

Description

Title of Invention: REFINING METHOD OF WASTE PLASTIC PYROLYSIS OIL USING SULFUR SOURCE AND MOLYBDENUM-BASED HYDROGENATION CATALYST, AND CONTINUOUS OPERATION METHOD THEREOF

Technical Field

- [1] The present disclosure relates to a refining method of a waste plastic pyrolysis oil using a sulfur source and a molybdenum-based hydrogenation catalyst, and a continuous operation method thereof.

Background Art

- [2] Waste plastics, which are manufactured using petroleum as a raw material, have a low recyclability and are mostly disposed of as garbage. These forms of wastes are decomposed in their natural state, and since the decomposition takes a long time, they pollute the soil and cause serious environmental pollution. As a method of recycling waste plastics, the waste plastics may be pyrolyzed and converted into usable oil, which is referred to as a waste plastic pyrolysis oil.
- [3] However, since a pyrolysis oil obtained by pyrolyzing waste plastics has a high content of impurities such as chlorine, nitrogen, and metal as compared with oils manufactured from crude oil by a common method, it may not be directly used as a high value-added fuel such as gasoline and diesel oil and should go through a refining process.
- [4] As a refining method for removing impurities such as chlorine, nitrogen, and metal contained in the waste plastic pyrolysis oil, a hydrotreating method by reacting waste plastic pyrolysis oil and hydrogen gas (H_2) in the presence of a hydrotreating catalyst, a method of removing chlorine contained in the waste plastic pyrolysis oil by adsorption using a chlorine adsorbent, and the like, are known.
- [5] In the hydrotreating method, the waste plastic pyrolysis oil has a high content of impurities such as metal so that it affects the catalyst in the hydrotreating process, and thus, the catalytic activity is rapidly decreased, so that the process may not be performed stably for a long time.
- [6] Therefore, a refining technology of a waste plastic pyrolysis oil which improves the catalytic activity in the waste plastic pyrolysis oil hydrotreating process and may operate the process stably for a long time is needed.
- [7] [Related Art Document]
- [8] [Patent Document]

- [9] Japanese Patent Laid-Open Publication No. 2003-034794 (February 7, 2003)

Disclosure of Invention

Technical Problem

- [10] An object of the present disclosure is to provide a refining method of a waste plastic pyrolysis oil, which may produce a refined oil having a significantly reduced content of impurities such as chlorine, nitrogen, oxygen, and metal.
- [11] Another object of the present disclosure is to provide a continuous operation method of waste plastic pyrolysis oil refining equipment, which allows operation of the refining equipment for a long time by continuously supplying sulfur from a sulfur source to maintain the activity of a molybdenum-based sulfide hydrogenation catalyst.

Solution to Problem

- [12] In one general aspect, a refining method of a waste plastic pyrolysis oil includes: (S1) mixing a waste plastic pyrolysis oil and a sulfur source to prepare a mixed oil fraction; (S2) hydrotreating the mixed oil fraction with a reaction gas including a hydrogen gas (H_2) in the presence of a molybdenum-based hydrogenation catalyst; and (S3) removing by-products of the hydrotreating from the product of (S2) to obtain a refined oil.
- [13] In an exemplary embodiment of the present disclosure, the sulfur source may include a sulfur-containing oil fraction.
- [14] In an exemplary embodiment of the present disclosure, the mixed oil fraction may include 100 ppm or more of sulfur.
- [15] In an exemplary embodiment of the present disclosure, the sulfur-containing oil fraction may be included at less than 100 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil.
- [16] In an exemplary embodiment of the present disclosure, the sulfur-containing oil fraction may be included at less than 50 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil.
- [17] In an exemplary embodiment of the present disclosure, the sulfur source may include one or two or more sulfur-containing organic compounds selected from disulfide-based compounds, sulfide-based compounds, sulfonate-based compounds, and sulfate-based compounds.
- [18] In an exemplary embodiment of the present disclosure, the reaction gas of (S2) may further include a hydrogen sulfide gas (H_2S).
- [19] In an exemplary embodiment of the present disclosure, the hydrogen sulfide gas (H_2S) may be separated from the by-products of the hydrotreating which has been removed in (S3) and then supplied again.
- [20] In an exemplary embodiment of the present disclosure, the molybdenum-based hy-

drogenation catalyst may be a catalyst in which a molybdenum-based metal, or a metal including any one or two or more selected from nickel, cobalt, and tungsten and a molybdenum-based metal are supported on a support.

[21] In an exemplary embodiment of the present disclosure, the molybdenum-based hydrogenation catalyst may include a molybdenum-based sulfide hydrogenation catalyst.

[22] In an exemplary embodiment of the present disclosure, (S2) may be performed at a pressure of 200 bar or less.

[23] In an exemplary embodiment of the present disclosure, (S2) may be performed at a temperature of 300°C or higher and lower than 450°C.

[24] In an exemplary embodiment of the present disclosure, (S2) may be performed at a liquid hourly space velocity (LHSV) of 0.1 to 5 h⁻¹.

[25] In another general aspect, a continuous operation method of waste plastic pyrolysis oil refining equipment includes: (S1) mixing a waste plastic pyrolysis oil and a sulfur source to prepare a mixed oil fraction; (S2) hydrotreating the mixed oil fraction with a reaction gas including a hydrogen gas (H₂) and a hydrogen sulfide gas (H₂S) at a pressure of 200 bar or less in the presence of a molybdenum-based sulfide hydrogenation catalyst; and (S3) removing by-products of the hydrotreating from the product of (S2) to obtain a refined oil, wherein the hydrogen sulfide gas (H₂S) of (S2) is separated from the by-products of the hydrotreating of (S3) and supplied again.

[26] In an exemplary embodiment of the present disclosure, the activity of the molybdenum-based sulfide hydrogenation catalyst may be maintained by continuously supplying sulfur from the sulfur source.

[27] In an exemplary embodiment of the present disclosure, the mixed oil fraction may include 100 ppm or more of sulfur. In an exemplary embodiment of the present disclosure, the sulfur source may include a sulfur-containing oil fraction.

[28] In an exemplary embodiment of the present disclosure, the sulfur-containing oil fraction may be included at less than 100 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil.

[29] In an exemplary embodiment of the present disclosure, the sulfur source may include one or two or more sulfur-containing organic compounds selected from disulfide-based compounds, sulfide-based compounds, sulfonate-based compounds, and sulfate-based compounds.

Advantageous Effects of Invention

[30] The refining method of a waste plastic pyrolysis oil according to the present disclosure may produce a refined oil having a significantly low content of impurities such as chlorine, nitrogen, oxygen, and metal.

[31] In addition, the continuous operation method of waste plastic pyrolysis oil refining

equipment according to the present disclosure may continuously operate refining equipment for a long time, by continuously supplying sulfur from a sulfur source to maintain the activity of a molybdenum-based sulfide hydrogenation catalyst.

Brief Description of Drawings

- [32] The above and other objects, features and advantages of the present invention will become apparent from the following description of preferred embodiments given in conjunction with the accompanying drawings, in which:
- [33] FIG. 1 illustrates refining equipment of a waste plastic pyrolysis oil according to the present disclosure including: a mixer where a waste plastic pyrolysis oil and a sulfur-containing oil fraction are introduced and mixed; a reactor where a mixed oil fraction is introduced from the mixer, a reaction gas including a hydrogen gas (H_2) is introduced, and a hydrotreatment is performed in the presence of a molybdenum-based hydrogenation catalyst; and a process of separating by-products of the hydrotreatment and a refined oil from the reactor,
- [34] FIG. 2 illustrates refining equipment of a waste plastic pyrolysis oil which is the same as the refining equipment of a waste plastic pyrolysis oil of FIG. 1, except that a sulfur-containing organic compound is introduced thereto instead of the sulfur-containing oil fraction,
- [35] FIG. 3 illustrates refining equipment of a waste plastic pyrolysis oil which is the same as the refining equipment of a waste plastic pyrolysis oil of FIG. 1, except that the reaction gas further includes a hydrogen sulfide gas (H_2S), and
- [36] FIG. 4 illustrates refining equipment of a waste plastic pyrolysis oil which is the same as the refining equipment of a waste plastic pyrolysis oil of FIG. 3, except that a gas separation unit which separates a hydrogen sulfide gas (H_2S) from by-products and a recirculation line which resupplies the separated hydrogen sulfide gas (H_2S) to the reactor are further included.

Best Mode for Carrying out the Invention

- [37] The drawings illustrated in the present specification are provided by way of example so that the idea of the present disclosure may be sufficiently conveyed to a person skilled in the art. Therefore, the present disclosure is not limited to the provided drawings, but may be embodied in many different forms, and the drawings may be exaggerated in order to clear the spirit of the present invention.
- [38] Technical terms and scientific terms used in the present specification have the general meaning understood by those skilled in the art to which the present invention pertains unless otherwise defined, and a description for the known function and configuration obscuring the gist of the present disclosure will be omitted in the following description and the accompanying drawings.

- [39] The singular form of the term used herein may be intended to also include a plural form, unless otherwise indicated.
- [40] The numerical range used in the present specification includes all values within the range including the lower limit and the upper limit, increments logically derived in a form and span in a defined range, all double limited values, and all possible combinations of the upper limit and the lower limit in the numerical range defined in different forms. Unless otherwise defined in the present specification, values which may be outside a numerical range due to experimental error or rounding of a value are also included in the defined numerical range.
- [41] The term "comprise" mentioned in the present specification is an open-ended description having a meaning equivalent to the term such as "is/are provided", "contain", "have", or "is/are characterized", and does not exclude elements, materials, or processes which are not further listed.
- [42] The unit of % used in the present specification without particular mention refers to % by weight, unless otherwise defined.
- [43] The unit of ppm used in the present specification without particular mention refers to ppm by mass, unless otherwise defined.
- [44] The boiling point used in the present specification refers to a boiling point at 1 atm, unless otherwise defined.
- [45] Since a pyrolysis oil obtained by pyrolyzing waste plastics has a high content of impurities such as chlorine, nitrogen, and metal as compared with oils manufactured from crude oil by a common method, it may not be directly used as a high value-added fuel such as gasoline and diesel oil and should go through a refining process.
- [46] As a refining method for removing impurities such as chlorine, nitrogen, and metal contained in the waste plastic pyrolysis oil, a hydrotreating method by reacting waste plastic pyrolysis oil and hydrogen gas (H₂) in the presence of a hydrotreating catalyst, a method of removing chlorine contained in the waste plastic pyrolysis oil by adsorption using a chlorine adsorbent, and the like, are known.
- [47] In the hydrotreating method, the waste plastic pyrolysis oil has a high content of impurities such as metal so that it affects the catalyst in the hydrotreating process, and thus, the catalytic activity is rapidly decreased, so that the process may not be performed stably for a long time.
- [48] Thus, the refining method of a waste plastic pyrolysis oil according to the present disclosure may use the means described later, thereby producing a refined oil having a significantly low content of impurities such as chlorine, nitrogen, oxygen, and metal, and may continuously operate the refining equipment for a long time by continuously supplying sulfur from a sulfur source to maintain the activity of a molybdenum-based sulfide hydrogenation catalyst.

- [49] The present disclosure provides a refining method of a waste plastic pyrolysis oil including: (S1) mixing a waste plastic pyrolysis oil and a sulfur source to prepare a mixed oil fraction; (S2) hydrotreating the mixed oil fraction with a reaction gas including a hydrogen gas (H_2) in the presence of a molybdenum-based hydrogenation catalyst; and (S3) removing by-products of the hydrotreating from the product of (S2) to obtain a refined oil.
- [50] The waste plastic pyrolysis oil refers to a hydrocarbon oil mixture produced by pyrolysis of waste plastic. Here, the waste plastics may include solid or liquid wastes related to synthetic polymer compounds such as waste synthetic resin, waste synthetic fiber, waste synthetic rubber, and waste vinyl. The hydrocarbon oil mixture may include impurities such as a chlorine compound, a nitrogen compound, and a metal compound, in addition to a hydrocarbon oil, may include impurities present in the form of a compound to which chlorine, nitrogen, or metal is bonded in the hydrocarbon, and may include hydrocarbons in the form of olefin.
- [51] As a specific example, the waste plastic pyrolysis oil may contain 300 ppm or more of nitrogen and 30 ppm or more of chlorine and may contain 20 vol% or more of olefin (1 atm, 25°C) and 1 vol% or more of conjugated diolefin (1 atm, 25°C), but the content of the impurities is only a specific example which may be included in the waste plastic pyrolysis oil and the composition of the waste plastic pyrolysis oil is not limited thereto.
- [52] The sulfur source refers to a sulfur source which may continuously supply a sulfur component during a refining process.
- [53] In (S1), a waste plastic pyrolysis oil and a sulfur source are mixed to prepare a mixed oil fraction, thereby suppressing the deactivation of the molybdenum-based hydrogenation catalyst due to the lack of the sulfur source and operation at a high temperature during the refining process and maintaining catalytic activity.
- [54] In an exemplary embodiment of the present disclosure, the sulfur source may include a sulfur-containing oil fraction. The sulfur-containing oil fraction refers to an oil fraction formed of a hydrocarbon containing sulfur obtained using crude oil as a raw material. The sulfur-containing oil fraction is not particularly limited as long as it is an oil fraction containing sulfur, and may be, for example, light gas oil, straight naphtha, decompression naphtha, pyrolysis naphtha, straight kerosene, decompression kerosene, pyrolysis kerosene, straight diesel, decompression diesel, pyrolysis diesel, a sulfur-containing waste tire oil fraction, and the like, or any mixture thereof.
- [55] According to a specific example, a waste tire oil fraction is included as a sulfur-containing oil fraction to convert a high content of sulfur included in the waste tire into an oil fraction with a hydrocarbon, and thus, may preferably act as the sulfur source of the waste plastic pyrolysis oil. In addition, it is advantageous to divert the waste tire oil

fraction to the sulfur source of the waste plastic pyrolysis oil, in terms of a decrease in an environmental load due to waste tire recycling and the long-term maintenance of the catalytic activity.

- [56] Specifically, the sulfur-containing oil fraction may be a light gas oil (LGO) having a gravity of 0.7 to 1. When used, it may be uniformly mixed with the waste plastic pyrolysis oil and has high hydrotreating efficiency. Specifically, the gravity may be 0.75 to 0.95, and more specifically, 0.8 to 0.9. The sulfur-containing oil fraction may include 100 ppm or more of sulfur. When the sulfur component is included at 100 ppm or less, the content of the sulfur component supplied is small, so that the effect of preventing the deactivation of the molybdenum-based hydrogenation catalyst may be insignificant. Specifically, the sulfur component may be included at 800 ppm or more, more specifically, 8,000 ppm or more, and unlimitedly, at 200,000 ppm or less.
- [57] In an exemplary embodiment of the present disclosure, the mixed oil fraction may include 100 ppm or more of sulfur. Like the sulfur-containing oil fraction, when the sulfur component is included at 100 ppm or less, the content of the sulfur component supplied is small, so that the effect of preventing the deactivation of the molybdenum-based hydrogenation catalyst may be insignificant. Specifically, the sulfur component may be included at 800 ppm or more, more specifically, 8,000 ppm or more, and unlimitedly, at 200,000 ppm or less.
- [58] In an exemplary embodiment of the present disclosure, the sulfur-containing oil fraction may be included at less than 100 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil. Specifically, the sulfur-containing oil fraction may be included at less than 70 parts by weight, more specifically, less than 50 parts by weight, and unlimitedly, at more than 25 parts by weight. Since the sulfur-containing oil fraction is included at less than 100 parts by weight, the concentration of chlorine (Cl) or nitrogen (N) included in the waste plastic pyrolysis oil may be lower to control the production rate of an ammonium salt (NH_4Cl) and improve process stability.
- [59] In an exemplary embodiment of the present disclosure, the sulfur source may include one or two or more sulfur-containing organic compounds selected from disulfide-based compounds, sulfide-based compounds, sulfonate-based compounds, and sulfate-based compounds. Specifically, the sulfur source may include one or a mixture of two or more selected from disulfide, dimethyl disulfide, dimethyl sulfide, polysulfide, dimethyl sulfoxide (DMSO), methyl methanesulfonate, ethyl methanesulfonate, propylsulfonate, propenyl propenesulfonate, propenyl cyanoethansulfonate, ethylene sulfate, bicycloglyoxal sulfate, and methyl sulfate, and these are only presented as an example, and the present disclosure is not limited thereto.
- [60] The sulfur-containing organic compound may be included at 1 to 25 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil. Specifically, it may be

included at 5 to 20 parts by weight, and more specifically, 10 to 15 parts by weight. When it is included at less than 1 part by weight, the content of the sulfur component is small, so that the effect of preventing the deactivation of the molybdenum-based hydrogenation catalyst may be insignificant.

- [61] The step of (S2) hydrotreating the mixed oil fraction with a reaction gas including a hydrogen gas (H_2) in the presence of a molybdenum-based hydrogenation catalyst refers to a hydrogenation reaction of adding a hydrogen gas (H_2) to a hydrocarbon oil fraction included in the mixed oil fraction. Specifically, the hydrotreating may refer to a conventionally known hydrotreatment including a hydrodesulfurization reaction, a hydrocracking reaction, a hydrodechlorination reaction, a hydrodenitrification reaction, and a hydrodemetalation reaction. By the hydrotreatment, a part of impurities including chlorine (Cl) and nitrogen (N) and olefins is removed, other metal impurities may be removed, and by-products including the impurities are produced.
- [62] The by-products are produced by reacting chlorine (Cl), nitrogen (N), sulfur (S), or oxygen (O) which is an impurity included in the waste plastic pyrolysis oil with a hydrogen gas (H_2), and specifically, may include hydrogen sulfide gas (H_2S), hydrogen chloride (HCl), ammonia (NH_3), water vapor (H_2O), and the like, and in addition, may include unreacted hydrogen gas (H_2), a trace amount of methane (CH_4) or ethane (C_2H_6), or the like.
- [63] In an exemplary embodiment of the present disclosure, the molybdenum-based hydrogenation catalyst may be a catalyst in which a molybdenum-based metal, or a metal including any one or two or more selected from nickel, cobalt, and tungsten and a molybdenum-based metal are supported on a support. The molybdenum-based hydrogenation catalyst has a high catalytic activity in the hydrotreating, and may be used alone or in the form of a binary-based catalyst combined with a metal such as nickel, cobalt, and tungsten, if necessary.
- [64] As the support, alumina, silica, silica-alumina, titanium oxide, a molecular sieve, zirconia, aluminum phosphate, carbon, niobia, or a mixture thereof may be used, but is not limited thereto.
- [65] In an exemplary embodiment of the present disclosure, the molybdenum-based hydrogenation catalyst may include a molybdenum-based sulfide hydrogenation catalyst. For example, molybdenum sulfide (MoS) or molybdenum disulfide (MoS_2) may be included, but the present disclosure is not limited thereto, and a known molybdenum-based sulfide hydrogenation catalyst may be included.
- [66] In an exemplary embodiment of the present disclosure, the reaction gas may further include a hydrogen sulfide gas (H_2S). The hydrogen sulfide gas (H_2S) included in the reaction gas may act as a sulfur source and regenerate the activity of the molybdenum-based hydrogenation catalyst deactivated during the refining process with the sulfur

source mixed with the waste plastic pyrolysis oil.

- [67] The step of (S3) removing by-products of the hydrotreating from the product of (S2) to obtain a refined oil may finally obtain a high-quality refined oil having reduced impurities from the mixed oil fraction.
- [68] As described above, the by-products are produced by reacting chlorine (Cl), nitrogen (N), sulfur (S), or oxygen (O) which is an impurity included in the waste plastic pyrolysis oil with a hydrogen gas (H_2), and specifically, may include hydrogen sulfide gas (H_2S), hydrogen chloride (HCl), ammonia (NH_3), water vapor (H_2O), and the like, and in addition, may include unreacted hydrogen gas (H_2), a trace amount of methane (CH_4) or ethane (C_2H_6), or the like.
- [69] As a method of removing the by-products, for example, the by-products may be removed from the product of (S2) by a method of exhausting a mixed gas, which is only described as an example of the method, and the present disclosure is not limited thereto. By the method, a high-quality refined oil having reduced impurities may be finally obtained from the mixed oil fraction.
- [70] In an exemplary embodiment of the present disclosure, the hydrogen sulfide gas (H_2S) may be separated from the by-products of the hydrotreating which has been removed in (S3) and then supplied again. Specifically, regarding the hydrogen sulfide gas (H_2S) included in the reaction gas of (S2), a hydrogen sulfide gas (H_2S) is separated by an adsorption removal step from the by-products of hydrotreating removed in (S3) and then supplied again to use it as the hydrogen sulfide gas (H_2S) of (S2). In the adsorption removal step, a hydrogen sulfide gas (H_2S) may be separated from the by-products using, for example, an adsorbent such as zeolite, carbon, and alumina, and also, a hydrogen gas (H_2) may also be separated.
- [71] In an exemplary embodiment of the present disclosure, the hydrotreating of (S2) may be performed at a pressure of 200 bar or less. When it is performed at a pressure of 200 bar or less, production of a NH_4Cl impurity may be suppressed to suppress a differential pressure increase rate in the reactor and improve reaction stability. Specifically, it may be performed at a pressure of 150 bar or less, more specifically, 100 bar or less, and unlimitedly, at a pressure of 60 bar or more.
- [72] In an exemplary embodiment of the present disclosure, the hydrotreating of (S2) may be performed at a temperature of 300°C or higher and lower than 450°C. When the range is satisfied, hydrotreating efficiency may be improved. Specifically, it may be performed at a temperature of 320 to 430°C, more specifically, 350 to 400°C.
- [73] In an exemplary embodiment of the present disclosure, the hydrotreating of (S2) may be performed at a liquid hourly space velocity (LHSV) of 0.1 to 5 h^{-1} . When LHSV satisfies the range, a refined oil from which impurities such as chlorine, nitrogen, or metal are removed may be more stably obtained. Specifically, it may be performed at

LHSV of 0.3 to 3 h⁻¹, more specifically, 0.5 to 1.5 h⁻¹.

- [74] In an exemplary embodiment of the present disclosure, the refined oil obtained by the refining method of a waste plastic pyrolysis oil may include less than 10 ppm of chlorine (Cl), less than 100 ppm of nitrogen (N), and less than 50 ppm of sulfur (S). In addition, the obtained refined oil may include less than 3 wt% of olefins and 0.5 wt% or less of conjugated diolefins.
- [75] The refining method of a waste plastic pyrolysis oil described above may be performed by pyrolysis oil refining equipment.
- [76] The pyrolysis oil refining equipment may include a mixer where a waste plastic pyrolysis oil and a sulfur source are introduced and mixed to prepare a mixed oil fraction; and a reactor where the mixed oil fraction is introduced from the mixer, a reaction gas including a hydrogen gas (H₂) is introduced, and a hydrotreatment is performed in the presence of a molybdenum-based hydrogenation catalyst. In addition, the configuration of the refining equipment is not necessarily limited thereto, and the refining equipment may be configured by including or changing other conventional known configurations.
- [77] The mixer may include a common mixer for uniform mixing. A pyrolysis oil and a sulfur source are introduced to the mixer and are stirred to prepare a uniform mixed oil fraction.
- [78] The reactor may include a reaction area in which the molybdenum-based hydrogenation catalyst is provided. In the reaction area, a dechlorination, denitrification, desulfurization, or demetallization reaction may be performed. The mixed oil fraction is introduced to the reactor and hydrotreated in the presence of a hydrotreating catalyst, and a reaction of removing a part of olefin and metal impurities may be performed together.
- [79] The reactor is provided with a gas outlet, and by-products of the hydrotreating may be discharged to the gas outlet.
- [80] In addition, the refining equipment may further include a gas separation unit where the by-products are introduced and a hydrogen sulfide gas (H₂S) is separated from the by-products of hydrotreating; and a recirculation line where the hydrogen sulfide gas (H₂S) separated from the gas separation unit is supplied to the reactor again. The gas separation unit may include an adsorbent, and separate the hydrogen sulfide gas (H₂S) from the by-products with the adsorbent. Other than that, unreacted hydrogen gas (H₂) may also be separated.
- [81] As shown in FIG. 4, the hydrogen sulfide gas (H₂S) separated from the gas separation unit may be supplied to the reactor again through the recirculation line. Other than that, unreacted hydrogen gas (H₂) may also be supplied to the reactor again through the recirculation line. Though not shown in FIG. 4, the recirculation line where the hydrogen

sulfide gas (H_2S) and hydrogen gas (H_2) are recirculated may further include a washing unit where washing with water is performed. By further including the washing unit, impurities remaining in the hydrogen sulfide gas (H_2S) and hydrogen gas (H_2), for example, hydrogen chloride (HCl) and ammonia (NH_3), are dissolved in water and removed, so that high-purity hydrogen sulfide gas (H_2S) and hydrogen gas (H_2) may be supplied to the reactor again.

- [82] In addition, the present disclosure provides a continuous operation method of waste plastic pyrolysis oil refining equipment including: (S1) mixing a waste plastic pyrolysis oil and a sulfur source to prepare a mixed oil fraction; (S2) hydrotreating the mixed oil fraction with a reaction gas including a hydrogen gas (H_2) and a hydrogen sulfide gas (H_2S) at a pressure of 200 bar or less in the presence of a molybdenum-based sulfide hydrogenation catalyst; and (S3) removing by-products of the hydrotreating from the product of (S2) to obtain a refined oil, wherein the hydrogen sulfide gas (H_2S) of (S2) is separated from the by-products of the hydrotreating of (S3) and supplied again.
- [83] The hydrotreating may be performed at a pressure of 200 bar or less. When it is performed at a pressure of 200 bar or less, production of a NH_4Cl impurity may be suppressed to suppress a differential pressure increase rate in the reactor and improve reaction stability. Specifically, it may be performed at a pressure of 150 bar or less, more specifically, 100 bar or less, and unlimitedly, at a pressure of 60 bar or more.
- [84] The hydrogen sulfide gas (H_2S) included in the reaction gas may act as a sulfur source and regenerate the activity of the molybdenum-based hydrogenation catalyst deactivated during the reaction process with the sulfur source mixed with the waste plastic pyrolysis oil.
- [85] The hydrogen sulfide gas (H_2S) may be separated from the by-products of the hydrotreating which has been removed in (S3) and then supplied again. Specifically, regarding the hydrogen sulfide gas (H_2S) included in the reaction gas of (S2), a hydrogen sulfide gas (H_2S) is separated by an adsorption removal step from the by-products of hydrotreating removed in (S3) and then supplied again to use it as the hydrogen sulfide gas (H_2S) of (S2). The amount of used hydrogen sulfide gas (H_2S) which is separately input may be reduced to improve process efficiency, and the cost of disposing the by-products of the hydrogenation reaction may be reduced to improve economic feasibility.
- [86] In an exemplary embodiment of the present disclosure, the activity of the molybdenum-based sulfide hydrogenation catalyst may be maintained by continuously supplying sulfur from the sulfur source. The sulfur source acts as a sulfur source which continuously supplies the sulfur component during the refining process, and may suppress the deactivation of the molybdenum-based sulfide hydrogenation catalyst and

regenerate the catalytic activity. As the catalytic activity is regenerated, the waste plastic pyrolysis oil refining equipment may be operated stably and continuously for a long time.

- [87] In an exemplary embodiment of the present disclosure, the mixed oil fraction may include 100 ppm or more of sulfur. When the sulfur component is included at 100 ppm or less, the content of the sulfur component supplied is small, so that the effect of preventing the deactivation of the molybdenum-based hydrogenation catalyst may be insignificant. Specifically, the sulfur component may be included at 800 ppm or more, more specifically, 8,000 ppm or more, and unlimitedly, at 200,000 ppm or less.
- [88] In an exemplary embodiment of the present disclosure, the sulfur source may include a sulfur-containing oil fraction. The sulfur-containing oil fraction refers to an oil fraction formed of a hydrocarbon containing sulfur obtained using crude oil as a raw material. The sulfur-containing oil fraction is not particularly limited as long as it is an oil fraction containing sulfur, and may be, for example, light gas oil, straight naphtha, decompression naphtha, pyrolysis naphtha, straight kerosene, decompression kerosene, pyrolysis kerosene, straight diesel, decompression diesel, pyrolysis diesel, a sulfur-containing waste tire oil fraction, and the like, or any mixture thereof.
- [89] In an exemplary embodiment of the present disclosure, the sulfur-containing oil fraction may be included at less than 100 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil. Specifically, the sulfur-containing oil fraction may be included at less than 70 parts by weight, more specifically, less than 50 parts by weight, and unlimitedly, at more than 25 parts by weight. Since the sulfur-containing oil fraction is included at less than 100 parts by weight, a nitrogen (N) impurity may be efficiently removed even when the hydrotreating is performed at a low pressure of 100 bar or less. When the sulfur-containing oil fraction is included at more than 100 parts by weight, the nitrogen (N) impurity removal efficiency is lowered in the hydrotreating at a low pressure of 100 bar or less. In addition, when the hydrotreating is performed at a high pressure of 100 bar or more for removing impurities, a NH_4Cl production rate is increased to deteriorate reaction stability.
- [90] In an exemplary embodiment of the present disclosure, the sulfur source may include one or two or more sulfur-containing organic compounds selected from disulfide-based compounds, sulfide-based compounds, sulfonate-based compounds, and sulfate-based compounds. Specifically, the sulfur source may include one or a mixture of two or more selected from dimethyl disulfide, dimethyl sulfide, polysulfide, dimethyl sulfoxide (DMSO), methyl methanesulfonate, ethyl methanesulfonate, propylsulfonate, propenyl propenesulfonate, propenyl cyanoethansulfonate, ethylene sulfate, bicycloglyoxal sulfate, and methyl sulfate, and is not limited thereto.
- [91] The sulfur-containing organic compound may be included at 1 to 25 parts by weight

based on 100 parts by weight of the waste plastic pyrolysis oil. Specifically, it may be included at 5 to 20 parts by weight, and more specifically, 10 to 15 parts by weight. When it is included at less than 1 part by weight, the content of the sulfur component is small, so that the effect of preventing the deactivation of the molybdenum-based hydrogenation catalyst may be insignificant.

[92] For the matters which are not further described for the continuous operation method of waste plastic pyrolysis oil refining equipment, see the descriptions for the refining method of a waste plastic pyrolysis oil described above.

[93] Hereinafter, the present disclosure will be described in detail by the examples, however, the examples are for describing the present disclosure in more detail, and the right scope is not limited to the following examples.

[94] **Example 1**

[95] A light gas oil (R-LGO) having a specific gravity of 0.85851 containing 20,000 ppm of a sulfur-containing oil fraction, specifically, sulfur as a sulfur source was used.

[96] A hydrocarbon oil mixture containing a high concentration of impurities of 200 ppm or more of nitrogen (N), 30 ppm or more of chlorine (Cl), 20 vol% or more of olefin, and 1 vol% or more of conjugated diolefin was used as a waste plastic pyrolysis oil.

[97] 70 parts by weight of the sulfur-containing oil fraction with respect to 100 parts by weight of the waste plastic pyrolysis oil was put into a mixer to prepare a mixed oil fraction. The mixed oil fraction prepared from the mixer was put into a reactor, a reaction gas including a hydrogen gas (H_2) was put into the reactor, and the reactor was operated for hydrotreating. Specifically, the mixed oil fraction was put into the reactor, and then was hydrotreated with the reaction gas including a hydrogen gas (H_2) under the conditions of 350°C and 60 bar in the presence of a NiMoS/ γ - Al_2O_3 hydrotreating catalyst. By-products were produced by the hydrotreatment, and the by-products included a hydrogen sulfide gas (H_2S), hydrogen chloride (HCl), ammonia (NH_3), water vapor (H_2O), and a trace amount of methane (CH_4) and ethane (C_2H_6). The by-products were discharged to a gas outlet of the reactor, and a high-quality refined oil from which impurities had been removed was finally obtained from the reactor.

[98] **Example 2**

[99] The hydrotreatment was performed under the same conditions as in Example 1, except that it was performed under the condition of 380°C in the presence of a hydrotreating catalyst. In addition, the by-products in the fluid removed from the reactor was put into the gas separation unit. A hydrogen sulfide gas (H_2S) and a hydrogen gas (H_2) were separated from the by-products by a zeolite adsorbent in the gas separation unit. The reaction was performed under the same conditions as in Example 1, except that the hydrogen sulfide gas (H_2S) and the hydrogen gas (H_2) separated above were supplied to the reactor again through a recirculation line to be included in the reaction

gas and were used, thereby finally obtaining a refined oil from which impurities had been removed.

[100] **Example 3**

[101] A refined oil from which impurities had been removed was finally obtained by performing the reaction under the same conditions as in Example 1, except that 50 parts by weight of the sulfur-containing oil fraction with respect to 100 parts by weight of the waste plastic pyrolysis oil was put into the mixer.

[102] **Example 4**

[103] A refined oil from which impurities had been removed was finally obtained by performing the reaction under the same conditions as in Example 1, except that the hydrotreatment was performed under the conditions of 320°C and 90 bar in the presence of a hydrotreating catalyst.

[104] **Example 5**

[105] A high-quality refined oil from which impurities had been removed was finally obtained by performing the reaction under the same conditions as in Example 1, except that a sulfur-containing oil fraction containing 50,000 ppm of sulfur was used as the sulfur source.

[106] **Example 6**

[107] A high-quality refined oil from which impurities had been removed was finally obtained by performing the reaction under the same conditions as in Example 1, except that a sulfur-containing oil fraction containing 2,000 ppm of sulfur was used as the sulfur source.

[108] **Example 7**

[109] A high-quality refined oil from which impurities had been removed was finally obtained by performing the reaction under the same conditions as in Example 2, except that a sulfur-containing oil fraction containing 2,000 ppm of sulfur was used.

[110] **Example 8**

[111] A high-quality refined oil from which impurities had been removed was finally obtained by performing the reaction under the same conditions as in Example 3, except that a sulfur-containing oil fraction containing 2,000 ppm of sulfur was used.

[112] **Example 9**

[113] A high-quality refined oil from which impurities had been removed was finally obtained by performing the reaction under the same conditions as in Example 5, except that a sulfur-containing oil fraction containing 5,000 ppm of sulfur was used.

[114] **Comparative Example 1**

[115] A refined oil from which impurities had been removed was finally obtained by performing the reaction under the same conditions as in Example 1, except that only the waste plastic pyrolysis oil was used.

[116] **Comparative Example 2**

[117] A high-quality refined oil from which impurities had been removed was finally obtained by performing the reaction under the same conditions as in Example 1, except that a sulfur-containing oil fraction containing 50 ppm of sulfur was used as the sulfur source.

[118] **Evaluation Example**

[119] **Measurement method**

[120] A chlorine (Cl) content (ppm) in the finally obtained refined oil was measured by ICP and XRF analysis methods and shown.

[121] Total nitrogen % sulfur (TNS element) analysis was performed for the refined oil, and catalytic activity maintenance time was measured in hours based on the time when a nitrogen content in the refined oil exceeded 10 ppm and shown.

[122] The measurement results are shown in the following Table 1.

[123] [Table 1]

	Exa mple 1	Exam ple 2	Exa mple 3	Exa mple 4	Exa mple 5	Exa mpl e 6	Exa mpl e 7	Exa mple 8	Exa mpl e 9	Compar ative Exempl e 1	Com parat ive Exa mple 2
Waste plastic pyrolysis oil (parts by weight)	100	100	100	100	100	100	100	100	100	100	100
Sulfur-containi ng oil fraction (parts by weight)	70	70	50	70	70	70	70	50	70	0	100
Sulfur content in mixed oil fraction (ppm)	8241	8241	6673	8241	2059 4	829	829	673	206 4	10	30
Hydrot reatme nt	Reaction gas compos ition	H ₂	H ₂ + H ₂ S	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂
	Reaction tem- perature (°C)	350	380	350	320	350	350	380	350	350	350
	Pressur e (bar)	60	60	60	90	60	60	60	60	60	60
		Results									
Cl (ppm)	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Catalytic activity maintenance time	1440	1560	1152	1200	1560	720	780	576	936	295	300

- [124] Referring to Table 1,
- [125] it may be confirmed that in Examples 1 to 5, the catalytic activity maintenance time was all 1100 hours or more, and thus, high catalytic activity was maintained for a long time, and in Examples 6 to 9 also, the catalytic activity maintenance time was also as long as 500 hours or more. In particular, in Example 2, it was confirmed that the catalytic activity maintenance time was as high as 1560 hours, and the main reason is considered as being that 100 parts by weight of the waste plastic pyrolysis oil and 70 parts by weight of the sulfur-containing oil fraction containing 20,000 ppm of sulfur were used, and $H_2 + H_2S$ was used as the reaction gas. In particular, in Example 5 also, it was confirmed that the catalytic activity maintenance time was as high as 1560 hours, and the main reason is considered as being that 100 parts by weight of the waste plastic pyrolysis oil and 70 parts by weight of the sulfur-containing oil fraction containing 50,000 ppm of sulfur were used.
- [126] However, when the hydrotreatment was performed under the same conditions as in Example 1, except using only the waste plastic pyrolysis oil in Comparative Example 1, it was confirmed that the catalytic activity maintenance time was as significantly short as 295 hours, and also, when the sulfur-containing oil fraction containing 50 ppm of sulfur was used in Comparative Example 2 also, it was confirmed that the catalytic activity was decreased due to the lack of a sulfur source, so that the catalytic activity maintenance time was as significantly short as 300 hours.
- [127] Although the exemplary embodiments of the present invention have been described above, the present invention is not limited to the exemplary embodiments but may be made in various forms different from each other, and those skilled in the art will understand that the present invention may be implemented in other specific forms without departing from the spirit or essential feature of the present invention. Therefore, it should be understood that the exemplary embodiments described above are not restrictive, but illustrative in all aspects.

Claims

- [Claim 1] A refining method of a waste plastic pyrolysis oil, the method comprising:
(S1) mixing a waste plastic pyrolysis oil and a sulfur source to prepare a mixed oil fraction;
(S2) hydrotreating the mixed oil fraction with a reaction gas including a hydrogen gas (H_2) in the presence of a molybdenum-based hydrogenation catalyst; and
(S3) removing by-products of the hydrotreating from a product of (S2) to obtain a refined oil.
- [Claim 2] The refining method of a waste plastic pyrolysis oil of claim 1, wherein the sulfur source includes a sulfur-containing oil fraction.
- [Claim 3] The refining method of a waste plastic pyrolysis oil of claim 1, wherein the mixed oil fraction includes 100 ppm or more of sulfur.
- [Claim 4] The refining method of a waste plastic pyrolysis oil of claim 2, wherein the sulfur-containing oil fraction is included at less than 100 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil.
- [Claim 5] The refining method of a waste plastic pyrolysis oil of claim 2, wherein the sulfur-containing oil fraction is included at less than 50 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil.
- [Claim 6] The refining method of a waste plastic pyrolysis oil of claim 1, wherein the sulfur source includes one or two or more sulfur-containing organic compounds selected from disulfide-based compounds, sulfide-based compounds, sulfonate-based compounds, and sulfate-based compounds.
- [Claim 7] The refining method of a waste plastic pyrolysis oil of claim 1, wherein the reaction gas of (S2) includes a hydrogen sulfide gas (H_2S).
- [Claim 8] The refining method of a waste plastic pyrolysis oil of claim 7, wherein the hydrogen sulfide gas (H_2S) is separated from the by-products of the hydrotreating which has been removed in (S3) and then supplied again.
- [Claim 9] The refining method of a waste plastic pyrolysis oil of claim 1, wherein the molybdenum-based hydrogenation catalyst is a catalyst in which a molybdenum-based metal, or a metal including any one or two or more selected from nickel, cobalt, and tungsten and a molybdenum-based metal are supported on a support.
- [Claim 10] The refining method of a waste plastic pyrolysis oil of claim 1, wherein the molybdenum-based hydrogenation catalyst includes a

- molybdenum-based sulfide hydrogenation catalyst.
- [Claim 11] The refining method of a waste plastic pyrolysis oil of claim 1, wherein (S2) is performed at a pressure of 200 bar or less.
- [Claim 12] The refining method of a waste plastic pyrolysis oil of claim 1, wherein (S2) is performed at a temperature of 300°C or higher and lower than 450°C.
- [Claim 13] The refining method of a waste plastic pyrolysis oil of claim 1, wherein (S2) is performed at a liquid hourly space velocity (LHSV) of 0.1 to 5 h⁻¹.
- [Claim 14] A continuous operation method of waste plastic pyrolysis oil refining equipment, the method comprising:
(S1) mixing a waste plastic pyrolysis oil and a sulfur source to prepare a mixed oil fraction;
(S2) hydrotreating the mixed oil fraction with a reaction gas including a hydrogen gas (H₂) and a hydrogen sulfide gas (H₂S) at a pressure of 200 bar or less in the presence of a molybdenum-based sulfide hydrogenation catalyst; and
(S3) removing by-products of the hydrotreating from a product of (S2) to obtain a refined oil,
wherein the hydrogen sulfide gas (H₂S) of (S2) is separated from the by-products of the hydrotreating of (S3) and supplied again.
- [Claim 15] The continuous operation method of waste plastic pyrolysis oil refining equipment of claim 14, wherein sulfur is continuously supplied from the sulfur source to maintain an activity of the molybdenum-based sulfide hydrogenation catalyst.
- [Claim 16] The continuous operation method of waste plastic pyrolysis oil refining equipment of claim 14, wherein the mixed oil fraction includes 100 ppm or more of sulfur.
- [Claim 17] The continuous operation method of waste plastic pyrolysis oil refining equipment of claim 14, wherein the sulfur source includes a sulfur-containing oil fraction.
- [Claim 18] The continuous operation method of waste plastic pyrolysis oil refining equipment of claim 17, wherein the sulfur-containing oil fraction is included at less than 100 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil.
- [Claim 19] The continuous operation method of waste plastic pyrolysis oil refining equipment of claim 14, wherein the sulfur source includes one or two or more sulfur-containing organic compounds selected from disulfide-

based compounds, sulfide-based compounds, sulfonate-based compounds, and sulfate-based compounds.