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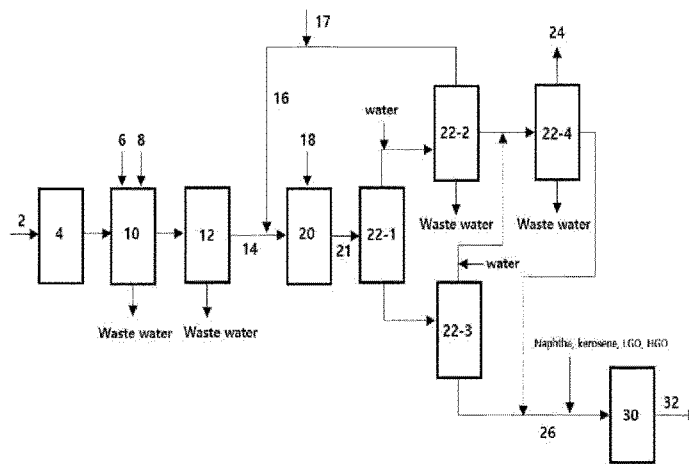
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(54) Title: METHOD AND SYSTEM FOR PRODUCING SYNGAS CONTAINING HYDROGEN FROM WASTE PLASTIC PYROLYSIS OIL



(57) Abstract: Embodiments of the present disclosure relate to a method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil. The method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil according to the embodiments of the present disclosure may minimize formation of an ammonium chloride salt (NH<sub>4</sub>Cl) and may prevent an adhesion phenomenon of impurity particles in a reactor in a refining process of waste plastic pyrolysis oil containing impurities including chlorine and nitrogen. The method and system for producing syngas containing hydrogen according to the present disclosure may have excellent refining efficiency and may implement a long-term operation of a process because a catalyst used in the process is prevented from being deactivated, and may produce lightened and refined hydrocarbons having a low content of impurities and olefins from waste plastic pyrolysis oil and may thus produce syngas containing hydrogen.



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## Description

### Title of Invention: METHOD AND SYSTEM FOR PRODUCING SYNGAS CONTAINING HYDROGEN FROM WASTE PLASTIC PYROLYSIS OIL

#### Technical Field

- [1] Embodiments of the present disclosure relate to a method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil.

#### Background Art

- [2] Waste plastics, which are produced by using petroleum as a feedstock, have a low rate of recycling, such as energy recovery in power generation, or mechanical recycling, and a significant amount of waste plastics is simply incinerated or landfilled. These wastes take a long time to degrade in nature, which causes contamination of the soil and serious environmental pollution. A method for recycling waste plastics includes pyrolysis of the waste plastics and converting the pyrolyzed waste plastics into usable oil. The oil produced by pyrolyzing waste plastics in this way is called waste plastic pyrolysis oil.
- [3] However, waste plastic pyrolysis oil may be blended in a limited amount with 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 than oil produced from crude oil by a general method. In particular, a chlorine component causes corrosion of a reactor itself or after being converted into HCl during a process of producing refined hydrocarbons.
- [4] A refining method for removing impurities such as chlorine, nitrogen, oxygen, and metals contained in waste plastic pyrolysis oil, a method of performing dechlorination, denitrification, and deoxygenation by reacting waste plastic pyrolysis oil with hydrogen in the presence of a hydrotreating catalyst, and a method of removing chlorine contained in waste plastic pyrolysis oil by adsorption using a chlorine adsorbent, or the like are known.
- [5] Specifically, U.S. Patent No. 3,935,295 discloses a technology for removing chloride contaminants from various hydrocarbon oils. The technology is a conventional technology of hydrotreating oil in the presence of a hydrotreating catalyst in a first reactor, introducing a fluid containing hydrogen chloride (HCl) produced at this time and refined oil into a second reactor, and then removing a chlorine component contained in the fluid by adsorption using an adsorbent.
- [6] However, as described in the conventional technology, when oil is allowed to react with hydrogen in the presence of a hydrotreating catalyst, a chlorine compound such as hydrogen chloride produced together with refined oil, and a nitrogen compound react

with each other to form an ammonium chloride salt ( $\text{NH}_4\text{Cl}$ ), and the ammonium chloride salt causes various process issues. Specifically, the ammonium chloride salt formed inside the reactor by the reaction of oil and hydrogen not only causes corrosion of the reactor to reduce durability, but also causes various process issues such as an occurrence of a differential pressure and a resulting reduction in process efficiency. In addition, when the process is operated for a long period of time, adhesion of impurity particles in the waste plastic pyrolysis oil occurs inside the reactor, causing various process issues.

- [7] Therefore, there is a need to develop a method capable of producing syngas containing hydrogen from waste plastic pyrolysis oil while solving the process problems described above.

## **Disclosure of Invention**

### **Technical Problem**

- [8] An embodiment of the present disclosure is directed to providing a method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil that may minimize formation of an ammonium chloride salt ( $\text{NH}_4\text{Cl}$ ) in a refining process of waste plastic pyrolysis oil containing impurities including chlorine and nitrogen.
- [9] Another embodiment of the present disclosure is directed to providing a method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil that have excellent refining efficiency and may implement a long-term operation because activity of a catalyst is maintained for a long time.
- [10] Still another embodiment of the present disclosure is directed to providing a method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil that may prevent an adhesion phenomenon of impurity particles in a reactor.
- [11] Still another embodiment of the present disclosure is directed to providing a method and system for producing syngas containing hydrogen with reduced impurities by significantly reducing a content of impurities such as chlorine, nitrogen, oxygen, and metals and a content of olefins from waste plastic pyrolysis oil.

### **Solution to Problem**

- [12] In one general aspect, a method for producing syngas containing hydrogen from waste plastic pyrolysis oil includes: applying a voltage to a first mixed solution obtained by mixing waste plastic pyrolysis oil, washing water, and a demulsifier to dehydrate the first mixed solution; hydrotreating a second mixed solution obtained by mixing the dehydrated first mixed solution and a sulfur source to produce refined oil from which impurities are removed; and gasifying the refined oil from which impurities are removed.
- [13] In the dehydration operation, the waste plastic pyrolysis oil may be mixed in a

- greater volume than the washing water.
- [14] In the dehydration operation, the waste plastic pyrolysis oil and the washing water may be mixed in the first mixed solution at a volume ratio of 1:0.001 to 1:0.5.
- [15] In the dehydration operation, the waste plastic pyrolysis oil and the demulsifier may be mixed in the first mixed solution at a volume ratio of 1:0.000001 to 1:0.001.
- [16] The voltage may be applied as an alternating current or a combination of an alternating current and a direct current.
- [17] The voltage may be applied through a vertical electrode.
- [18] The method for producing syngas containing hydrogen from waste plastic pyrolysis oil may further include, after the application of the voltage in the dehydration operation, removing a rag layer from the first mixed solution.
- [19] The dehydration operation may be performed under a temperature condition of 20°C to 300°C.
- [20] A ratio of a content of moisture in the waste plastic pyrolysis oil to a content of moisture in the first mixed solution dehydrated in the dehydration operation may be 1:0.0001 to 1:0.9.
- [21] In the dehydration operation, the dehydrated first mixed solution may be additionally dehydrated by condensation of moisture.
- [22] A weight ratio of nitrogen to chlorine in the second mixed solution may be 1:1 to 1:10.
- [23] The sulfur source may include sulfur-containing oil.
- [24] The sulfur-containing oil may be included in an amount of less than 0.5 parts by weight with respect to 100 parts by weight of the first mixed solution dehydrated in the dehydration operation.
- [25] The sulfur source may include one or two or more sulfur-containing organic compounds selected from a disulfide-based compound, a sulfide-based compound, a sulfonate-based compound, and a sulfate-based compound.
- [26] The hydrotreating operation may be performed in the presence of a molybdenum-based hydrotreating catalyst.
- [27] 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.
- [28] The molybdenum-based hydrotreating catalyst may include a molybdenum-based sulfide hydrotreating catalyst.
- [29] The hydrotreating may be performed under a pressure condition of 50 bar to 150 bar.
- [30] The method for producing syngas containing hydrogen from waste plastic pyrolysis oil may further include, after the hydrotreating operation, subjecting a stream including

the refined oil from which impurities are removed to gas-liquid separation and then washing the gas-liquid separated stream with water.

[31] In an embodiment, the gasification operation a refined fraction separated by distilling the refined oil from which impurities are removed in the hydrotreating operation may be gasified.

[32] In an embodiment, the gasification operation is gasification a mixed oil obtained by mixing the refined oil from which impurities are removed in the hydrotreating operation and petroleum hydrocarbons may be gasified.

[33] Other features and aspects will be apparent from the following detailed description, the drawings, and the claims.

### **Advantageous Effects of Invention**

[34] The method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil according to the embodiments of the present disclosure may minimize formation of an ammonium chloride salt ( $\text{NH}_4\text{Cl}$ ) and may prevent an adhesion phenomenon of impurity particles in a reactor in a refining process of waste plastic pyrolysis oil containing impurities including chlorine and nitrogen.

[35] The method and system for producing syngas containing hydrogen according to the present disclosure may have excellent refining efficiency and may implement a long-term operation of a process because a catalyst used in the process is prevented from being deactivated, and may produce lightened and refined hydrocarbons having a low content of impurities and a low content of olefins from waste plastic pyrolysis oil and may thus produce syngas containing hydrogen.

### **Brief Description of Drawings**

[36] FIG. 1 is a process diagram of a method for producing syngas containing hydrogen from waste plastic pyrolysis oil according to an embodiment of the present disclosure.

[37] FIG. 2 is a diagram of dehydrator used in a system for producing syngas containing hydrogen from waste plastic pyrolysis oil according to an embodiment of the present disclosure.

### **Best Mode for Carrying out the Invention**

[38] Various embodiments of the present disclosure will be described in greater detail with reference to the accompanying drawings. The drawings are schematic illustrations of various embodiments (and intermediate structures). As such, variations from the configurations and shapes of the illustrations as a result, for example, of manufacturing techniques and/or tolerances, are to be expected. Thus, the described embodiments should not be construed as being limited to the particular configurations and shapes illustrated herein but may include deviations in configurations and shapes which do not depart from the spirit and scope of the present disclosure as defined in the appended

claims.

- [39] It will be understood that, although the terms "first", "second", "third", and so on may be used herein to describe various elements, these elements are not limited by these terms. These terms are used to distinguish one element from another element. Thus, a first element described below could also be termed as a second or third element without departing from the spirit and scope of the present disclosure.
- [40] It should be understood that the drawings are simplified schematic illustrations of the described processes and apparatuses and may not include well known details to avoid obscuring the features of the embodiments of the present disclosure.
- [41] It should also be noted that features present in one embodiment may be used with one or more features of another embodiment without departing from the scope of the present disclosure.
- [42] It is further noted, that in the various drawings, like reference numbers designate like elements.
- [43] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the present disclosure.
- [44] As used herein, singular forms are intended to include the plural forms as well, unless the context clearly indicates otherwise.
- [45] It will be further understood that the terms "comprises," "comprising," "includes," and "including" when used in this specification, specify the presence of the stated elements and do not preclude the presence or addition of one or more other elements. As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.
- [46] Unless otherwise defined, all terms including technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the embodiments belong in view of the present disclosure.
- [47] It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the present disclosure and the relevant art and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.
- [48] The advantages and features of the embodiments of the present disclosure and methods for accomplishing them will become apparent from embodiments described below in detail with reference to the accompanying drawings. However, the embodiments of the present disclosure is not limited to embodiments to be disclosed below, but may be implemented in various different forms. These embodiments are provided in order to make the present disclosure complete and allow those skilled in the art to better recognize the scope of the present disclosure. Therefore, the present disclosure is not limited by the embodiments disclosed herein.

- [49] Unless defined otherwise, all terms (including technical and scientific terms) used in the present specification have the same meanings as commonly understood by those skilled in the art to which the present disclosure pertains.
- [50] 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 this specification, values out of the numerical range that may occur due to experimental errors or rounded values also fall within the defined numerical range.
- [51] The term "reactor" used in the present specification may refer to a device that may be used in processes such as production, refining, separation, and mixing of waste plastic pyrolysis oil. For example, the reactor may be interpreted to mean a device such as a dehydrator, a coalescer, a hydrotreating reactor, or a separator used in a refining process of waste plastic pyrolysis oil.
- [52] The term "vertical electrode" used in the present specification may refer to an electrode erected in a vertical direction with respect to the ground, and the term "horizontal electrode" may refer to an electrode laid horizontally with respect to the ground.
- [53] In a method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil according to embodiments of the present disclosure, a dehydration operation is performed in a dehydrator 10 as a shown in FIG. 1. The dehydration operation includes water washing, demulsification, voltage application, and the like for reducing problems such as catalyst deactivation due to moisture dispersed in the form of an emulsion in the waste plastic pyrolysis oil 2, and corrosion of a reactor due to chlorine contained in moisture and a low pH of moisture. A demulsifier 8 may be added in the dehydrator or in a feed tank 4 and mixed with the pyrolysis oil 2 before the mixture is fed to the dehydrator 10. Following the dehydration operation, the dehydrated pyrolysis oil may be fed to a hydrotreating reactor 20 for subjecting it to a hydrotreating operation whereby impurities contained in the dehydrated waste plastic pyrolysis oil 14 are removed through a hydrotreating reaction and a gasification operation of gasifying refined oil from which impurities are removed through the above processes are performed. The method for producing syngas containing hydrogen from waste plastic pyrolysis oil according to the present disclosure may stably produce syngas containing hydrogen having a low content of impurities from waste plastic pyrolysis oil by organically combining the above series of temporal processes.
- [54] Hereinafter, the method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil will be described in detail.

- [55] The present disclosure provides a method for producing syngas containing hydrogen from waste plastic pyrolysis oil, the method including: applying a voltage to a first mixed solution obtained by mixing waste plastic pyrolysis oil, washing water, and a demulsifier to dehydrate the first mixed solution; a hydrotreating operation hydrotreating a second mixed solution obtained by mixing the first mixed solution dehydrated in the dehydration operation and a sulfur source to produce refined oil from which impurities are removed; and gasifying the refined oil from which impurities are removed.
- [56] First, is a step of applying a voltage to a first mixed solution obtained by mixing waste plastic pyrolysis oil, washing water, and a demulsifier to dehydrate the first mixed solution.
- [57] Waste plastic pyrolysis oil contains moisture, and moisture in pyrolysis oil may cause problems such as deactivation of a hydrotreating catalyst and corrosion of a reactor. In addition, since water-soluble impurities are contained in moisture, it is required to remove moisture. Moisture present in the form of an emulsion in waste plastic pyrolysis oil may be easily removed by performing the step S1).
- [58] The waste plastic pyrolysis oil according to an embodiment of the present disclosure may be a mixture of hydrocarbon oils produced by pyrolyzing waste plastics, and in this case, the waste plastics may include solid or liquid wastes related to synthetic polymer compounds such as waste synthetic resins, waste synthetic fibers, waste synthetic rubber, and waste vinyl.
- [59] The mixture of hydrocarbon oils according to an embodiment of the present disclosure may contain impurities such as a chlorine compound, a nitrogen compound, an oxygen compound, a metal compound, and char-derived particles, may contain impurities in the form of compounds in which chlorine, nitrogen, oxygen, or a metal is bonded to hydrocarbons, and may contain paraffinic, olefinic, naphthenic, or aromatic hydrocarbons.
- [60] The washing water according to an embodiment of the present disclosure may serve to increase the probability of contact between emulsion-type moisture present in the waste plastic pyrolysis oil. In addition, a basic compound may be added to the washing water to remove a water-soluble acidic material contained in moisture, and the basic compound may be sodium hydroxide (NaOH), but is not limited thereto. The waste plastic pyrolysis oil according to an embodiment of the present disclosure may be mixed in a greater volume than the washing water. In an embodiment, the waste plastic pyrolysis oil and the washing water may be mixed in the first mixed solution at a volume ratio of 1:0.001 to 1:0.5, 1:0.005 to 1:0.4, or 1:0.01 to 1:0.3. When the volume ratio satisfies the above range, water washing is sufficiently performed, and thus, impurities in the pyrolysis oil may be significantly reduced, and costs required to remove

washing water to be mixed may be minimized.

- [61] The demulsifier according to an embodiment of the present disclosure may be one or a mixture of two or more selected from the group consisting of polyethylene glycol, tert-butanol, acetone, alkylnaphthalene sulfonate, alkylbenzene sulfonate, a nonionic alkoxyated alkyl phenol resin, polyalkylene oxide, and polyoxyethylene sorbitan ester, but is not limited thereto. In an embodiment, the demulsifier may be added with the washing water.
- [62] In the first mixed solution according to an embodiment of the present disclosure, the waste plastic pyrolysis oil and the demulsifier may be mixed at a volume ratio of 1:0.000001 to 1:0.001, 1:0.000002 to 1:0.0005, or 1:0.000003 to 1:0.0001. When the volume ratio satisfies the above range, the emulsion may be decomposed with minimal impact on the quality of pyrolysis oil.
- [63] The demulsifier according to an embodiment of the present disclosure may have a weight average molecular weight of 200 to 2,000, 300 to 1,000, or 400 to 800. When the weight average molecular weight satisfies the above range, it is easy to mix the demulsifier with the waste plastic pyrolysis oil and the washing water under conditions where the dehydration operation is performed, and thus, the decomposition efficiency of the moisture emulsion is increased.
- [64] The moisture in the form of an emulsion contained in the first mixed solution in which the waste plastic pyrolysis oil, the washing water, and the demulsifier are mixed is still difficult to remove because it is stable. Therefore, a voltage may be applied to the first mixed solution to facilitate removal of moisture.
- [65] The voltage according to an embodiment of the present disclosure may be applied a dual polarity, alternating current, direct current or a combination of an alternating current and a direct current. Some impurity particles contained in the waste plastic pyrolysis oil have polarities, and therefore, when a direct current voltage is applied, polarized impurity particles accumulate on a specific electrode, and when the process is performed for a long period of time, the impurities may adhere to the electrode. However, when an alternating current voltage is applied, the polarity of the electrode changes periodically, and therefore, the adhesion phenomenon of the impurity particles may be prevented. In addition, a frequency of the alternating current according to an embodiment of the present disclosure may be a single frequency or a combination of two or more frequencies. As a specific example, in the case of the single frequency, an alternating current with a frequency of 60 Hz may be applied, and in the case of the combination of two or more frequencies, alternating currents with frequencies of 50 Hz and 60 Hz may be applied alternately, but the embodiments of the present disclosure are not limited thereto.
- [66] The voltage according to an embodiment of the present disclosure may be applied

through a vertical electrode. In a case where the impurity particles accumulate on the electrode during a mixed solution preparation process or a voltage application process, when the impurities particles are not artificially washed, the impurity particles may adhere to the electrode after a long period of time. However, when a vertical electrode is used, the adhesion phenomenon of the impurity particles may be prevented in advance because the impurity particles do not accumulate on the electrode but fall to the bottom of the reactor due to gravity even without an additional washing operation.

[67] A magnitude of the voltage according to an embodiment of the present disclosure may be 0.1 to 50 kV, 1 to 30 kV, or 5 to 20 kV, but is not limited thereto.

[68] The dehydration according to an embodiment of the present disclosure may be performed by any method known in the art. As a non-limiting example, after the application of the voltage, water may be removed by draining a water layer which is oil-water separated. Water may also be removed in a gas-liquid separator.

[69] Metal impurities in the waste plastic pyrolysis oil stabilize the emulsion, hinder oil-water separation, and help form a stable emulsion layer, commonly called a rag layer. Such a rag layer may be formed between a desalinated oil layer at an upper portion of the first mixed solution and a water layer at a lower portion of the first mixed solution, and may be gradually thickened during a continuous dehydration operation. An excessively thickened rag layer may be discharged to equipment at the hydrotreating operation together with desalinated oil. This reduces the desalination effect of the desalinated oil and reduces the efficiency of the process. In addition, the rag layer may be discharged together with water and may cause issues in a wastewater treatment process. Therefore, in an embodiment, the rag layer formed between the desalinated oil layer and the water layer may be removed.

[70] Therefore, the method for producing syngas containing hydrogen from waste plastic pyrolysis oil according to an embodiment of the present disclosure may further include, after the application of the voltage in the dehydration operation, removing a rag layer from the first mixed solution. The removal of the rag layer may be performed through a pipe penetrating through a wall of a dehydrator and connected to the outside after measuring a change in density of the mixed solution by a density meter in the dehydrator to determine a formation location and a thickness of the rag layer, but is not limited thereto.

[71] In the dehydration operation according to an embodiment of the present disclosure, after dehydrating the first mixed solution, the dehydrated first mixed solution may be additionally dehydrated by condensation of moisture.

[72] The additional dehydration according to an embodiment of the present disclosure may be performed by supplying the dehydrated first mixed solution to a coalescer. In an embodiment, the residual moisture contained in the dehydrated first mixed solution

may be removed through condensation by a collection filter in the coalescer, but this is only a specific example and the embodiments of the present disclosure are not limited thereto. As the content of moisture in the waste plastic pyrolysis oil is further reduced through the additional dehydration, deactivation of the catalyst due to moisture may be significantly reduced or prevented, and the process stability and the quality of syngas containing hydrogen may be improved.

- [73] A ratio of a content of moisture in the waste plastic pyrolysis oil to a content of moisture in the dehydrated first mixed solution according to an embodiment of the present disclosure may be 1:0.0001 to 1:0.9, 1:0.0005 to 1:0.5, or 1:0.001 to 1:0.1. When the ratio satisfies the above range, a risk of issues occurring in subsequent processes such as during hydrotreating may be significantly reduced, and high-quality refined oil that can satisfy specifications may be produced as a feedstock, but embodiments of the present disclosure are not limited thereto.
- [74] The dehydration operation according to an embodiment of the present disclosure may be performed at a pressure of 50 bar or less. When the dehydration operation is performed at a pressure of 50 bar or less, moisture in the pyrolysis oil may be easily removed, and the process stability may be secured. In an embodiment, the dehydration operation may be performed at a pressure of 30 bar or less, or 20 bar or less, and 5 bar or more.
- [75] The dehydration operation according to an embodiment of the present disclosure may be performed at a temperature of 20°C to 300°C. When the temperature satisfies the above range, the decomposition of the emulsion and the condensation of moisture are smoothly performed, and thus, the dehydration efficiency may be improved. In an embodiment, the dehydration operation may be performed at a temperature of 50°C to 250°C, or 80°C to 200°C.
- [76] In order to improve the dehydration efficiency in the dehydration operation according to an embodiment of the present disclosure, one or more additional processes selected from the group consisting of centrifugation and distillation may be performed before and/or after the dehydration. The additional centrifugation and distillation processes described above may be performed by known methods and are not limited to any particular method.
- [77] Next, a hydrotreating operation may be performed. The hydrotreating operation hydrotreats a second mixed solution obtained by mixing the first mixed solution dehydrated in the dehydration operation and a sulfur source to produce refined oil from which impurities are removed.
- [78] The second mixed solution according to an embodiment of the present disclosure may have a concentration of chlorine (Cl) of 10 ppm or more, 100 ppm or more, or 200 ppm or more. In an embodiment, the second mixed solution may have a concentration

of chlorine (Cl) of 3,000 ppm or less. The embodiment of the present disclosure, however, is not limited thereto.

[79] In the second mixed solution according to an embodiment of the present disclosure, a weight ratio of nitrogen to chlorine may be 1:0.1 to 1:10, 1:0.5 to 1:5, or 1:1 to 1:2, but the above weight ratio is only a specific example of what may be included in the waste plastic pyrolysis oil, and a composition of the waste plastic pyrolysis oil is not limited thereto.

[80] The hydrotreating operation, according to an embodiment of the present disclosure, may be performed under a condition in which a ratio of hydrogen to the second mixed solution is  $100 \text{ Nm}^3/\text{Sm}^3$  to  $5,000 \text{ Nm}^3/\text{Sm}^3$ ,  $500 \text{ Nm}^3/\text{Sm}^3$  to  $3,000 \text{ Nm}^3/\text{Sm}^3$ , or  $1,000 \text{ Nm}^3/\text{Sm}^3$  to  $1,500 \text{ Nm}^3/\text{Sm}^3$ . When this condition is satisfied, impurities may be effectively removed, the high activity of the hydrotreating catalyst may be maintained for a long period of time, and the process efficiency may be improved.

[81] The sulfur source refers to a sulfur source capable of continuously supplying a sulfur component during the refining process.

[82] In the hydrotreating operation, the second mixed solution containing the sulfur source may be prepared, such that during the refining process, deactivation of a molybdenum-based hydrotreating catalyst due to lack of the sulfur source and high-temperature operation may be suppressed, and the catalytic activity may be maintained.

[83] The sulfur source according to an embodiment of the present disclosure may include a sulfur-containing oil. The sulfur-containing oil refers to oil composed of hydrocarbons containing sulfur obtained from crude oil as a feedstock. The sulfur-containing oil is not particularly limited and may include oil containing sulfur. In an embodiment, 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.

[84] When waste tire oil is included as the sulfur-containing oil according to an embodiment of the present disclosure, a high content of sulfur contained in waste tires may be converted into oil together with hydrocarbons and may serve as a sulfur source for the waste plastic pyrolysis oil. In addition, diverting the waste tire oil into the sulfur source for the waste plastic pyrolysis oil is advantageous in terms of reducing the environmental load due to recycling of waste tires and maintaining the catalytic activity for a long period of time.

[85] In an embodiment, the sulfur-containing oil may be light gas oil (LGO) with a specific gravity of 0.7 to 1. When this sulfur-containing oil is used, the sulfur-containing oil may be uniformly mixed with the dehydrated first mixed solution, and

high hydrotreating efficiency may be exhibited. In an embodiment, the specific gravity may be 0.75 to 0.95, or, 0.8 to 0.9. The sulfur-containing oil may contain 100 ppm or more of sulfur. When the sulfur component is contained in an amount of less than 100 ppm, a content of the sulfur component supplied may be small, such that the effect of preventing deactivation of the molybdenum-based hydrotreating catalyst may be insufficient. In an embodiment, the sulfur component may be contained in an amount of 800 ppm or more, or 8,000 ppm or more, and 200,000 ppm or less.

[86] The second mixed solution according to an embodiment of the present disclosure may contain 100 ppm or more of sulfur. As in the case of the sulfur-containing oil, when the sulfur component is contained in the second mixed solution in an amount of less than 100 ppm, the content of the sulfur component supplied may be small, such that the effect of preventing deactivation of the molybdenum-based hydrotreating catalyst may be insufficient. In an embodiment, the sulfur component may be contained in an amount of 800 ppm or more, or 8,000 ppm or more, and 200,000 ppm or less.

[87] The sulfur-containing oil according to an embodiment of the present disclosure may be included in an amount of less than 0.5 parts by weight with respect to 100 parts by weight of the first mixed solution dehydrated in the dehydration operation. In an embodiment, the sulfur-containing oil may be included in an amount of less than 0.1 parts by weight, more specifically, less than 0.05 parts by weight, and without limitation, more than 0.01 parts by weight. As the sulfur-containing oil is included in an amount of less than 0.5 parts by weight, the concentration of chlorine (Cl) or nitrogen (N) contained in the waste plastic pyrolysis oil may be diluted, such that a formation rate of an ammonium chloride salt ( $\text{NH}_4\text{Cl}$ ) may be controlled, and the process stability may be improved.

[88] The sulfur source according to an embodiment of the present disclosure may include one or two or more sulfur-containing organic compounds selected from a disulfide-based compound, a sulfide-based compound, a sulfonate-based compound, and a sulfate-based compound. 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, propyl methanesulfonate, propenyl propenesulfonate, propenyl cyanoethanesulfonate, ethylene sulfate, bicyclo-glyoxal sulfate, and methyl sulfate. However, these compounds are only presented as examples and the embodiments of the present disclosure are not limited thereto.

[89] The sulfur-containing organic compound according to an embodiment of the present disclosure may be included in an amount of 0.01 to 0.1 parts by weight with respect to 100 parts by weight of the first mixed solution dehydrated in the dehydration

operation. Specifically, the sulfur-containing organic compound may be included in an amount of 0.02 to 0.08 parts by weight, and or, 0.03 to 0.06 parts by weight with respect to 100 parts by weight of the first mixed solution dehydrated in the dehydration operation. When the sulfur-containing organic compound is included in an amount of less than 0.01 parts by weight, the content of the sulfur component supplied may be small, such that the effect of preventing deactivation of the molybdenum-based hydrotreating catalyst may be insufficient.

- [90] The hydrotreating refers to a hydrogenation reaction that occurs by adding a reaction gas including hydrogen gas ( $H_2$ ) to the second mixed solution in which the first mixed solution dehydrated in the dehydration operation and the sulfur source are mixed in the presence of a molybdenum-based hydrotreating catalyst. Specifically, the hydrotreating may refer to hydrotreating, which is known in the related art, including a hydrodesulfurization reaction, a hydrocracking reaction, a hydro-dechlorination reaction, a hydro-denitrogenation reaction, a hydro-deoxygenation reaction, and a hydro-demetalization reaction. Through the hydrotreating, impurities including chlorine (Cl), nitrogen (N), and oxygen (O), and some olefins may be removed, other metal impurities may also be removed, and a by-product containing the impurities may be produced.
- [91] The by-product may be produced by reacting impurities such as chlorine (Cl), nitrogen (N), sulfur (S), or oxygen (O) contained in the waste plastic pyrolysis oil with the hydrogen gas ( $H_2$ ). In an embodiment, for example, the by-product may include hydrogen sulfide gas ( $H_2S$ ), hydrogen chloride (HCl), ammonia ( $NH_3$ ), water vapor ( $H_2O$ ), or the like, and in addition, may include unreacted hydrogen gas ( $H_2$ ), and a trace of methane ( $CH_4$ ), ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ), butane ( $C_4H_{10}$ ), or the like.
- [92] The molybdenum-based hydrotreating catalyst according to an embodiment of the present disclosure 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.
- [93] As the support according to an embodiment of the present disclosure, alumina, silica, silica-alumina, titanium oxide, a molecular sieve, zirconia, aluminum phosphate, carbon, niobia, or a mixture thereof may be used, but the embodiments of the present disclosure are not limited thereto.
- [94] The molybdenum-based hydrotreating catalyst according to an embodiment of the present disclosure may include a molybdenum-based sulfide hydrotreating catalyst. For example, the molybdenum-based hydrotreating catalyst may include molybdenum sulfide ( $MoS$ ) or molybdenum disulfide ( $MoS_2$ ), but is not limited thereto, and may

include a known molybdenum-based sulfide hydrotreating catalyst.

[95] The reaction gas according to an embodiment of the present disclosure may further include hydrogen sulfide gas (H<sub>2</sub>S). The hydrogen sulfide gas (H<sub>2</sub>S) included in the reaction gas may act as a sulfur source, and may regenerate the activity of the molybdenum-based hydrotreating catalyst deactivated during the refining process together with the sulfur source mixed with the waste plastic pyrolysis oil.

[96] The hydrotreating according to an embodiment of the present disclosure may be performed at a pressure of 150 bar or less. In an embodiment, the hydrotreating may be performed at a pressure of 120 bar or less, or 100 bar or less, and 50 bar or more. It has been observed, that when the hydrotreating operation is performed under a pressure condition of more than 150 bar, ammonia and hydrogen chloride are produced in excess during the hydrotreating, an ammonium chloride salt formation temperature increases, and as a result, a differential pressure of the hydrotreating reactor (an or other process equipment) may increase, and the process stability may be significantly reduced. By controlling the contents of nitrogen and chlorine in the waste plastic pyrolysis oil, the increase in ammonium chloride salt formation temperature may be partially suppressed even under a condition of a pressure of more than 150 bar. However, this case is not appropriate because the waste plastic pyrolysis oil targeted in the refining process according to the present disclosure may be extremely limited thereto.

[97] The hydrotreating operation according to an embodiment of the present disclosure may be performed at a temperature of 150°C to 500°C. This temperature refers to the temperature of the mixed solution in the hydrotreating reactor. When the temperature satisfies the above range, the hydrotreating efficiency may be improved. In an embodiment, the hydrotreating may be performed at a temperature of 200°C to 400°C.

[98] The hydrotreating according to an embodiment of the present disclosure may be performed in multiple stages, and as a specific example, may be performed in two stages. When the hydrotreating is performed in two stages, a first stage may be performed at a lower temperature than a second stage. In this case, the first stage may be performed at a temperature of 150°C to 300°C, or 200°C to 250°C, and the second stage may be performed at a temperature of 300°C to 500°C, or 350°C to 400°C, but the present disclosure is not limited thereto.

[99] A method for producing syngas containing hydrogen from waste plastic pyrolysis oil according to an embodiment of the present disclosure may further include, after the hydrotreating operation, subjecting a stream including the refined oil from which impurities are removed to gas-liquid separation (see separators 22-1 to 22-4) and then washing the gas-liquid separated stream with water.

[100] The stream including the refined oil from which impurities are removed according to

an embodiment of the present disclosure may contain hydrogen chloride, ammonia, unreacted hydrogen gas, and the like, in addition to the refined oil from which impurities are removed discharged from a rear end of the hydrotreating reactor where the hydrotreating operation is performed.

- [101] Through the gas-liquid separation according to an embodiment of the present disclosure, from the stream including the refined oil from which impurities are removed, ammonia and hydrogen chloride produced by the hydrotreating may be removed, and unreacted hydrogen gas may be recovered.
- [102] The gas-liquid separation according to an embodiment of the present disclosure may be performed by a method known in the art using a separator (see separator 22-1), but is not particularly limited.
- [103] The gas-liquid separation according to an embodiment of the present disclosure may be performed two to four times, three or four times, or four times as illustrated as an example in FIG.1 which shows four separators 22-1, 22-2, 22-3 and 22-4. When the above range is satisfied, the formation of the ammonium chloride salt may be minimized even under a low-temperature condition for oil-water separation because the refined oil contains traces of  $\text{NH}_3$  and  $\text{HCl}$ . In addition, oil refining and petrochemical processes using the refined oil as a feedstock may be stably performed without adding an additional salt remover agent to the refined oil later.
- [104] A gas stream produced as a result of the gas-liquid separation according to an embodiment of the present disclosure may include off-gas containing light hydrocarbons, hydrogen sulfide, ammonia, hydrogen chloride, or the like, and unreacted hydrogen gas. According to a method known in the art, the off-gas and the unreacted hydrogen gas are separated, the separated unreacted hydrogen gas is recirculated in the process, and the off-gas is treated through an operation described below and may be used as a feedstock or discharged into the atmosphere.
- [105] Through the water washing according to an embodiment of the present disclosure, a salt included in the gas stream may be dissolved and removed, or salt formation may be suppressed by dissolving gas that may form a salt. The water washing may be performed by a method known in the art, but is not limited thereto.
- [106] The water washing according to an embodiment of the present disclosure may be performed two to four times, and specifically, two or three times. When the above range is satisfied, the salt removal and salt formation suppression effect may be sufficiently exhibited, such that high-quality refined oil may be obtained, and the process stability may be secured.
- [107] A method for producing syngas containing hydrogen from waste plastic pyrolysis oil according to an embodiment of the present disclosure may further include, after the subjecting of the stream including the refined oil from which impurities are removed to

the gas-liquid separation and then the washing of the gas-liquid separated stream with water: combusting the separated off-gas; and processing uncombusted off-gas.

[108] The off-gas according to an embodiment of the present disclosure may contain C1-C4 light hydrocarbons, hydrogen sulfide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>), and the like. Therefore, in order to use the off-gas as fuel, it is required to combust the off-gas to remove hydrogen sulfide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>), and the like. Exhaust gas containing sulfur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), and the like, produced by combustion of the off-gas may be discharged into the atmosphere after performing caustic scrubbing to meet emission standards.

[109] In addition, after the combusting of the separated off-gas, uncombusted off-gas may be discharged as wastewater by being subjected to sour water stripping, adsorption, biological treatment, oxidation, amine scrubbing, or caustic scrubbing.

[110] Next, the a gasification operation for gasifying the refined oil from which impurities are removed is performed.

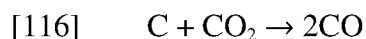
[111] In the present disclosure, "gasification" refers to a thermo-chemical conversion process through changes in chemical structures of carbonaceous materials in the presence of a gasifying agent (air, oxygen, water vapor, carbon dioxide, or a mixture thereof) in a broad sense, and refers to a process of converting carbonaceous materials into syngas mainly containing hydrogen and carbon monoxide in a narrower sense.

[112] The gasification according to an embodiment of the present disclosure may typically produce syngas (may consist of hydrogen and carbon monoxide, and may contain a small amount of carbon dioxide) through a water vapor gasification reaction and/or a carbon dioxide gasification reaction according to the following Reaction Formulas 1 and 2.

[113] [Reaction Formula 1]



[115] [Reaction Formula 2]



[117] The gasification according to an embodiment of the present disclosure may be performed using a gasification reactor known in the art. For example, the water vapor gasification reaction may be performed using a counter-current fixed bed reactor, a co-current fixed bed reactor, a fluidized bed reactor, a moving bed reactor, an entrained bed reactor, or the like. In addition, in the case of the carbon dioxide gasification reaction, for example, a fluidized bed reactor may be used, and examples of the fluidized bed reactor include a riser, bubbling, or turbulent type reactor. However, the type and detailed configuration of the reactor may be appropriately selected or adjusted from various gasification reactors known in the art depending on an intended gasification reaction route (for example, the water vapor gasification reaction, the carbon

dioxide gasification reaction, or both reactions). In addition, reaction conditions may also be appropriately selected considering the target reaction route and the like.

[118] The gasification according to an embodiment of the present disclosure may be performed at a temperature of 400 to 1,200°C, specifically, 500 to 1,000°C, and more specifically, 550 to 800°C, but is not limited thereto.

[119] The gasification according to an embodiment of the present disclosure is not particularly limited, and may be performed at a pressure of, for example, 1 to 5 bar, and more specifically, 1 to 5 bar. In this case, the reaction gas mainly contains water vapor, but may optionally contain oxygen or air (for example, through air blowing), and furthermore, may contain a small amount of carbon dioxide. In some cases, the amount of water vapor in a reaction region may be controlled by controlling a partial pressure using an inert gas such as nitrogen or argon. In this case, a supply ratio of water vapor/carbon may be, for example, within 4, specifically, 0.1 to 3, and more specifically, 0.5 to 2, on a molar basis.

[120] In the gasification operation according to an embodiment of the present disclosure, a refined fraction separated by distilling the refined oil from which impurities are removed in the hydrotreating operation may be gasified. The refined fraction according to an embodiment of the present disclosure may be at least one selected from the group consisting of naphtha, kerosene, light gas oil, vacuum gas oil (VGO), and residue, but is not limited thereto.

[121] In the gasification operation according to an embodiment of the present disclosure, mixed oil obtained by mixing the refined oil from which impurities are removed in the hydrotreating operation and petroleum hydrocarbons may be gasified. In addition, mixed oil obtained by mixing the refined fraction and petroleum hydrocarbons may also be gasified.

[122] The petroleum hydrocarbon refers to a mixture of naturally occurring hydrocarbons or oil separated from the mixture, and specifically, may be one or a mixture of two or more selected from the group consisting of kerosene, light gas oil, heavy gas oil, and vacuum gas oil (VGO) derived from crude oil, but is not limited thereto.

[123] The mixed oil according to an embodiment of the present disclosure may include the refined oil from which impurities are removed in the hydrotreating operation in an amount of 5 wt% or more, 10 wt% or more, 20 wt% or more, 40 wt% or more, or 50 wt% or more, with respect to the total weight of the mixed oil, and an upper limit of the content of the refined oil from which impurities are removed in the hydrotreating operation may be 95 wt% or less, but is not limited thereto. The present disclosure is not limited to the above range. However, in general, the lower the content of impurities in the refined oil, the higher the proportion of refined oil that may be included in the mixed oil.

- [124] In addition, the present disclosure provides a system for producing syngas containing hydrogen from waste plastic pyrolysis oil, the system including: a dehydrator performing dehydration by applying a voltage to a first mixed solution obtained by mixing waste plastic pyrolysis oil, washing water, and a demulsifier; a hydrotreating reactor into which the first mixed solution dehydrated in the dehydrator and hydrogen gas are introduced and in which refined oil from which impurities are removed is produced by hydrotreating the first mixed solution in the presence of a hydrotreating catalyst; and a gasification reactor for gasifying the refined oil from which impurities are removed.
- [125] The contents described for the method for producing syngas containing hydrogen from waste plastic pyrolysis oil may be equally applied to the description of the system for producing syngas containing hydrogen from waste plastic pyrolysis oil to the extent of overlap.
- [126] The dehydrator according to an embodiment of the present disclosure may be provided with a vertical electrode. The number of vertical electrodes provided in the dehydrator according to an embodiment of the present disclosure may be at least two, specifically, four or more, more specifically, six or more, and as an upper limit, twenty or fewer, but is not limited thereto.
- [127] The dehydrator according to an embodiment of the present disclosure may include a coalescer therein. The coalescer is a device that collects fine droplets to form large droplets, and any device commonly used in the industry may be used. The coalescer is not particularly limited.
- [128] The first mixed solution dehydrated in the dehydrator may be introduced into the coalescer according to an embodiment of the present disclosure, and an additionally dehydrated first mixed solution may be produced. When a dehydrator including the coalescer is used, the additionally dehydrated first mixed solution is also introduced into the hydrotreating reactor together with the hydrogen gas.
- [129] The system for producing syngas containing hydrogen from waste plastic pyrolysis oil according to an embodiment of the present disclosure may further include a separator 22-1 for subjecting the refined oil from which impurities are removed to gas-liquid separation, the refined oil being produced in the hydrotreating reactor.
- [130] The number of separators according to an embodiment of the present disclosure may be two to four, specifically, three or four, or four as illustrated in FIG. 1 with separators 22-1 to 22-4. four. When the above range is satisfied, the formation of the ammonium chloride salt may be minimized even under a low-temperature condition for oil-water separation because the refined oil contains traces of  $\text{NH}_3$  and  $\text{HCl}$ . In addition, oil refining and petrochemical processes using the refined oil as a feedstock may be stably performed without adding an additional salt remover to the refined oil

later.

- [131] The system for producing syngas containing hydrogen from waste plastic pyrolysis oil according to an embodiment of the present disclosure may further include a recycle gas compressor recovering unreacted hydrogen gas from the separated gas stream from the separator and adding the recovered unreacted hydrogen gas as recycle gas 16 to the hydrotreating reactor 20.

### **Mode for the Invention**

- [132] Hereinafter, the method and system for producing syngas containing hydrogen from waste plastic pyrolysis oil according to embodiments of the present disclosure will be described in more detail with reference to Examples. However, the following Examples are only reference examples for describing the embodiments of the present disclosure in detail, and the embodiment of the present disclosure is not limited thereto and may be implemented in various forms. Unless otherwise defined, all technical terms and scientific terms used herein have the same meaning as commonly understood by those skilled in the art to which the present disclosure pertains. In addition, the terms used in the present disclosure are only to effectively describe specific Examples, but are not intended to limit the present disclosure.

[133] **[Example 1]**

- [134] Waste plastic pyrolysis oil, washing water, and polyethylene glycol having a weight average molecular weight of 500 were added to a dehydrator under conditions of 150°C and 10 bar at a volume ratio of 1:0.25:0.0001, and stirring was performed, thereby preparing a first mixed solution. The first mixed solution was separated into oil and water by applying an alternating current voltage of 15 kV through a vertical electrode, and then dehydration was performed by removing the water layer.

- [135] At this time, in the waste plastic pyrolysis oil, the content of moisture was about 5,000 ppm or more, and impurities at high concentrations of 500 ppm or more of nitrogen (N), 200 ppm or more of chlorine (Cl), and 20 vol% or more of olefins were contained.

- [136] A second mixed solution was prepared by mixing dimethyl disulfide in an amount of 0.04 parts by weight with respect to 100 parts by weight of the first mixed solution dehydrated in the dehydrator, and then the second mixed solution was hydrotreated under conditions of 300°C and 70 bar, thereby producing refined oil from which impurities were removed.

- [137] Mixed oil obtained by mixing the refined oil from which impurities were removed and atmospheric residue having a boiling point of 380°C or higher derived from crude oil at a weight ratio of 1:1 was gasified under conditions of 600°C and 2 bar, thereby obtaining syngas containing hydrogen.

[138] **[Examples 2 and 3]**

[139] Syngas containing hydrogen was obtained under the same conditions as those in Example 1, except that the waste plastic pyrolysis oil, washing water, and polyethylene glycol were introduced into the dehydrator at the volume ratio shown in Table 1.

[140] **[Example 4]**

[141] Syngas containing hydrogen was obtained under the same conditions as those in Example 1, except that a direct current voltage was applied through a horizontal electrode.

[142] **[Example 5]**

[143] Syngas containing hydrogen was obtained under the same conditions as those in Example 1, except that the dehydration of the first mixed solution was performed under a temperature condition of 120°C.

[144] **[Example 6]**

[145] Syngas containing hydrogen was obtained under the same conditions as those in Example 1, except that the waste plastic pyrolysis oil and polyethylene glycol were introduced at a volume ratio of 1:0.00001 and the hydrotreating was performed under a condition of a pressure of 180 bar in Example 5.

[146] **[Example 7]**

[147] Syngas containing hydrogen was obtained under the same conditions as those in Example 1, except that after the first mixed solution was dehydrated, the first mixed solution was additionally dehydrated through a coalescer.

[148] **[Comparative Example 1]**

[149] Syngas containing hydrogen was obtained under the same conditions as those in Example 1, except that washing water was not added as in Example 1.

[150] **[Comparative Example 2]**

[151] Syngas containing hydrogen was obtained under the same conditions as those in Example 1, except that polyethylene glycol was not introduced as in Example 1.

[152] **[Comparative Example 3]**

[153] Syngas containing hydrogen was obtained under the same conditions as those in Example 1, except that a voltage was not applied in Example 1.

[154] **[Comparative Example 4]**

[155] Syngas containing hydrogen was obtained under the same conditions as those in Example 1, except that dimethyl disulfide was not mixed with the dehydrated first mixed solution as in Example 1.

[156] **Evaluation Examples**

[157] **Measurement Methods**

[158] After the dehydration operation was completed, the contents of moisture and chlorine in the obtained mixed solution and the content of chlorine in the refined oil from which



Dehydration	Washing water (volume ratio)	0.25	0.50	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	
	Demulsifier (volume ratio)	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	
	Temperature (°C)	150	150	150	150	120	120	150	150	150	150	150	
	Pressure (bar)	10	10	10	10	10	10	10	10	10	10	10	
	Voltage	Type	AC	AC	AC	DC	AC	AC	AC	AC	AC	-	AC
		Electrode	Vertical	Vertical	Vertical	Horizontal	Vertical	Vertical	Vertical	Vertical	Vertical	-	Vertical
	Presence or absence of coalescer	X	X	X	X	X	X	X	O	X	X	X	X
Hydrotreating	Whether sulfur source is mixed or not	O	O	O	O	O	O	O	O	O	O	X	
	Temperature (°C)	300	300	300	300	300	300	300	300	300	300	300	
	Pressure (bar)	70	70	70	70	70	180	70	70	70	70	70	
Content of moisture after de-		592	783	672	595	721	895	510	2485	4416	3840	610	

hydration (ppm)											
Content of Cl after dehydration (ppm)	562	552	614	560	646	739	483	1024	1118	1105	564
Catalyst life (hr)	>72 0	>72 0	>72 0	>72 0	>72 0	>72 0	>72 0	<576	<576	<576	<336
Content of Cl in refined oil (ppm)	<1	<1	<1	<1	<1	<1	<1	13.7	18.0	16.8	11.7
Particle adhesion rate (%)	0.20	0.18	0.20	3.5	0.21	0.20	0.1 8	0.24	0.21	-	0.20

[165] As shown in Table 1, in Comparative Examples 1 to 3, the introduction of washing water, introduction of demulsifier, and application of voltage were set differently from Examples, and as a result, the effect of removing moisture and Cl by the dehydration operation was poor. As waste plastic pyrolysis oil containing a large amount of impurities was hydrotreated, the content of Cl in the refined oil was high, and the hydrotreating catalyst was deactivated relatively quickly. In Comparative Example 4, it was confirmed that although moisture and some impurities in the waste plastic pyrolysis oil were sufficiently removed in the dehydration operation, the hydrotreating catalyst was deactivated within a short time due to an insufficient content of sulfur, and thus, when the refining process was maintained for a long period time, the content of Cl in the refined oil was high as in other Comparative Examples. In addition, it may be expected that the content of refined oil in the gasified mixed oil is inevitably limited because Cl contained in a large amount in the refined oil has a potential to cause corrosion of the gasification reactor.

[166] However, in Examples 1 to 7 according to the method for producing syngas containing hydrogen from waste plastic pyrolysis oil of the present disclosure, a significant amount of moisture contained in the waste plastic pyrolysis oil was removed through the dehydration operation, and a sulfur source was added, and as a result, the activity of the hydrotreating catalyst was maintained for a remarkably long time. In addition, since some water-soluble impurities were preemptively removed in the dehydration operation and hydrotreating was performed, a content of impurities such as Cl in the refined oil was low. Therefore, it was confirmed that a large amount of refined oil was added in the gasification process even when the impurities were not ad-

ditionally removed.

- [167] Meanwhile, when an alternating current voltage was applied using a vertical electrode, it was confirmed that the adhesion rate of impurity particles derived from char in the pyrolysis oil to the electrode surface was significantly low even when the process was continued for longer than three months. Through this, it was appreciated that when an alternating current voltage was applied or a vertical electrode was used, there was no need to stop the process for washing the inside of the reactor, and as a result, process efficiency was significantly improved.
- [168] In addition, in the case of Example 6, although the dehydration result was poor compared to other Examples, the content of Cl impurities in the refined hydrocarbons was significantly low as the hydrotreating was performed under a high pressure condition. However, since ammonia and hydrogen chloride were produced in excess due to the high pressure, it was confirmed that a relatively large amount of ammonium chloride salt was formed even at the temperature at which the hydrotreating was performed.
- [169] In Example 7, as the additional dehydration was performed using a coalescer, the contents of moisture and chlorine after the dehydration were lower than those in other Examples. Therefore, it may be expected that the activation time of the catalyst, the process stability, and the quality of syngas containing hydrogen are relatively superior to those in other Examples.
- [170] As set forth above, the method and system for producing syngas containing hydrogen according to the present disclosure may minimize formation of an ammonium chloride salt ( $\text{NH}_4\text{Cl}$ ) in a refining process of waste plastic pyrolysis oil containing impurities including chlorine and nitrogen.
- [171] The method and system for producing syngas containing hydrogen according to the embodiments of the present disclosure may prevent deactivation of the catalyst due to moisture, such that the refining efficiency may be excellent, and the process may be operated for a long period of time.
- [172] The method and system for producing syngas containing hydrogen according to the embodiments of the present disclosure may significantly reduce a content of impurities such as chlorine, nitrogen, oxygen, and metals and a content of olefins from waste plastic pyrolysis oil and may thus produce syngas containing hydrogen.
- [173] The method and system for producing syngas containing hydrogen according to the present disclosure may be used in production of eco-friendly syngas containing hydrogen using waste plastics as a feedstock.
- [174] Although the embodiments of the present disclosure have been described, the present disclosure is not limited to these embodiments, and those skilled in the art will appreciate that various modifications and alterations may be made without departing

from the concept and scope of the claims described below.

[175] While the present disclosure has been shown and described with reference to certain embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the present disclosure and any equivalents. Therefore, the scope of the present disclosure should not be limited to the above-described embodiments but should include the equivalents thereof.

[176] In the above-described embodiments, all operations may be selectively performed, or part of the operations may be omitted. In each embodiment, the operations are not necessarily performed in accordance with the described order and may be rearranged. The embodiments disclosed in this specification and drawings are only examples to facilitate an understanding of the present disclosure, and the present disclosure is not limited thereto. That is, it should be apparent to those skilled in the art that various modifications can be made on the basis of the technological scope of the present disclosure.

[177] The embodiments of the present disclosure have been described in the drawings and specification. Although specific terminologies are used here, those are only to describe the embodiments of the present disclosure. Therefore, the present disclosure is not restricted to the above-described embodiments and many variations are possible within the scope of the present disclosure. It should be apparent to those skilled in the art that various modifications can be made on the basis of the technological scope of the present disclosure in addition to the embodiments disclosed herein. Furthermore, the embodiments may be combined to form additional embodiments.

[178] List of Numerals in the Figures

[179] 2 waste plastic pyrolysis oil

[180] 4 feed tank

[181] 6 water

[182] 8 demulsifier

[183] 10 dehydrator

[184] 12 coalescer

[185] 14 dehydrated first mixed solution

[186] 16 recycle gas

[187] 17 H<sub>2</sub>

[188] 18 Sulfur source

[189] 20 hydrotreating reactor

[190] 21 hydrotreated second mixed solution

[191] 22-1 to 22-4 gas liquid separators

[192] 24 off-gas

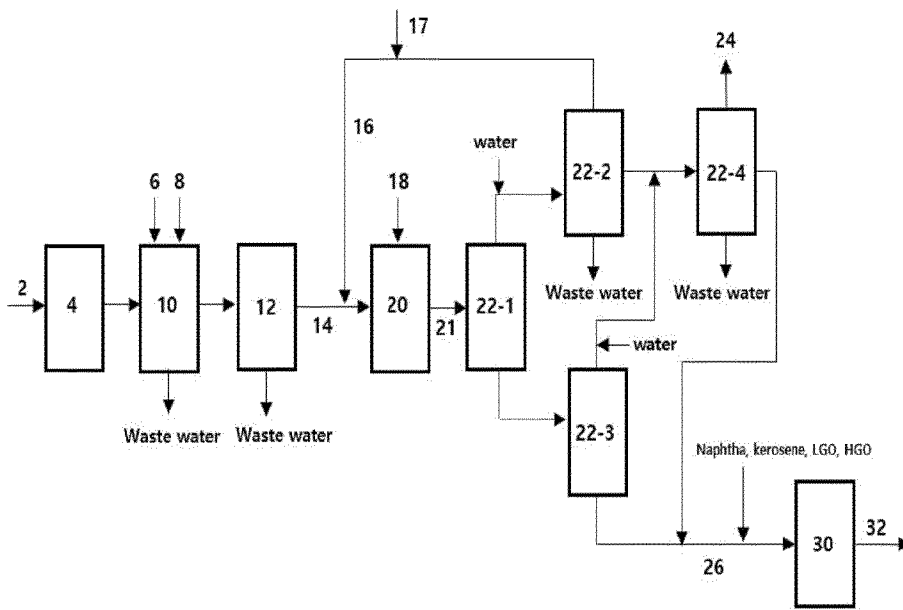
- [193] 26 refined oil
- [194] 30 gasification unit
- [195] 32 syngas

## Claims

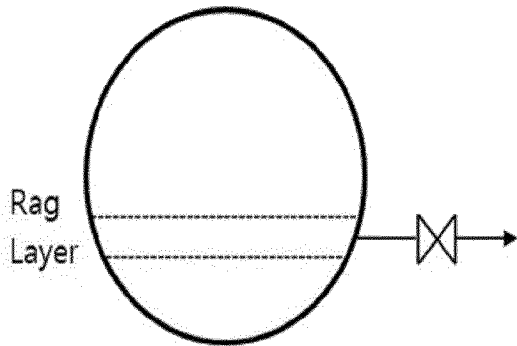
- [Claim 1] a method for producing syngas containing hydrogen from waste plastic pyrolysis oil, the method comprising:  
a dehydration operation of applying a voltage to a first mixed solution obtained by mixing the waste plastic pyrolysis oil, washing water, and a demulsifier to dehydrate the first mixed solution;  
a hydrotreating operation of hydrotreating a second mixed solution obtained by mixing the first mixed solution dehydrated in the dehydration operation and a sulfur source to produce refined oil from which impurities are removed; and  
a gasification operation of gasifying the refined oil from which impurities are removed.
- [Claim 2] The method of claim 1, wherein in the dehydration operation, the waste plastic pyrolysis oil is mixed in a greater volume than the washing water.
- [Claim 3] The method of claim 2, wherein in the dehydration operation, the waste plastic pyrolysis oil and the washing water are mixed in the first mixed solution at a volume ratio of 1:0.001 to 1:0.5.
- [Claim 4] The method of claim 1, wherein in the dehydration operation, the waste plastic pyrolysis oil and the demulsifier are mixed in the first mixed solution at a volume ratio of 1:0.000001 to 1:0.001.
- [Claim 5] The method of claim 1, wherein the voltage is applied as an alternating current or a combination of an alternating current and a direct current.
- [Claim 6] The method of claim 1, wherein the voltage is applied through at least one pair of vertical electrodes.
- [Claim 7] The method of claim 1, further comprising, after the application of the voltage in the dehydration operation, removing a rag layer from the first mixed solution.
- [Claim 8] The method of claim 1, wherein the dehydration operation is performed under a temperature condition of 20°C to 300°C.
- [Claim 9] The method of claim 1, wherein a ratio of a content of moisture in the waste plastic pyrolysis oil to a content of moisture in the first mixed solution dehydrated in the dehydration operation is 1:0.0001 to 1:0.9.
- [Claim 10] The method of claim 1, wherein the first mixed solution in the dehydration operation is additionally dehydrated by condensation of moisture.
- [Claim 11] The method of claim 1, wherein a weight ratio of nitrogen to chlorine

- in the second mixed solution is 1:1 to 1:10.
- [Claim 12] The method of claim 1, wherein the sulfur source includes sulfur-containing oil.
- [Claim 13] The method of claim 12, wherein the sulfur-containing oil is included in an amount of less than 0.5 parts by weight with respect to 100 parts by weight of the first mixed solution dehydrated in the dehydration operation.
- [Claim 14] The method of claim 1, wherein the sulfur source includes one or two or more sulfur-containing organic compounds selected from a disulfide-based compound, a sulfide-based compound, a sulfonate-based compound, and a sulfate-based compound.
- [Claim 15] The method of claim 1, wherein the hydrotreating is performed in the presence of a molybdenum-based hydrotreating catalyst.
- [Claim 16] The method of claim 15, wherein the molybdenum-based hydrotreating catalyst is 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.
- [Claim 17] The method of claim 1, wherein the hydrotreating operation is performed under a pressure condition of 50 bar to 150 bar.
- [Claim 18] The method of claim 1, further comprising, after the hydrotreating operation, subjecting a stream including the refined oil from which impurities are removed to gas-liquid separation and then washing the gas-liquid separated stream with water.
- [Claim 19] The method of claim 1, wherein in the gasification operation, a refined fraction separated by distilling the refined oil from which impurities are removed is gasified.
- [Claim 20] The method of claim 1, wherein in the gasification operation, mixed oil obtained by mixing the refined oil from which impurities are removed in the hydrotreating operation and petroleum hydrocarbons is gasified.

[Fig. 1]



[Fig. 2]



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2024/003437

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
C01B 3/34(2006.01); C10G 1/00(2006.01); C10G 1/10(2006.01); C10G 33/02(2006.01); C10G 45/06(2006.01); C10G 67/02(2006.01)		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) C01B 3/34(2006.01); C07C 1/00(2006.01); C10B 53/07(2006.01); C10G 1/02(2006.01); C10G 1/10(2006.01); C10G 25/00(2006.01); C10G 33/02(2006.01); C10G 33/04(2006.01); C10G 47/00(2006.01)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models Japanese utility models and applications for utility models		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS(KIPO internal) & Keywords: syngas, hydrogen, waste pyrolysis oil, dehydration, hydrotreating		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2021-204820 A1 (TOTAL RESEARCH & TECHNOLOGY FELUY) 14 October 2021 (2021-10-14) claims 1-10; page 8-42; figure 2	1-20
Y	EP 3907267 A1 (BASF SE) 10 November 2021 (2021-11-10) claims 1-15; paragraphs [0105]-[0118]	1-20
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A	US 8277643 B2 (HUBER, G. W. et al.) 02 October 2012 (2012-10-02) the whole document	1-20
A	US 2022-0380680 A1 (EASTMAN CHEMICAL COMPANY) 01 December 2022 (2022-12-01) the whole document	1-20
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search <b>24 June 2024</b>		Date of mailing of the international search report <b>26 June 2024</b>
Name and mailing address of the ISA/KR <b>Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea</b> Facsimile No. +82-42-481-8578		Authorized officer <b>HEO, Joo Hyung</b> Telephone No. +82-42-481-5373

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/KR2024/003437**

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