

Description

Title of Invention: METHOD OF TREATING PYROLYSIS OIL FROM WASTE PLASTICS

Technical Field

- [1] The present disclosure relates to a method of treating 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 take a long time to degrade in nature, causing contamination of the soil and serious environmental pollution. As a method for recycling waste plastics, waste plastics may be pyrolyzed and converted into usable oil, which is called waste plastic pyrolysis oil.
- [3] However, pyrolysis oil obtained by pyrolyzing waste plastics 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 by a general method.
- [4] A refinery process such as hydrotreating has been performed to remove the impurities. However, the waste plastic pyrolysis oil contains water, chlorine, and nitrogen, which causes problems such as equipment corrosion, a reduction in the activity of a catalyst, and deterioration of properties of a product during hydrotreating. In addition, ammonia and hydrogen chloride formed during hydrotreating react with each other to produce an ammonium chloride salt (NH_4Cl), and the ammonium chloride salt causes corrosion of a subsequent Equipment, which causes a reduction in durability and a lot of process problems such as a reduction in process efficiency due to occurrence of a differential pressure. In addition, waste plastic pyrolysis oil has a high content of impurities such as metals, which affects the catalyst in the hydrotreating process, and accordingly, the activity of the catalyst is rapidly reduced, and thus the process may not be stably performed for a long period of time.
- [5] Therefore, there is a demand for a process of treating waste plastic pyrolysis oil by which high-quality high-value-added fuel with minimized impurities may be stably obtained for a long period of time from a waste plastic pyrolysis oil raw material containing impurities without process trouble issues.

Disclosure of Invention

Technical Problem

- [6] An object of the present disclosure is to provide a method of treating waste plastic pyrolysis oil that may implement a stable operation for a long period of time without a reduction in the activity of a hydrotreating catalyst.

- [7] Another object of the present disclosure is to provide a method of treating waste plastic pyrolysis oil that may implement a stable operation for a long period of time by suppressing or minimizing formation of an ammonium chloride salt (NH_4Cl) throughout a process of treating waste plastic pyrolysis oil.
- [8] Still another object of the present disclosure is to provide a method of treating waste plastic pyrolysis oil by which high-quality high-value-added fuel having a significantly reduced content of impurities such as chlorine, nitrogen, oxygen, and metals may be obtained.

Solution to Problem

- [9] In one general aspect, a method of treating waste plastic pyrolysis oil includes: a first step of washing waste plastic pyrolysis oil with water and then removing moisture; a second step of mixing the waste plastic pyrolysis oil from which the moisture is removed and a sulfur source to prepare a mixed oil; a third step of hydrotreating the mixed oil with hydrogen gas in the presence of a hydrotreating catalyst; a fourth step of separating the hydrotreated mixed oil into a liquid stream and a gas stream to obtain liquid pyrolysis oil; and a fifth step of recovering hydrogen gas from the separated gas stream and recycling the recovered hydrogen gas to the third step.
- [10] In an embodiment, the waste plastic pyrolysis oil that is subjected to the first step may contain moisture in an amount of 300 to 2,000 ppm.
- [11] In an embodiment, the sulfur source in the second step may contain sulfur-containing oil.
- [12] In an embodiment, the sulfur source in the second step may be contained in an amount of less than 50 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil.
- [13] In an embodiment, the mixed oil in the second step may contain sulfur in an amount of 100 ppm or more.
- [14] In an embodiment, the third step may include a 3-1st step of hydrotreating the mixed oil at a first temperature in the presence of a hydrotreating catalyst to produce a fluid from which olefin, nitrogen, chlorine is removed; and a 3-2nd step of hydrotreating the fluid at a second temperature higher than the first temperature in the presence of a hydrotreating catalyst to produce refined oil from which impurities are removed.
- [15] In an embodiment, the first reaction temperature may be higher than 100°C and lower than 400°C , and the second reaction temperature may be higher than 300°C and lower than 450°C .
- [16] In an embodiment, a reaction pressure in the hydrotreating in each of the 3-1st step and the 3-2nd step may be more than 10 bar and less than 200 bar.
- [17] In an embodiment, liquid hourly space velocities (LHSVs) in the hydrotreating in the

3-1st step and the hydrotreating in the 3-2nd step may be 1:0.1 to 1:2.0.

- [18] In an embodiment, in the fourth step, the hydrotreated mixed oil may be introduced into a high-temperature and high-pressure separator to separate the hydrotreated mixed oil into a liquid stream and a gas stream.
- [19] In an embodiment, the gas stream separated in the high-temperature and high-pressure separator may be sequentially introduced into a low-temperature and high-pressure separator and a low-temperature and low-pressure separator, and the liquid stream separated in the high-temperature and high-pressure separator may be introduced into a high-temperature and low-pressure separator.
- [20] In an embodiment, the gas stream separated in the high-temperature and high-pressure separator may be washed with water to suppress formation of a salt.
- [21] In an embodiment, the method may further include a step of performing distillation on the liquid pyrolysis oil separated in the fourth step, and in the distillation step, formation of a salt may be suppressed using a salt remover.
- [22] In an embodiment, in the fifth step, the recovered hydrogen gas may be purified to remove impurities, and then the hydrogen gas from which the impurities are removed may be recycled to the third step.

Advantageous Effects of Invention

- [23] As set forth above, the method of treating waste plastic pyrolysis oil according to the present disclosure may implement a stable operation for a long period of time without a reduction in the activity of a hydrotreating catalyst.
- [24] The method of treating waste plastic pyrolysis oil according to the present disclosure may implement a stable operation for a long period of time by suppressing or minimizing formation of an ammonium chloride salt (NH_4Cl) throughout a process.
- [25] In the method of treating waste plastic pyrolysis oil according to the present disclosure, high-quality high-value-added fuel having a significantly reduced content of impurities such as chlorine, nitrogen, oxygen, and metals may be obtained.
- [26] In the method of treating waste plastic pyrolysis oil according to the present disclosure, hydrogen gas is recovered from the separated waste gas and the recovered hydrogen gas is reused, such that cost-effectiveness may be improved.

Best Mode for Carrying out the Invention

- [27] 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.
- [28] A numerical range used in the present specification includes upper and lower limits and all values within these limits, 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.

- [29] 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.
- [30] Unless otherwise defined, a unit of "%" used in the present specification unless specifically mentioned refers to "wt%"
- [31] Unless otherwise defined, a unit of "ppm" used in the present specification unless specifically mentioned refers to "wtppm"
- [32] The present disclosure provides a method of treating waste plastic pyrolysis oil, the method including: a first step of washing waste plastic pyrolysis oil with water and then removing moisture; a second step of mixing the waste plastic pyrolysis oil from which the moisture is removed and a sulfur source to prepare a mixed oil; a third step of hydrotreating the mixed oil with hydrogen gas in the presence of a hydrotreating catalyst; a fourth step of separating the hydrotreated mixed oil into a liquid stream and a gas stream to obtain liquid pyrolysis oil; and a fifth step of recovering hydrogen gas from the separated gas stream and recycling the recovered hydrogen gas to the third step. Through this, it is possible to obtain high-quality high-value-added fuel with minimized impurities stably for a long period of time from a waste plastic pyrolysis oil raw material without process trouble issues.
- [33] The waste plastic pyrolysis oil may be a mixture of hydrocarbon oils produced by pyrolyzing waste plastics at a high temperature. In this case, the waste plastics may include solid or liquid waste related to synthetic polymer compounds such as a waste synthetic resin, a waste synthetic fiber, waste synthetic rubber, and waste vinyl. The waste plastics may be household waste plastics or industrial or agricultural waste plastics.
- [34] The waste plastic pyrolysis oil may contain impurities such as a chlorine compound, a nitrogen compound, and a metal compound in addition to the hydrocarbon oil, and may contain an excessive amount of moisture. Both organic chlorine and inorganic chlorine may be present in the chlorine compound.
- [35] A content of the chlorine compound in the waste plastic pyrolysis oil may be 50 ppm or more, and specifically, may be 300 ppm or more. An upper limit of the content of the chlorine compound is not particularly limited, and may be, for example, 3,000 ppm or less, and specifically, 1,500 ppm or less.
- [36] The waste plastic pyrolysis oil may contain an excessive amount of moisture. Since waste plastics are usually collected or discarded in a state of containing moisture, pyrolysis oil produced from the waste plastics contains an excessive amount of

moisture. A content of the moisture contained in the waste plastic pyrolysis oil may be 300 ppm or more, and specifically, 500 ppm or more. An upper limit of the content of the moisture is not particularly limited, and for example, may be 3,000 ppm or less.

- [37] As a specific example, the waste plastic pyrolysis oil may contain 500 ppm or more of nitrogen, 100 ppm of chlorine, and 2,000 ppm or more of moisture, or may contain 20 vol% or more (based on 1 atm and 25°C) of olefins and 1 vol% or more (based on 1 atm and 25°C) of conjugated diolefins, but a content of the impurities is merely a specific example that may be included in the waste plastic pyrolysis oil, and a composition of the waste plastic pyrolysis oil is not limited thereto.
- [38] The excessive amount of moisture and the impurities such as chlorine and nitrogen contained in the waste plastic pyrolysis oil may cause deactivation of the catalyst in a hydrogenation process or may cause problems such as equipment corrosion. Accordingly, the first step of washing the waste plastic pyrolysis oil with water and then removing the moisture is performed to simultaneously remove impurities and moisture contained in the pyrolysis oil, such that process stability and quality improvement of refined oil may be promoted.
- [39] Specifically, in the first step, washing water is supplied to the waste plastic pyrolysis oil and the waste plastic pyrolysis oil is washed with water to discharge an aqueous solution containing chlorine and nitrogen, such that impurities including chlorine in the waste plastic pyrolysis oil may be removed. Moisture remaining in the waste plastic pyrolysis oil may be removed by performing a drying dehydration process such as hot air drying or by an oil-water separation, centrifugal separation, or distillation method.
- [40] The first step may be performed at 30 to 250°C and 2 to 50 bar. The first step may be performed in an inert atmosphere, for example, a nitrogen atmosphere, and in a case where a water treatment process is performed under the above conditions, impurity removal efficiency may be improved.
- [41] In an embodiment, the waste plastic pyrolysis oil that is subjected to the first step may contain moisture in an amount of 300 to 2,000 ppm. Moisture present in the waste plastic pyrolysis oil may be effectively reduced through the first step.
- [42] The waste plastic pyrolysis oil and the sulfur source are mixed to prepare the mixed oil in the second step, such that deactivation of the hydrotreating catalyst due to an insufficient sulfur source and a high-temperature operation during the reaction and the separation and refinery processes may be suppressed, and the activity of the catalyst may be maintained. The sulfur source refers to a sulfur source capable of continuously supplying a sulfur component during the refinery process.
- [43] In this case, the hydrotreating catalyst may refer to a commonly used hydrotreating catalyst, but as described below, the hydrotreating catalyst may refer to a molybdenum-based hydrotreating catalyst, and specifically, a molybdenum-based

sulfide hydrotreating catalyst, in terms of improving the activity of the catalyst by the sulfur source.

- [44] In an embodiment, the sulfur source may contain sulfur-containing oil. The sulfur-containing oil refers to oil composed of hydrocarbons containing sulfur obtained from crude oil as a raw material. The sulfur-containing oil is not particularly limited as long as it is an oil containing sulfur, and the sulfur-containing oil may be, for example, light gas oil, straight-run naphtha, vacuum naphtha, pyrolysis naphtha, straight-run kerosene, vacuum kerosene, pyrolysis kerosene, straight-run gas oil, vacuum gas oil, pyrolysis gas oil, sulfur-containing waste tire oil, and any mixture thereof.
- [45] In an embodiment, the sulfur-containing oil may be contained in an amount of less than 50 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil. Specifically, the sulfur-containing oil may be contained in an amount of less than 40 parts by weight.
- [46] The sulfur source may contain a sulfur-containing organic compound instead of or together with sulfur-containing oil. Specifically, the sulfur-containing organic compound may be one or two or more compounds selected from a disulfide-based compound, a sulfide-based compound, a sulfonate-based compound, and a sulfate-based compound. Specifically, the sulfur-containing organic compound 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, propyl methanesulfonate, propenyl propenesulfonate, propenyl cyanoethansulfonate, ethylene sulfate, bicyclo-glyoxal sulfate, and methyl sulfate. However, these compounds are only presented as examples and the present disclosure is not limited thereto. The sulfur-containing organic compound may be contained in an amount of 0.001 to 50 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil. When the sulfur-containing organic compound is contained in an amount of less than 0.01 parts by weight, a content of sulfur component supplied is small, such that the effect of preventing deactivation of the hydrotreating catalyst may be insufficient.
- [47] The third step of hydrotreating the mixed oil with the hydrogen gas in the presence of the hydrotreating catalyst refers to hydrogenation in which hydrogen gas is added to the hydrocarbon oil included in the mixed oil. Specifically, the hydrotreating may refer to conventionally known hydrotreating including hydrodesulfurization, hydrocracking, hydrodechlorination, hydrodenitrogenation, and hydrodemetallization. Impurities including chlorine (Cl) and nitrogen (N), olefins, and other metal impurities may be removed by the hydrotreating.
- [48] In an embodiment, the third step may include a 3-1st step of hydrotreating the mixed oil at a first temperature in the presence of a hydrotreating catalyst to produce a fluid

from which olefins are removed; and a 3-2nd step of hydrotreating the fluid at a second temperature higher than the first temperature in the presence of a hydrotreating catalyst to produce refined oil from which impurities are removed.

- [49] The type of each component removed in the hydrotreating may be determined by a reaction temperature. The hydrotreating in the 3-1st step may be performed at a first temperature to mainly remove olefins, and the hydrotreating in the 3-2nd step may be performed at a second temperature higher than the first temperature to mainly remove impurities including chlorine and nitrogen.
- [50] The hydrotreating in the 3-1st step and the hydrotreating in the 3-2nd step may be performed consecutively, but olefins are first removed in the 3-1st step, and then impurities including chlorine and nitrogen are removed in the 3-2nd step, such that it is possible to minimize formation and accumulation of materials that cause a differential pressure, such as oligomers, in the reactor.
- [51] In an embodiment, the first temperature may be higher than 100°C and lower than 400°C, and the second temperature may be higher than 300°C and lower than 450°C. A difference between the first temperature and the second temperature may be 50 to 350°C, and specifically, 50 to 280°C, but this is only an example, and the difference between the first temperature and the second temperature is not limited thereto.
- [52] When the hydrotreating is performed in a range of the first temperature, olefins may be intensively removed. Specifically, hydrogenation of the waste plastic pyrolysis oil is performed in the presence of a hydrotreating catalyst, and most of the olefins from the waste plastic pyrolysis oil are saturated to produce paraffins. In addition, some impurities such as chlorine are removed from the waste plastic pyrolysis oil, and other metal impurities are removed. The first temperature may be 100 to 400°C.
- [53] When the hydrotreating is performed in a range of the second temperature, impurities including chlorine and nitrogen may be removed. When the second temperature is 300°C or lower, the impurities in the waste plastic pyrolysis oil may not be effectively removed, which may cause deterioration of product quality. When the second temperature is 450°C or higher, a side reaction of thermal cracking excessively occurs, which may cause deactivation of the catalyst such as coking. Specifically, when the second temperature is 320 to 420°C, the activity of the catalyst may be maintained, which is preferable.
- [54] In an embodiment, a reaction pressure in the hydrotreating in each of the 3-1st step and the 3-2nd step may be more than 10 bar and less than 200 bar. Under a low pressure condition of 10 bar or less, impurities including chlorine and nitrogen may not be effectively removed. Under a high pressure condition of 200 bar or more, formation of an ammonium chloride salt (NH_4Cl) is promoted. Specifically, the reaction pressure may be 30 bar to 180 bar.

- [55] In an embodiment, liquid hourly space velocities (LHSVs) in the hydrotreating in the 3-1st step and the hydrotreating in the 3-2nd step may be 1:0.1 to 1:2.0. When this is satisfied, the impurities may be effectively removed by the hydrotreating of each of the 3-1st step and the 3-2nd step, the activity of the hydrotreating catalyst may be maintained at high activity for a long period of time, and the process efficiency is improved.
- [56] As the hydrotreating catalyst, various types of known catalysts may be used as long as they are catalysts for performing hydrogenation in which hydrogen is added to the hydrocarbon oil of the waste plastic pyrolysis oil. As a specific example, the hydrotreating catalyst may include one or two or more selected from a hydrodesulfurization catalyst, a hydrodenitrogenation catalyst, a hydrodechlorination catalyst, and a hydrodemetallization catalyst. Such a catalyst allows a demetallization reaction to be performed and allows a denitrification reaction or a dechlorination reaction to be performed at the same time according to conditions such as the temperature described above. Specifically, the hydrotreating catalyst may contain an active metal having the hydrotreating catalytic ability, and preferably, an active metal may be supported on a support. As the active metal, any active metal may be used as long as it has a required catalytic ability, and for example, the active metal may include one or more selected from molybdenum and nickel. As the support, any support may be used as long as it has durability enough to support an active metal.
- [57] It may be advantageous that the hydrotreating catalyst is a molybdenum-based hydrotreating catalyst, and specifically, a molybdenum-based sulfide hydrotreating catalyst, in terms of improving the activity of the catalyst by the sulfur source. The molybdenum-based hydrotreating catalyst may be a catalyst in which a molybdenum-based metal, or a metal including one or two or more selected from nickel, cobalt, and tungsten and a molybdenum-based metal are supported on a support. The molybdenum-based hydrotreating catalyst has high catalytic activity during hydrotreating, and the molybdenum-based hydrotreating catalysts may be used alone or, if necessary, in the form of a two-way catalyst combined with a metal such as nickel, cobalt, or tungsten. 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 the present disclosure is not limited thereto. The molybdenum-based sulfide hydrotreating catalyst may contain, for example, molybdenum sulfide (MoS) or molybdenum disulfide (MoS₂), but is not limited thereto, and may include a known molybdenum-based sulfide hydrotreating catalyst.
- [58] Through the fourth step, the mixed oil hydrotreated in the third step may be separated into a liquid stream and a gas stream to obtain liquid pyrolysis oil.
- [59] In an embodiment, the hydrotreated mixed oil may be introduced into a high-

temperature and high-pressure separator to separate the hydrotreated mixed oil into a liquid stream and a gas stream. A gas stream and a liquid stream separated from impurities may be obtained from the mixed oil through the high-temperature and high-pressure separator. Before the hydrotreated mixed oil is introduced into the high-temperature and high-pressure separator, a cooling process may be performed.

- [60] In an embodiment, the gas stream separated in the high-temperature and high-pressure separator may be sequentially introduced into a low-temperature and high-pressure separator and a low-temperature and low-pressure separator, and the liquid stream separated in the high-temperature and high-pressure separator may be introduced into a high-temperature and low-pressure separator.
- [61] The gas stream separated in the high-temperature and high-pressure separator may be sequentially introduced into a low-temperature and high-pressure separator and a low-temperature and low-pressure separator to finally discharge and remove gas, and in this process, a part of the gas stream may be liquefied again and recovered as a liquid stream. The liquid stream separated in the high-temperature and high-pressure separator may be introduced into a high-temperature and low-pressure separator to finally recover a high-quality liquid stream.
- [62] In an embodiment, the gas stream separated in the high-temperature and high-pressure separator may be washed with water to suppress formation of a salt. The gas stream is washed with water, such that it is possible to prevent formation of an ammonium chloride salt (NH_4Cl) by ammonia and hydrogen chloride. The water washing process may be performed at least twice.
- [63] The fifth step is a step of recovering hydrogen gas from the separated gas stream and recycling the recovered hydrogen gas to the third step, and the gas stream may contain unreacted hydrogen gas, a trace of methane (CH_4) or ethane (C_2H_6), and the like. In addition to this, the gas stream may contain hydrogen sulfide gas (H_2S), hydrogen chloride (HCl), ammonia (NH_3), or water vapor (H_2O) generated by reacting chlorine (Cl), nitrogen (N), sulfur (S), or oxygen (O) with hydrogen gas. Hydrogen gas is recovered from the gas stream and the recovered hydrogen gas is recycled to the third step, such that cost-effectiveness may be enhanced and reaction efficiency may be improved.
- [64] In an embodiment, in the fifth step, the recovered hydrogen gas may be purified to remove impurities, and then the hydrogen gas from which the impurities are removed may be recycled to the third step. The recovered hydrogen gas may contain other impurities such as hydrogen chloride (HCl), and ammonia (NH_3). Therefore, a purification step is performed, such that the purity of the hydrogen gas may be improved by 90% or more and the hydrogen gas with improved purity may be recycled to the third step. The purification may be performed by washing the hydrogen gas with water,

and the water washing process may be performed at least once.

- [65] In an embodiment, the method may further include a step of performing distillation on the liquid pyrolysis oil separated in the fourth step, and in the distillation step, formation of a salt may be suppressed using a salt remover. Specifically, the liquid pyrolysis oil separated in the fourth step contains minimized impurities, and may contain less than 10 ppm of chlorine (Cl), less than 10 ppm of nitrogen (N), and less than 2,000 ppm of moisture. The liquid pyrolysis oil may contain less than 3 wt% of olefins, and may contain 0.5 wt% or less of conjugated diolefins. The pyrolysis oil is introduced into a fractionator to perform distillation, such that a petroleum product with minimized impurities may be finally recovered. The petroleum product may be recovered at different boiling points, for example, may be recovered as 5 to 35 wt% of Naphtha (bp 150°C or lower), 10 to 60 wt% of Kerosene (bp 150 to 265°C), 20 to 40 wt% of Light gas oil (bp 265 to 380°C), and 5 to 40 wt% of Atmospheric Residue (bp 380°C or higher), but is not limited thereto. In the distillation step, the gas stream is washed with water using a salt remover, such that it is possible to prevent formation of an ammonium chloride salt (NH_4Cl) by ammonia and hydrogen chloride. As the salt remover, a known salt remover capable of suppressing formation of an ammonium chloride salt (NH_4Cl) may be used.

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

[67] **Example 1**

- [68] Waste plastics were pyrolyzed to prepare 1,000 g of a waste plastic pyrolysis oil raw material. 560 ppm of chlorine, 1,080 ppm of nitrogen, and 2,200 ppm of moisture were contained in the waste plastic pyrolysis oil raw material.

- [69] The waste plastic pyrolysis oil was washed with 200 g of washing water. Thereafter, the washed waste plastic pyrolysis oil was dried with hot air at 130°C and 5 bar to remove moisture, and then only oil was recovered.

- [70] 100 parts by weight of oil of the recovered pyrolysis oil and 0.1 parts by weight of hydrocarbon oil containing 20,000 ppm of sulfur were mixed to prepare a mixed oil.

- [71] The prepared mixed oil and hydrogen gas were put into a reactor, and the reactor was operated, thereby hydrotreating the mixed oil. The mixed oil was hydrotreated with a reaction gas containing hydrogen gas (H_2) in the presence of a NiMo hydrotreating catalyst at 350°C and 60 bar.

- [72] The hydrotreated mixed oil was separated into a liquid stream and a gas stream. Specifically, the hydrotreated mixed oil was put into a high-temperature and high-pressure separator to separate the hydrotreated mixed oil into a liquid stream and a gas

stream so as to recover the liquid stream, thereby obtaining refined oil with minimized impurities. In addition, the hydrogen gas was recovered from the separated gas stream, and the recovered hydrogen gas was recycled to the hydrotreating reactor.

[73] **Comparative Example 1**

[74] In Example 1, the waste plastic pyrolysis oil raw material was directly put into the reactor to perform hydrotreating. That is, the reaction was performed under the same conditions as those of Example 1, except that the water washing and moisture removal processes and the process of mixing with the sulfur-containing hydrocarbon oil were omitted.

[75] **Evaluation Examples**

[76] The content (ppm) of chlorine (Cl) in the finally obtained refined oil was measured by an IC analysis method, and the results were shown.

[77] The catalytic activity retention time was measured and expressed in days based on the time point when the content of nitrogen in the refined oil exceeded 10 ppm by performing a Total Nitrogen & Sulfur (TNS element) analysis on the refined oil.

[78] [Table 1]

	Example 1	Comparative Example 1
Chlorine content (ppm)	< 9	> 320
Moisture content (ppm)	< 330	> 1,500
Catalytic activity retention time (day)	> 18	4

[79] In Example 1, as the method of treating waste plastic pyrolysis oil of the present disclosure was performed, it could be confirmed that the content of chlorine in the finally obtained waste plastic pyrolysis oil was removed to a level of a few ppm or less and high-quality refined oil with minimized impurities was obtained. In addition, it could be confirmed that the catalytic activity was continuously maintained for 18 days or longer. On the other hand, in Comparative Example 1, as the water washing and moisture removal processes and the process of mixing with the sulfur-containing hydrocarbon oil were omitted, it could be confirmed that the content of chlorine in the pyrolysis oil was 320 ppm and the catalytic activity retention time was significantly reduced to 4 days or shorter.

[80] Although embodiments of the present invention have been described, the present invention is not limited to the embodiments, but may be implemented in various different forms, and it will be apparent to those skilled in the art to which the present invention pertains that the embodiments 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 embodiments described hereinabove are illustrative rather than being restrictive in all aspects.

Claims

- [Claim 1] A method of treating waste plastic pyrolysis oil, comprising:
a first step of washing waste plastic pyrolysis oil with water and then removing moisture;
a second step of mixing the waste plastic pyrolysis oil from which the moisture is removed and a sulfur source to prepare a mixed oil;
a third step of hydrotreating the mixed oil with hydrogen gas in the presence of a hydrotreating catalyst;
a fourth step of separating the hydrotreated mixed oil into a liquid stream and a gas stream to obtain liquid pyrolysis oil; and
a fifth step of recovering hydrogen gas from the separated gas stream and recycling the recovered hydrogen gas to the third step.
- [Claim 2] The method of claim 1, wherein the waste plastic pyrolysis oil that is subjected to the first step contains moisture in an amount of 300 to 2,000 ppm.
- [Claim 3] The method of claim 1, wherein the sulfur source in the second step contains sulfur-containing oil.
- [Claim 4] The method of claim 1, wherein the sulfur source in the second step is contained in an amount of less than 50 parts by weight based on 100 parts by weight of the waste plastic pyrolysis oil.
- [Claim 5] The method of claim 1, wherein the mixed oil in the second step contains sulfur in an amount of 100 ppm or more.
- [Claim 6] The method of claim 1, wherein the third step includes:
a 3-1st step of hydrotreating the mixed oil at a first temperature in the presence of a hydrotreating catalyst to produce a fluid from which olefin, nitrogen, chlorine is removed; and
a 3-2nd step of hydrotreating the fluid at a second temperature higher than the first temperature in the presence of a hydrotreating catalyst to produce refined oil from which impurities are removed.
- [Claim 7] The method of claim 6, wherein the first temperature is higher than 100°C and lower than 400°C, and the second temperature is higher than 300°C and lower than 450°C.
- [Claim 8] The method of claim 6, wherein a reaction pressure in the hydrotreating in each of the 3-1st step and the 3-2nd step is more than 10 bar and less than 200 bar.
- [Claim 9] The method of claim 6, wherein liquid hourly space velocities (LHSVs) in the hydrotreating in the 3-1st step and the hydrotreating in the 3-2nd

- step is 1:0.1 to 1:2.0.
- [Claim 10] The method of claim 1, wherein in the fourth step, the hydrotreated mixed oil is introduced into a high-temperature and high-pressure separator to separate the hydrotreated mixed oil into a liquid stream and a gas stream.
- [Claim 11] The method of claim 10, wherein the gas stream separated in the high-temperature and high-pressure separator is sequentially introduced into a low-temperature and high-pressure separator and a low-temperature and low-pressure separator, and the liquid stream separated in the high-temperature and high-pressure separator is introduced into a high-temperature and low-pressure separator.
- [Claim 12] The method of claim 10, wherein the gas stream separated in the high-temperature and high-pressure separator is washed with water to suppress formation of a salt.
- [Claim 13] The method of claim 1, further comprising a step of performing distillation on the liquid pyrolysis oil separated in the fourth step, wherein in distillation step, formation of a salt is suppressed using a salt remover.
- [Claim 14] The method of claim 1, wherein in the fifth step, the recovered hydrogen gas is purified to remove impurities, and then the hydrogen gas from which the impurities are removed is recycled to the third step.