branching reaction may be performed in the presence of a catalyst of zeolite having a one-dimensional pore structure (hereinafter, 1-D zeolite). In a case of using the 1-D zeolite, a side reaction such as a cracking reaction is suppressed, and a selectivity of the olefin branching reaction is improved in the presence of impurities such as chlorine and nitrogen, such that the reaction efficiency may be maximized. Specifically, the 1-D zeolite may be zeolite having a 10-membered ring structure such as EU-2, ZSM-23, or ZSM-48 zeolite. The 1-D zeolite may have a BET specific surface area of 150 m²/g or more, an average pore size of 5 nm or more, and a total pore volume of 0.3 cc/g or more. When the above ranges are satisfied, the olefin branching reaction efficiency may be improved. Specifically, the BET specific surface area may be 180 to 400 m²/g (more specifically, 200 to 300 m²/g), the average pore size may be 6 to 20 nm (more specifically, 7 to 15 nm), and the total pore volume may be 0.4 to 2.0 cc/g (more specifically, 0.5 to 1.3 cc/g).
- [57] In an embodiment, a weight ratio of the weak acid site catalyst to the 1-D zeolite catalyst may be 60:40 to 90:10. Specifically, the weight ratio may be 60:40 to 80:20, and more specifically, the weight ratio may be 60:40 to 70:30.
- [58] The impurities in the waste plastic pyrolysis oil may be effectively reduced through the third step of hydrotreating the product obtained in the second step in the presence of the hydrotreating catalyst. Through the hydrotreating process, chlorine or nitrogen in the pyrolysis oil may be effectively removed, and in addition, other impurities such as sulfur, oxygen, and olefins may also be removed. The impurities in the waste plastic pyrolysis oil are removed through the hydrotreating process, such that deactivation of the catalyst is prevented in the hydrocracking process. Therefore, the refinery process may be performed for a long period of time, and impurities in the produced aviation fuel may be minimized.
- [59] In an embodiment, the hydrotreating catalyst in the third step may be a catalyst in which an active metal including one or two or more selected from molybdenum, nickel, cobalt, and tungsten is supported on a support. The hydrotreating catalyst may be a catalyst in which an active metal having a hydrotreating catalytic ability is supported on a support, and the active metal may include, for example, one or more selected from molybdenum, nickel, and cobalt. Any support may be used as the support as long as it has durability enough to support an active metal, and for example, the support may include one or two or more selected from alumina, zirconia, and titanium. Specifically, the hydrotreating catalyst may be a catalyst in which an active metal containing 0.1 to 10 wt% of nickel and 0.1 to 30 wt% of molybdenum with respect to a total weight of the hydrotreating catalyst is supported on a γ -alumina

support. However, this is only an example of the present disclosure, but the present disclosure is not limited thereto.

- [60] The fourth step of hydrocracking the product obtained in the third step in the presence of the hydrocracking catalyst is performed, such that it is possible to finally produce aviation fuel in accordance with the aviation fuel standard JET A-1 or JP-8 from the waste plastic pyrolysis oil.
- [61] In an embodiment, the hydrocracking catalyst may be a catalyst in which an active metal including one or two or more selected from molybdenum, nickel, cobalt, and tungsten is supported on zeolite. The support is preferably zeolite in terms of degradation reaction activity, and specifically, the support may contain ZSM-5, zeolite Y, or β -zeolite. The zeolite may be contained in an amount of 10 to 30 wt% with respect to the total weight of the hydrocracking catalyst.
- [62] In an embodiment, a freezing point of the produced aviation fuel may be -45°C or lower, and a yield of the produced aviation fuel may be 75% or more. Through the continuous refinery process including the first step to the fourth step, it is possible to produce aviation fuel having a freezing point of -45 to -55°C from waste plastic pyrolysis oil. In a case of oil obtained through a hydrogenation dewaxing process in the presence of a general noble metal catalyst, for example, a PtPd/1-D zeolite catalyst, according to the related art, a freezing point is about -25°C , which does not satisfy the JET A-1 or JP-8 standard. In order to satisfy this, it is possible to further improve the low-temperature properties of the pyrolysis oil by inducing hydrodewaxing and hydrocracking at the same time through a reaction at a high temperature reaction condition of 450°C or higher. However, in this case, the reaction is performed under excessive conditions, which causes a decrease in yield of 50% or more. On the other hand, in the method for producing aviation fuel including the first step to the fourth step of the present disclosure, it is possible to produce aviation fuel having a freezing point in accordance with the aviation fuel standard JET A-1 or JP-8 with a high yield from waste plastic pyrolysis oil. Specifically, the freezing point of the aviation fuel may be -50°C or lower (more specifically, -50°C to -60°C), and the yield of the aviation fuel may be 75% or more (more specifically, 80 or more and 90 or less).
- [63] In an embodiment, the produced aviation fuel may have a chlorine content of 10 ppm or less and a nitrogen content of 10 ppm or less. The aviation fuel finally obtained by the method for producing aviation fuel including the first step to the fourth step may be high-quality aviation fuel having an extremely low content of impurities, and may contain, for example, 10 ppm (weight) or less of chlorine, 30 ppm (weight) or less of nitrogen, 10 ppm (weight) or less of sulfur, 10 ppm (weight) or less of other metal components, 0.1 wt% or less of oxygen, 10 vol% or less of olefins, and 0.2 vol% or less of conjugated diolefins.

- [64] In an embodiment, the first step and the second step may be performed at a reaction temperature of higher than 300°C. In a case where the reaction is performed within the above temperature range, a side reaction such as a cracking reaction is suppressed, such that a change in molecular weight distribution and a weight loss may be minimized, and the efficiency of the olefin migration reaction and the olefin branching reaction may be maximized. The weight loss (reduction in weight) may be 5% or less, and a case where the reaction is performed in a relatively high temperature zone in the reaction temperature range may be advantageous in controlling a degree of positional migration of a double bond. Specifically, the reaction temperature may be 330 to 430°C, and more specifically, may be 330 to 400°C.
- [65] In an embodiment, the first step and the second step may be performed under conditions of a reaction pressure of 5 to 70 bar and a gas/oil ratio (GOR) of 100 to 3,000 in an inert atmosphere. In a high pressure condition of 70 bar or more, the reaction activity is reduced. On the other hand, a loss of the raw material may occur at a low reaction pressure of 5 bar or less. Therefore, it is preferable to control the pressure to an appropriate range. In addition, the first step and the second step may be performed in an inert atmosphere without supply of hydrogen required in common dewaxing. For example, various inert carrier gases such as nitrogen, argon, helium, and a mixture thereof may be selected without particular limitation, and specifically, nitrogen gas may be used. A flow rate of the inert carrier gas is one of the factors for controlling the reaction activity. Since the steps are performed by contact between the catalyst and the reactant, a retention time may be considered to control the reaction. A degree of the olefin migration reaction and branching reaction and a degree of occurrence of the side reaction may be controlled depending on the gas flow rate. Specifically, it is preferable that the reaction pressure is 5 to 50 bar (more specifically, 10 to 40 bar) and the GOR is 400 to 2,500 (more specifically, 500 to 2,000).
- [66] In an embodiment, the third step may be performed under conditions of a reaction temperature of lower than 300°C, a reaction pressure of 100 bar or less, and a gas/oil ratio (GOR) of 100 to 3,000 in hydrogen gas. In a case where the hydrotreating is performed under the above conditions, chlorine, nitrogen, and other impurities may be effectively removed while minimizing formation of an ammonium salt (NH_4Cl). Specifically, the temperature may be 250°C or lower (more specifically, 100°C or higher and 250°C or lower), the reaction pressure may be 30 bar to 90 bar (more specifically, 50 bar to 80 bar), and the GOR may be 400 to 2,500 (more specifically, 500 to 2,000).
- [67] In an embodiment, the fourth step may be performed under conditions of a reaction temperature of higher than 300°C, a reaction pressure of 100 bar or less, and a gas/oil ratio (GOR) of 100 to 3,000 in hydrogen gas. In a case where the hydrocracking is

performed under the above conditions, the low-temperature properties of the pyrolysis oil may be effectively improved, and aviation fuel may be obtained with a high yield. In particular, the low-temperature properties of the pyrolysis oil are primarily improved through the first step and the second step, and then the hydrocracking is performed, such that it is possible to obtain desired aviation fuel having a freezing point in accordance with the aviation fuel standard JET-A or JP-8 with a high yield even when the hydrocracking is performed under milder conditions. Specifically, the temperature may be 350°C or higher (more specifically, 350°C or higher and 450°C or lower), the reaction pressure may be 30 bar to 90 bar (more specifically, 50 bar to 80 bar), and the GOR may be 400 to 2,500 (more specifically, 500 to 2,000).

[68] In an embodiment, the method for producing aviation fuel may further include a fifth step of hydrofinishing a product obtained in the fourth step under conditions of a reaction temperature of higher than 300°C, a reaction pressure of 100 bar or less, and a gas/oil ratio (GOR) of 100 to 3,000 in the presence of a hydrofinishing catalyst. Olefins and aromatic components of oil are removed according to the specifications required for each product by performing the hydrofinishing process, such that stability may be secured, and an aromatic content and gas hygroscopicity may be controlled. In particular, when the fourth step is performed at 370°C or higher, since olefins are additionally produced by the cracking reaction, it is more preferable to perform the fifth step of hydrofinishing the product to remove the olefins. Specifically, the reaction temperature may be 330°C to 430°C, the reaction pressure may be 10 to 90 bar, and the gas/oil ratio (GOR) may be 500 to 2,500.

[69] The catalyst used in the hydrofinishing process may be a catalyst in which an active metal including one or two or more selected from molybdenum, nickel, cobalt, and tungsten is supported on a support. Specifically, the hydrofinishing catalyst may be a catalyst in which an active metal having a hydrotreating catalytic ability is supported on a support, and the active metal may include, for example, one or more selected from molybdenum, nickel, and cobalt. Any support may be used as the support as long as it has durability enough to support an active metal, and for example, the support may include alumina, zirconia, and titanium.

[70] In addition, the present disclosure provides an apparatus for producing aviation fuel including: a first reactor into which waste plastic pyrolysis oil is introduced and in which an olefin migration reaction and an olefin branching reaction are sequentially performed; a second reactor into which a reaction product and hydrogen gas are introduced from the first reactor and in which hydrotreating is performed in the presence of a hydrotreating catalyst; and a third reactor into which a reaction product and hydrogen gas are introduced from the second reactor and in which hydrocracking is performed in the presence of a hydrocracking catalyst.

- [71] In an embodiment, the first reactor may include a first zone filled with a weak acid site catalyst, and a second zone filled with a catalyst of zeolite having a one-dimensional pore structure (1-D zeolite), and the waste plastic pyrolysis oil may be refined by sequentially passing through the first zone and the second zone.
- [72] An inert carrier gas may be supplied into the first reactor. As the inert carrier gas, for example, various carrier gases known in the art, such as nitrogen, argon, helium, and a mixture thereof, may be selected and supplied without particular limitation, and specifically, nitrogen gas may be supplied.
- [73] In an embodiment, the first reactor to the third reactor may be fixed bed reactors. The fixed bed reactor has an advantage of high productivity and may be operated in a continuous mode.
- [74] The first reactor to the third reactor are filled with the catalysts, respectively. As illustrated in FIG. 1, the waste plastic pyrolysis oil may be introduced into the first reactor, and the waste plastic pyrolysis oil may be subjected to the refinery process by sequentially passing through the second reactor and the third reactor.
- [75] A pipe is connected to each of the reactors, and a reaction product may be introduced from each of the reactors through the pipe.
- [76] A reaction zone provided with a hydrotreating catalyst exists in the second reactor. The reaction product and hydrogen gas are introduced into the reaction zone from the first reactor and the reaction product and hydrogen gas are subjected to hydrotreating, such that chlorine and nitrogen may be removed from the waste plastic pyrolysis oil, and some olefins and other impurities may be removed together.
- [77] A reaction zone provided with a hydrocracking catalyst exists in the third reactor. The reaction product and hydrogen gas are introduced into the reaction zone from the second reactor and the reaction product and hydrogen gas are subjected to hydrocracking, such that aviation fuel may be finally obtained from the waste plastic pyrolysis oil.
- [78] In an embodiment, the apparatus for producing aviation fuel may further include a fourth reactor into which a reaction product and hydrogen gas are introduced from the third reactor and in which hydrofinishing is performed in the presence of a hydrofinishing catalyst. As illustrated in FIG. 2, the apparatus further includes the fourth reactor, such that olefins and aromatic components of oil are removed according to the specifications required for each product. Therefore, stability may be secured, and an aromatic content and gas hygroscopicity may be controlled. In particular, when the temperature condition of the third reactor is set to 370°C or higher, since olefins are additionally produced by the cracking reaction, it is more preferable to further include the fourth reactor for performing hydrofinishing to remove the olefins.
- [79] As for matters that are not further described in the apparatus for producing aviation

fuel, the contents described in the method for producing aviation fuel described above may be used for reference.

[80] Hereinafter, the present disclosure will be described in detail with reference to Examples. However, these Examples are intended to describe the present disclosure in more detail, and the scope of the present disclosure is not limited by the following Examples.

[81] **Example 1**

[82] A mixture of hydrocarbon oils containing a high concentration of impurities including 1,000 ppm of nitrogen and 700 ppm of chlorine was prepared as a waste plastic pyrolysis oil raw material. 20 wt% of naphtha (bp 180°C or lower, to C8) and 80 wt% of Kero (bp 180 to 220°C, C8 to C10) were included in the mixture of hydrocarbon oils, and a content of total olefins contained in the mixture of hydrocarbon oils was 20 vol%.

[83] The waste plastic pyrolysis oil was introduced into a first reactor, and an olefin migration reaction and an olefin branching reaction were performed. Specifically, 70 g of a TiO₂ catalyst was introduced into a first zone of the first reactor, and 30 g of a ZSM-48 zeolite catalyst was introduced into a second zone of the first reactor, thereby filling the first reactor with the catalysts. The remaining part of the reactor was filled with silica beads, and then a thermocouple was installed in contact with the part filled with the catalyst. At this time, as the zeolite, zeolite having a BET specific surface area of 260 m²/g, an average pore size of 10 nm, and a pore volume of 0.83 cc/g was used.

[84] Under conditions of N₂ and 5 bar, the temperature of the reactor was raised at a rate of 5°C/min and maintained at 250°C for 3 hours to remove water or adsorbed gas present on a surface of the catalyst. Thereafter, the temperature was raised to 350°C, and then the reactor was operated under conditions of a N₂/oil ratio (GOR) of 700 and a weight hourly space velocity (WHSV) of 0.5 hr⁻¹, thereby performing an olefin migration reaction and an olefin branching reaction of the waste plastic pyrolysis oil.

[85] The reaction product produced in the first reactor was introduced into a second reactor, and then the reaction product was subjected to hydrotreating. The inside of the second reactor was filled with NiMo/γ-Al₂O₃ as a hydrotreating catalyst, each of the reaction product and hydrogen gas was introduced into the second reactor, and then hydrotreating was performed under conditions of 230°C, 60 bar, a H₂/Oil ratio of 860, and LHSV of 1 h⁻¹, thereby obtaining a reaction product obtained by removing impurities such as chlorine and nitrogen from the waste plastic pyrolysis oil.

[86] The reaction product produced in the second reactor was introduced into a third reactor, and then hydrocracking was performed. The inside of the third reactor was filled with NiMo/Zeolite (10%) as a hydrocracking catalyst, each of the reaction product and hydrogen gas was introduced into the third reactor, and then hydro-

cracking was performed under conditions of 360°C, 60 bar, a H₂/Oil ratio of 860, and LHSV of 1 h⁻¹, thereby finally obtaining aviation fuel which was refined oil.

[87] **Example 2**

[88] Aviation fuel which was refined oil was obtained in the same manner as that of Example 1, except that the operation was performed by changing the temperature conditions and the pressure conditions of the first reactor, the second reactor, and the third reactor as shown in Table 1.

[89] **Example 3**

[90] Aviation fuel which was refined oil was obtained in the same manner as that of Example 1, except that a step of hydrofinishing the obtained aviation fuel was further performed.

[91]

[92] **Example 4**

[93] Aviation fuel which was refined oil was obtained in the same manner as that of Example 1, except that the first reactor was operated by changing the reaction temperature and the reaction pressure to 320°C and 70 bar, respectively, in hydrogen gas.

[94] **Comparative Example 1**

[95] Aviation fuel which was refined oil was obtained in the same manner as that of Example 1, except that the reaction was performed by directly introducing the waste plastic pyrolysis oil into the second reactor without the first reactor of the production apparatus.

[96] **Comparative Example 2**

[97] Aviation fuel which was refined oil was obtained in the same manner as that of Example 1, except that the reaction was performed without the third reactor of the production apparatus.

[98] **Comparative Example 3**

[99] Aviation fuel which was refined oil was obtained in the same manner as that of Example 1, except that the reaction was performed without the second reactor of the production apparatus.

[100] **Comparative Example 4**

[101] Aviation fuel which was refined oil was obtained in the same manner as that of Example 1, except that the order of the first reactor and the second reactor of the production apparatus was changed and the reaction was performed by first adding the waste plastic pyrolysis oil into the second reactor.

[102] **Comparative Example 5**

[103] Aviation fuel which was refined oil was obtained in the same manner as that of Example 1, except that the reaction was performed by applying only the 1-D zeolite catalyst without the TiO₂ catalyst in the first reactor of the production apparatus.

[104] **Evaluation Examples**

[105] The freezing point and yield were measured by performing analysis on the aviation fuel which was refined oil according to the JET A-1 standard.

[106] The chlorine and nitrogen contents (ppm) and the olefin content (wt%) were measured by performing ICP and XRF analysis on the aviation fuel which was refined oil.

[107] While continuously producing refined oil, the maximum operating time (operating life) at which deactivation of the catalyst did not occur was measured.

[108] The measured results are shown in Table 1.

[109] (Table 1)

[110]

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
First reactor	Temperature (°C) Pressure (bar)	350 5	370 15	370 15	370 15	370 15	370 15	370 15	370 15
Second reactor	Temperature (°C) Pressure (bar)	230 60	270 80	270 80	270 80	270 80	270 80	270 80	270 80
Third reactor	Temperature (°C) Pressure (bar)	340 60	400 80	400 80	400 80	400 80	400 80	400 80	400 80
Fourth reactor	Temperature (°C) Pressure (bar)	- -	- -	- -	- -	- -	- -	- -	- -
Freezing point (°C)	-47	-46	-48	-48	-48	-48	-48	-48	-48
Yield (%)	82	85	87	87	87	87	87	87	87
Cl (ppm)	1	1	1	1	1	1	1	1	1
N (ppm)	1	1	1	1	1	1	1	1	1
Olefin content (wt%)	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Operating life (day)	> 15	> 16	> 15	> 15	> 15	> 15	> 15	> 15	> 15

[111]

Evaluation

[112]

As for the freezing point and the yield of the obtained aviation fuel, it could be confirmed that, in Examples 1 and 2, as the waste plastic pyrolysis oil was sequentially subjected to the olefin migration reaction by TiO₂ in N₂ gas and the olefin branching reaction by ZSM-48 in the first reactor, the hydrotreating in the second reactor, and the hydrocracking in the third reactor, aviation fuel having a freezing point of -45°C or

lower was finally obtained at a yield of 82% or more. It could be confirmed that, in Example 3, as the temperature of the first reactor was set to -37°C or higher, the reaction was performed by further including hydrofinishing in the fourth reactor, and aviation fuel having a freezing point of -48°C was finally obtained at a yield of 87%.

- [113] On the other hand, in Example 4, as the reaction was performed in hydrogen gas in the first reactor, aviation fuel having a freezing point of -35°C was finally obtained at a yield of 70%. It could be confirmed from this that the freezing point and the yield of the aviation fuel were reduced compared to the reaction performed in N₂ gas in Example 1.
- [114] As for the Cl, N, and olefin contents and the operating life of the obtained aviation fuel, it could be confirmed that, in Examples 1 to 4, as the olefin migration reaction and the olefin branching reaction in the first reactor, the hydrotreating in the second reactor, and the hydrocracking in the third reactor were sequentially performed, all of the Cl, N, and olefin contents which were impurities in the obtained aviation fuel were minimized, and the operating life was 15 days or longer, which showed that the aviation fuel production process was stably performed for a long period of time.
- [115] In Comparative Example 1, the reaction was performed except for the olefin migration reaction and the olefin branching reaction in the first reactor, in Comparative Example 2, the reaction was performed except for the hydrocracking in the third reactor, and it could be confirmed that the freezing point and the yield of the obtained aviation fuel were -25°C or higher and 65% or less, respectively, which were significantly reduced. In addition, it could be confirmed that as the Cl, N, and olefin contents in the aviation fuel obtained in each of Comparative Examples 1 and 2 were 35 to 38 ppm, 117 to 125 ppm, and 5 to 7 wt%, respectively, the quality of the aviation fuel was reduced, and the operating life was also reduced to 7 days or shorter.
- [116] It could be confirmed that, in Comparative Example 3, as the reaction was performed except for the hydrotreating process in the second reactor, the Cl, N, and olefin contents in the obtained aviation fuel were 384 ppm, 754 ppm, and 8 wt%, respectively, which showed that the quality of the aviation fuel was significantly reduced, and the operating life was also significantly reduced to 3 days or shorter.
- [117] It could be confirmed that, in Comparative Example 4, as the order of the first reactor and the second reactor was changed, that is, the hydrotreating process of the waste plastic pyrolysis oil was performed, and then the olefin migration reaction and the olefin branching reaction were performed, the freezing point and the yield of the obtained aviation fuel were -32°C and 55%, respectively, which showed that the reaction order of the present disclosure had a significant effect on production of aviation fuel. In addition, it could be confirmed that as the Cl, N, and olefin contents in the obtained aviation fuel were 24 ppm, 97 ppm, and 3 wt%, respectively, the quality

of the aviation fuel was reduced, and the operating life was also reduced to 9 days or shorter.

[118] It could be confirmed, in Comparative Example 5, as the aviation fuel production process was performed except for the olefin migration reaction in the first reactor, the freezing point and the yield of the obtained aviation fuel were reduced to -25°C and 63%, respectively. In addition, it could be confirmed that as the Cl, N, and olefin contents in the obtained aviation fuel were 26 ppm, 88 ppm, and 3 wt%, respectively, the quality of the aviation fuel was reduced, and the operating life was also reduced to 10 days or shorter.

[119] Although Examples and Comparative Examples have been described, the present invention is not limited to the above Examples, but may be prepared in various different forms, and it will be apparent to those skilled in the art to which the present invention pertains that the Examples may be implemented in other specific forms without departing from the spirit or essential feature of the present invention. Therefore, it is to be understood that the Examples described hereinabove are illustrative rather than being restrictive in all aspects.

Claims

- [Claim 1] A method for producing aviation fuel, comprising:
a first step of subjecting waste plastic pyrolysis oil to an olefin migration reaction;
a second step of subjecting a product obtained in the first step to an olefin branching reaction;
a third step of hydrotreating a product obtained in the second step in the presence of a hydrotreating catalyst; and
a fourth step of hydrocracking a product obtained in the third step in the presence of a hydrocracking catalyst.
- [Claim 2] The method of claim 1, wherein the first step is performed in the presence of a weak acid site catalyst, and the second step is performed in the presence of a catalyst of zeolite having a one-dimensional pore structure.
- [Claim 3] The method of claim 2, wherein the weak acid site catalyst includes a titanium oxide catalyst.
- [Claim 4] The method of claim 2, wherein a weight ratio of the weak acid site catalyst to the catalyst of zeolite having a one-dimensional pore structure is 60:40 to 90:10.
- [Claim 5] The method of claim 1, wherein the hydrotreating catalyst in the third step is a catalyst in which an active metal including one or two or more selected from molybdenum, nickel, cobalt, and tungsten is supported on a support.
- [Claim 6] The method of claim 1, wherein the hydrocracking catalyst in the fourth step is a catalyst in which an active metal including one or two or more selected from molybdenum, nickel, cobalt, and tungsten is supported on zeolite.
- [Claim 7] The method of claim 1, wherein the produced aviation fuel has a freezing point of -45°C or lower and a yield of 75% or more.
- [Claim 8] The method of claim 1, wherein the produced aviation fuel has a chlorine content of 10 ppm or less and a nitrogen content of 10 ppm or less.
- [Claim 9] The method of claim 1, wherein the first step and the second step are performed at a reaction temperature of higher than 300°C .
- [Claim 10] The method of claim 1, wherein the first step and the second step are performed under conditions of a reaction pressure of 5 to 70 bar and a gas/oil ratio (GOR) of 100 to 3,000 in an inert atmosphere.

- [Claim 11] The method of claim 1, wherein the third step is performed under conditions of a reaction temperature of lower than 300°C, a reaction pressure of 100 bar or less, and a gas/oil ratio (GOR) of 100 to 3,000 in hydrogen gas.
- [Claim 12] The method of claim 1, wherein the fourth step is performed under conditions of a reaction temperature of higher than 300°C, a reaction pressure of 100 bar or less, and a gas/oil ratio (GOR) of 100 to 3,000 in hydrogen gas.
- [Claim 13] The method of claim 1, further comprising a fifth step of hydrofinishing a product obtained in the fourth step under conditions of a reaction temperature of higher than 300°C, a reaction pressure of 100 bar or less, and a gas/oil ratio (GOR) of 100 to 3,000 in the presence of a hydrofinishing catalyst.
- [Claim 14] An apparatus for producing aviation fuel, comprising:
a first reactor into which waste plastic pyrolysis oil is introduced and in which an olefin migration reaction and an olefin branching reaction are sequentially performed;
a second reactor into which a reaction product and hydrogen gas are introduced from the first reactor and in which hydrotreating is performed in the presence of a hydrotreating catalyst; and
a third reactor into which a reaction product and hydrogen gas are introduced from the second reactor and in which hydrocracking is performed in the presence of a hydrocracking catalyst.
- [Claim 15] The apparatus of claim 14, wherein the first reactor includes a first zone filled with a weak acid site catalyst, and a second zone filled with a catalyst of zeolite having a one-dimensional pore structure, and the waste plastic pyrolysis oil is refined by sequentially passing through the first zone and the second zone.
- [Claim 16] The apparatus of claim 14, wherein the first reactor to the third reactor are fixed bed reactors.
- [Claim 17] The apparatus of claim 14, further comprising a fourth reactor into which a reaction product and hydrogen gas are introduced from the third reactor and in which hydrofinishing is performed in the presence of a hydrofinishing catalyst.