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(54) METHOD AND DEVICE FOR REFINING WASTE PLASTIC PYROLYSIS OIL

(57) The present invention provides a method and device for refining waste plastic pyrolysis oil, the method including: (S1) subjecting a waste plastic pyrolysis oil feedstock to a heat treatment by charging the waste plastic pyrolysis oil feedstock into a rotary kiln reactor and increasing a temperature of the rotary kiln reactor; (S2) recovering a gas component from a product in the step (S1); (S3) separating a high boiling point wax component from the recovered gas component and re-supplying the separated high boiling point wax component to the rotary kiln reactor in the step (S1); and (S4) recovering refined oil from the gas component from which the high boiling point wax component is removed.

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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a method and device for refining waste plastic pyrolysis oil.

BACKGROUND

[0002] Waste plastics, which are produced using petroleum as a feedstock, are difficult to recycle and are mostly disposed of as garbage. These wastes take a long time to degrade in nature, which causes contamination of the soil and serious environmental pollution. As a method for recycling waste plastics, there is a method for pyrolyzing waste plastics and converting the pyrolyzed waste plastics into usable oil, and the obtained oil is called waste plastic pyrolysis oil.

[0003] However, pyrolysis oil obtained by pyrolyzing waste plastics cannot be directly 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 than oil produced from crude oil by a general method, and therefore, pyrolysis oil needs to go through a post-treatment process.

[0004] As a post-treatment process according to the related art, a process of hydrotreating waste plastic pyrolysis oil in the presence of a hydrotreating catalyst to remove impurities such as chlorine, nitrogen, and other metals has been performed. However, in this process, an excessive amount of HCl is produced due to a high content of chlorine contained in the waste plastic pyrolysis oil, which causes equipment corrosion, abnormal reactions, deterioration of product properties, and the like. In particular, HCl reacts with a nitrogen compound to produce an ammonium salt (NH_4Cl), and the ammonium salt causes corrosion of a reactor, which causes not only a reduction in durability but also various process problems such as a differential pressure, blockage of a reactor, and a reduction in process efficiency.

[0005] Meanwhile, since waste plastic pyrolysis oil is a mixture of hydrocarbon oils having various boiling points and various molecular weight distributions, and a composition of impurities in the pyrolysis oil or reaction activity varies depending on the boiling point and molecular weight distribution characteristics of the mixture of hydrocarbon oils, the waste plastic pyrolysis oil cannot be directly used in the petrochemical industry or in the field, and needs to go through a high-value-adding process such as a separation process by boiling point or a lightening process. In the mixture of hydrocarbon oils, olefins, in particular, light olefins such as ethylene and propylene, have been widely used in the petrochemical industry.

[0006] A hydrocracking process has been performed as a lightening process to realize high-value-added waste plastic pyrolysis oil. However, waste plastic pyrolysis oil contains an excessive amount of impurities such as chlorine, nitrogen, sulfur, oxygen, and metals compared to crude oil, natural gas, naphtha oil, and the like. Therefore, during the hydrocracking process, reaction activity is significantly reduced due to the impurities, and process efficiency is also reduced because the hydrocracking process is performed separately from the hydrotreating process.

[0007] Therefore, there is a need for a technique that may effectively remove impurities in pyrolysis oil and achieve lightening of pyrolysis oil without using a post-treatment process such as hydrotreating or hydrocracking.

SUMMARY

[0008] The present invention aims to providing a method and device for refining waste plastic pyrolysis oil that may effectively reduce impurities in waste plastic pyrolysis oil, and at the same time, may realize high-value-added pyrolysis oil.

[0009] The present invention further aims to providing a method and device for refining waste plastic pyrolysis oil that may implement a stable process without corrosion or blockage of a reactor.

[0010] Against this background, the invention relates to a method for refining waste plastic pyrolysis oil includes: (S1) subjecting a waste plastic pyrolysis oil feedstock to a heat treatment by charging the waste plastic pyrolysis oil feedstock into a rotary kiln reactor and increasing a temperature of the rotary kiln reactor; (S2) recovering a gas component from a product in the step (S1); (S3) separating a high boiling point wax component from the recovered gas component and re-supplying the separated high boiling point wax component to the rotary kiln reactor in the step (S1); and (S4) recovering refined oil from the gas component from which the high boiling point wax component is removed.

[0011] The waste plastic pyrolysis oil feedstock may be liquid pyrolysis oil containing 10 to 30 wt% of Naphtha, 20 to 30 wt% of KERO, 10 to 30 wt% of LGO, and 30 to 50 wt% of VGO.

[0012] In the step (S1), the heat treatment may be performed by increasing the temperature of the rotary kiln reactor to a third temperature.

[0013] The third temperature may be 400 to 600°C.

[0014] When the temperature of the rotary kiln reactor is increased to the third temperature in the step (S1), a temperature increase rate may be 0.5°C/min to 5°C/min.

[0015] The method may further include, before the step (S1): (S1-1) subjecting the waste plastic pyrolysis oil feedstock

to a first heat treatment by increasing a temperature of the rotary kiln reactor to a first temperature; and (S1-2) subjecting the waste plastic pyrolysis oil feedstock to a second heat treatment by increasing a temperature of the rotary kiln reactor to a second temperature, wherein the temperature of the rotary kiln reactor is increased by sequentially heating the rotary kiln reactor from the first temperature to the third temperature.

[0016] The first temperature may be 50 to 150°C.

[0017] The second temperature may be 220 to 300°C.

[0018] In the step (S1), the heat treatment may be performed by adding an additive.

[0019] The additive may include a metal oxide catalyst or a composite catalyst in which an active metal is supported on a metal oxide carrier.

[0020] The method may further include, before the step (S1), (S0) charging waste plastics into a pyrolysis reactor and pyrolyzing the waste plastics at a temperature of 300 to 600°C in a non-oxidizing atmosphere to produce a waste plastic pyrolysis oil feedstock.

[0021] The pyrolysis reactor may include a rotary kiln reactor.

[0022] The refined oil recovered in the step (S4) may have a content of chlorine reduced by 50% or more compared to the waste plastic pyrolysis oil feedstock in the step (S1).

[0023] The refined oil recovered in the step (S4) may have a content of each of nitrogen, sulfur, and oxygen reduced by 20% or more compared to the waste plastic pyrolysis oil feedstock in the step (S1).

[0024] A weight ratio of the refined oil recovered in the step (S4) to light oil in the waste plastic pyrolysis oil feedstock in the step (S1) may be 1.3 or more.

[0025] Further, the present invention relates to a device for refining waste plastic pyrolysis oil, wherein the device includes: a rotary kiln reactor configured to receive a waste plastic pyrolysis oil feedstock; a gas separator configured to receive a gas component from the rotary kiln reactor; a condenser configured to receive a light gas component from the gas separator; and a re-supply line configured to re-supply a high boiling point wax component separated in the gas separator to the rotary kiln reactor.

[0026] The rotary kiln reactor is preferably configured for carrying out a method of the invention.

[0027] The rotary kiln reactor may sequentially include a first zone, a second zone, and a third zone in a direction from a feedstock inlet to an outlet.

[0028] The rotary kiln reactor may include a batch reactor.

[0029] Other features and aspects will be apparent from the following detailed description, the drawings, and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030]

FIG. 1 illustrates a block diagram of a method and device for refining waste plastic pyrolysis oil according to an exemplary embodiment.

FIG. 2 illustrates a block diagram of a method and device for refining waste plastic pyrolysis oil that separate a solid component 5 containing char and the like from a rotary kiln reactor 100 and re-supply the separated solid component 5 to the rotary kiln reactor 100 together with a high boiling point wax component 3 according to an exemplary embodiment.

FIG. 3 illustrates a block diagram of a method and device for refining waste plastic pyrolysis oil that pyrolyze waste plastics 6 in a pyrolysis reactor 400 to produce a waste plastic pyrolysis oil feedstock 1 according to an exemplary embodiment.

FIG. 4 illustrates a block diagram of a method and device for refining waste plastic pyrolysis oil that re-supply refined oil 10 recovered from a condenser 300 to a rotary kiln reactor 100 together with a high boiling point wax component 3 according to an exemplary embodiment.

FIG. 5A illustrates a rotary kiln reactor according to an exemplary embodiment, and FIG. 5B illustrates a rotary kiln reactor including a first zone, a second zone, and a third zone according to an exemplary embodiment.

DETAILED DESCRIPTION OF EMBODIMENTS

[0031] As used herein, unless otherwise defined, a unit of "%" mentioned in the present specification refers to "wt%".

[0032] Further, unless otherwise defined, a unit of "ppm" mentioned in the present specification refers to "mass ppm".

[0033] Further, unless otherwise defined, a boiling point mentioned in the present specification refers to a boiling point at 1 atm and 25°C.

[0034] Further, unless otherwise defined, a density mentioned in the present specification refers to a density at 1 atm and 25°C.

[0035] Further, unless otherwise defined, a high boiling point wax component mentioned in the present specification

refers to a mixture of hydrocarbons that may exist in a solid state without being dissolved in water during a reaction process or a transfer process.

[0036] Yet further, unless otherwise defined, impurities mentioned in the present specification include chlorine impurities, nitrogen impurities, oxygen impurities, or sulfur impurities.

[0037] Pyrolysis oil obtained by pyrolyzing waste plastics cannot be directly 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 than oil produced from crude oil by a general method, and therefore, pyrolysis oil needs to go through a post-treatment process.

[0038] As a post-treatment process according to the related art, a process of hydrotreating waste plastic pyrolysis oil in the presence of a hydrotreating catalyst to remove chlorine, nitrogen, and other metal impurities has been performed. However, an excessive amount of HCl is produced due to a high content of chlorine impurities contained in the waste plastic pyrolysis oil, which causes equipment corrosion, abnormal reactions, deterioration of product properties, and the like. In particular, HCl reacts with a nitrogen compound to produce an ammonium salt (NH_4Cl), and the ammonium salt causes corrosion of a reactor, which causes not only a reduction in durability but also various process problems such as a differential pressure and a reduction in process efficiency. In addition, a hydrocracking process has been performed as a lightening process to realize high-value-added waste plastic pyrolysis oil. However, as described above, waste plastic pyrolysis oil contains an excessive amount of impurities such as chlorine, nitrogen, and metals compared to crude oil, natural gas, naphtha oil, and the like. Therefore, during the hydrocracking process, reaction activity is significantly reduced due to the impurities, and process efficiency is also reduced because the hydrocracking process is performed separately from the hydrotreating process.

[0039] The present invention provides a method for refining waste plastic pyrolysis oil, the method including: (S1) subjecting a waste plastic pyrolysis oil feedstock to a heat treatment by charging the waste plastic pyrolysis oil feedstock into a rotary kiln reactor and increasing a temperature of the rotary kiln reactor; (S2) recovering a gas component from a product in the step (S1); (S3) separating a high boiling point wax component from the recovered gas component and re-supplying the separated high boiling point wax component to the rotary kiln reactor in the step (S1); and (S4) recovering refined oil from the gas component from which the high boiling point wax component is removed. Through this, it is possible to effectively remove impurities in waste plastic pyrolysis oil and improve a degree of lightening, such that high-value-added pyrolysis oil may be realized, and the process may be stably performed without corrosion or blockage of a reactor.

[0040] Specifically, the step (S1) is a step of subjecting a waste plastic pyrolysis oil feedstock 1 to a heat treatment by charging the waste plastic pyrolysis oil feedstock 1 into a rotary kiln reactor 100 and increasing a temperature of the rotary kiln reactor 100, and in this case, the waste plastic pyrolysis oil feedstock 1 may be a mixture of liquid hydrocarbon oils to be produced by pyrolyzing waste plastics in a step (S0), which will be described below.

[0041] Considering the rotary kiln reactor 100 that performs a reaction through rotation while heating the bottom of the reactor and unique characteristics of liquid pyrolysis oil, impurity removal efficiency and lightening efficiency may be significantly improved by using liquid waste plastic pyrolysis oil as a feedstock rather than solid waste plastics.

[0042] That is, the present invention relates to a refining method for producing refined oil 10 using waste plastic pyrolysis oil as a feedstock, rather than producing pyrolysis oil using solid waste plastics as a feedstock, and in particular, to a method for refining waste plastic pyrolysis oil having significantly improved impurity removal efficiency and lightening efficiency.

[0043] The waste plastic pyrolysis oil feedstock 1 may contain various impurities in addition to the hydrocarbon oil. For example, the waste plastic pyrolysis oil feedstock 1 may contain impurities such as a chlorine compound, a nitrogen compound, a sulfur compound, an oxygen compound, and a metal compound, and specifically, may contain 500 ppm or more of nitrogen, 100 ppm or more of chlorine, 30 ppm or more of sulfur, 0.7 wt% or more of oxygen, 20 vol% or more of olefins, and 1 vol% or more of conjugated diolefins.

[0044] The mixture of hydrocarbon oils present in the waste plastic pyrolysis oil feedstock 1 may contain Naphtha having 8 or fewer carbon atoms and a boiling point of 150°C or lower, KERO having 9 to 17 carbon atoms and a boiling point of 150 to 265°C, LGO having 18 to 20 carbon atoms and a boiling point of 265 to 340°C, and VGO having 21 or more carbon atoms and a boiling point of 340°C or higher in various ranges. Typically, the mixture of hydrocarbon oils contains an excessive amount of heavy oil such as LGO or VGO/AR compared to light oil such as Naphtha or KERO.

[0045] In an exemplary embodiment, the waste plastic pyrolysis oil feedstock 1 may be liquid pyrolysis oil containing 10 to 30 wt% of Naphtha, 20 to 30 wt% of KERO, 10 to 30 wt% of LGO, and 30 to 50 wt% of VGO. Specifically, the waste plastic pyrolysis oil feedstock 1 may be liquid pyrolysis oil containing 10 to 30 wt% of Naphtha having 8 or fewer carbon atoms and a boiling point of 150°C or lower, 20 to 30 wt% of KERO having 9 to 17 carbon atoms and a boiling point of 150 to 265°C, 10 to 30 wt% of LGO having 18 to 20 carbon atoms and a boiling point of 265 to 340°C, and 30 to 50 wt% of VGO having 21 or more carbon atoms and a boiling point of 340°C or higher. Using liquid pyrolysis oil that satisfies the above composition ratio may be advantageous because the impurity removal efficiency and lightening efficiency are improved.

[0046] Hereinafter, the method and device for refining waste plastic pyrolysis oil will be described with reference to

FIGS. 1 to 4.

[0047] In the step (S1), when the waste plastic pyrolysis oil feedstock 1 is charged into the rotary kiln reactor 100 and then subjected to a heat treatment by increasing the temperature of the rotary kiln reactor 100, a solid component 5 containing char, and pyrolysis gas, which is a gas component, are produced. Through the heat treatment, impurities such as chlorine, nitrogen, sulfur, and oxygen contained in the waste plastic pyrolysis oil feedstock 1 may be removed.

[0048] In an exemplary embodiment, in the step (S1), the heat treatment may be performed by increasing the temperature of the rotary kiln reactor 100 to a third temperature.

[0049] In an exemplary embodiment, the third temperature may be 400 to 600°C. The heat treatment is performed by increasing the temperature of the rotary kiln reactor 100 to the third temperature, such that impurities may be removed and lightening may be performed. Specifically, the third temperature may be 400 to 550°C, and more specifically, 400 to 500°C. In addition, as described below, before the step (S1), a heat treatment process including steps (S1-1) and (S1-2) is further performed, such that production of a high boiling point wax component 3 may be minimized, and the lightening efficiency may be further improved in conjunction with the steps (S2) to (S4).

[0050] In an exemplary embodiment, when the temperature of the rotary kiln reactor 100 is increased to the third temperature in the step (S1), a temperature increase rate may be 0.5°C/min to 5°C/min. When the heat treatment is performed by increasing the temperature of the rotary kiln reactor 100 at the above temperature increase rate, the impurity removal efficiency and lightening efficiency may be improved. Specifically, the temperature increase rate may be 0.5°C/min to 3°C/min, and more specifically, 0.5°C/min to 2°C/min.

[0051] The step (S2) is a step of recovering a gas component from a product in the step (S1), and specifically, the solid component 5 and the gas component are respectively separated at an outlet of the rotary kiln reactor 100, and the gas component may be recovered. As illustrated in FIG. 2, the separated solid component 5 may be re-treated by being re-supplied to the reactor in the step (S1) together with the high boiling point wax component 3 separated in the step (S3). Therefore, waste disposal costs may be reduced to improve economic efficiency, and at the same time, the process efficiency may be improved.

[0052] The gas component recovered in the step (S2) contains a mixture of hydrocarbon oils having various molecular weight distributions, and also contains the high boiling point wax component 3. The high boiling point wax component 3 refers to a hydrocarbon mixture that is insoluble in water during a reaction process or a transfer process or has a relatively high boiling point, and may refer to, for example, a wax component having a high molecular weight of C20 or higher. However, this is merely an example, and the standard of the high boiling point wax component 3 may vary depending on the environment in which it is to be separated and removed, such as production conditions or use environment of pyrolysis oil. In a case where the refined oil 10 is recovered by performing a refining process while containing the high boiling point wax component 3 as is, problems such as blockage of the reactor or difficulty in transfer may occur, and a content of heavy oil in the recovered refined oil 10 is high, which makes it difficult to realize high-value-added waste plastic pyrolysis oil. As illustrated in FIG. 1, (S3) separating a high boiling point wax component 3 from the recovered gas component and re-supplying the separated high boiling point wax component 3 to the rotary kiln reactor 100 in the step (S1) and (S4) recovering refined oil 10 from the gas component from which the high boiling point wax component 3 is removed are performed, such that refined oil 10 having improved impurity removal efficiency and an improved degree of lightening may be obtained, and process trouble problems such as blockage of the reactor may be solved. In this case, the process of separating the high boiling point wax component 3 and re-supplying the separated high boiling point wax component 3 to the rotary kiln reactor 100 in the step (S3) may be repeated one or more times.

[0053] That is, a series of processes including the steps (S1) to (S4) is performed, such that refined oil 10 having significantly reduced impurities and a significantly improved degree of lightening may be obtained without process troubles such as blockage of the reactor.

[0054] In the step (S1), before the temperature of the rotary kiln reactor 100 is increased to the third temperature, a preliminary heat treatment is performed, such that the impurity removal efficiency and lightening efficiency may be further improved.

[0055] In an exemplary embodiment, the method may further include, before the step (S1): (S1-1) subjecting the waste plastic pyrolysis oil feedstock 1 to a first heat treatment by increasing a temperature of the rotary kiln reactor 100 to a first temperature; and (S1-2) subjecting the waste plastic pyrolysis oil feedstock 1 to a second heat treatment by increasing a temperature of the rotary kiln reactor 100 to a second temperature, wherein the temperature of the rotary kiln reactor 100 may be increased by sequentially heating the rotary kiln reactor 100 from the first temperature to the third temperature.

[0056] In an exemplary embodiment, the first temperature in the step (S1-1) may be 50 to 150°C. Specifically, the first heat treatment may be performed at the first temperature in an oxygen-free atmosphere for 20 to 300 minutes. The waste plastic pyrolysis oil feedstock 1 may contain solid impurities such as a solid component formed by agglomeration of pyrolysis oil or a solid component unmelted during the waste plastic pyrolysis process. Accordingly, the first heat treatment process in the step (S1-1) is performed, such that uniformity and homogeneity of waste plastic pyrolysis oil may be improved, resulting in improvement of the process efficiency. Specifically, the first temperature may be 70 to 130°C, and more specifically, 90 to 110°C.

[0057] The second temperature in the step (S1-2) may be 220 to 300°C. Specifically, the second heat treatment may be performed at the second temperature in an oxygen-free atmosphere for 120 to 360 minutes. The second heat treatment of holding the second temperature for a predetermined time is performed, such that an impurity removal reaction such as a chlorine dissociation reaction from the waste plastic pyrolysis oil feedstock 1 may be sufficiently performed, and a resynthesis reaction of dissociated chlorine and pyrolyzed olefins may be suppressed. Specifically, the second temperature may be 230 to 290°C, and more specifically, 240 to 280°C.

[0058] As described above, before the step (S1), the preliminary heat treatment including the steps (S1-1) and (S1-2) is performed, such that impurities such as chlorine, nitrogen, sulfur, and oxygen may be effectively removed through a multi-stage temperature increase process of the rotary kiln reactor 100. In addition, production of the high boiling point wax component 3 may be minimized, and accordingly, the process efficiency may be further improved in conjunction with the steps (S2) to (S4). The steps (S1-1) and (S1-2) may be performed after a step (S0), which will be described below.

[0059] In an exemplary embodiment, when the multi-stage temperature increase process including the steps (S1-1), (S1-2), and (S1) is performed, a pressure of the rotary kiln reactor 100 may be maintained at 0.02 MPa or less, and specifically, 0.01 MPa or less.

[0060] The multi-stage temperature increase process including the steps (S1-1), (S1-2), and (S1) may be performed in various ways. For example, the temperature of the entire rotary kiln reactor 100 may be increased. As illustrated in FIG. 5A, the temperature of the entire rotary kiln reactor 100 may be increased. Specifically, the step (S1-1) of subjecting the waste plastic pyrolysis oil feedstock 1 to the first heat treatment by increasing the temperature of the entire rotary kiln reactor 100 to the first temperature, the step (S1-2) of subjecting the waste plastic pyrolysis oil feedstock 1 to the second heat treatment by increasing the temperature of the entire rotary kiln reactor 100 to the second temperature, and the step (S1) of subjecting the waste plastic pyrolysis oil feedstock 1 to the heat treatment by increasing the temperature of the entire rotary kiln reactor 100 to the third temperature may be sequentially performed.

[0061] In another exemplary embodiment, the temperature of the rotary kiln reactor 100 may be increased by sequentially heating the rotary kiln reactor 100 from the first temperature to the third temperature in a direction from a feedstock inlet to an outlet. The temperature of the rotary kiln reactor 100 is increased by sequentially heating the rotary kiln reactor 100 from the first temperature to the third temperature in the direction from the feedstock inlet to the outlet of the rotary kiln reactor 100, such that an optimal temperature gradient in the reactor is formed, and as a result, problems such as an increase in pressure and deterioration of pyrolysis efficiency may be solved. In the case of the pyrolysis technique using the rotary kiln reactor 100 in the related art, a process of increasing a temperature of the reactor by heating the reactor from the outlet side has been performed to avoid an increase in pressure. However, in this case, the pyrolysis efficiency is reduced due to uneven heating. In the case as illustrated in FIG. 5B, (S1-1) forming a first zone in which a burner 1 is located, a second zone in which a burner 2 is located, and a third zone in which a burner 3 is located in the direction from the feedstock inlet to the outlet of the rotary kiln reactor 100 and subjecting the waste plastic pyrolysis oil feedstock 1 to a first heat treatment by increasing the temperature of the rotary kiln reactor 100 to a first temperature in the first zone, (S1-2) subjecting the waste plastic pyrolysis oil feedstock 1 to a second heat treatment by increasing the rotary kiln reactor 100 to a second temperature in the second zone, and (S1) subjecting the waste plastic pyrolysis oil feedstock 1 to a heat treatment by increasing the rotary kiln reactor 100 to a third temperature in the third zone may be sequentially performed. Through this, an optical temperature gradient may be formed, which may be advantageous, and production of the high boiling point wax component 3 is minimized, such that the process efficiency may be further improved in conjunction with the steps (S2) to (S4).

[0062] In an exemplary embodiment, in the step (S1), the heat treatment may be performed by adding an additive. The heat treatment is performed by adding an additive, such that the impurity removal efficiency and lightening efficiency may be further improved. As the additive, a known additive that may be used in the pyrolysis process of the waste plastic pyrolysis oil feedstock 1 may be used.

[0063] In an exemplary embodiment, the additive may include a metal oxide catalyst or a composite catalyst in which an active metal is supported on a metal oxide carrier. The metal oxide catalyst may be magnesium oxide, calcium oxide, potassium oxide, sodium oxide, or the like. In terms of the impurity removal efficiency and lightening efficiency, the composite catalyst in which an active metal is supported on a metal oxide carrier may be preferable. The active metal may include at least one metal selected from copper, molybdenum, tungsten, and nickel. The metal oxide carrier may contain the metal oxide catalyst described above. Considering the impurity removal efficiency and lightening efficiency, a composite catalyst in which copper is supported on a calcium oxide carrier may be most preferable.

[0064] In an exemplary embodiment, the method may further include, before the step (S1), (S0) charging waste plastics 6 into a pyrolysis reactor 400 and pyrolyzing the waste plastics 6 at a temperature of 300 to 600°C in a non-oxidizing atmosphere to produce a waste plastic pyrolysis oil feedstock 1. As illustrated in FIG. 3, the waste plastic pyrolysis oil feedstock 1 may be produced by charging the solid waste plastics 6 into the pyrolysis reactor 400 and pyrolyzing the waste plastics 6, the produced waste plastic pyrolysis oil feedstock 1 may be charged into the rotary kiln reactor 100, and the heat treatment process in the step (S1) may be performed. The waste plastics may be domestic waste plastic or industrial waste plastic. The domestic waste plastic is a plastic in which PVC, PS, PET, PBT, and the like in addition

to PE and PP are mixed, and specifically, may be a mixed waste plastic containing 3 wt% or more of PVC together with PE and PP. The industrial waste plastic is industrial waste such as scrap or a defective product generated in a manufacturing process in industries, and mainly includes PE and PP. The non-oxidizing atmosphere is an atmosphere in which waste plastics do not oxidize (combust), and efficient pyrolysis may be stably performed in the above atmosphere. The pyrolysis may be performed at a temperature of 300 to 600°C in a non-oxidizing atmosphere for 150 minutes to 350 minutes, and when the holding time is satisfied, activation of the composition of the non-oxidizing atmosphere and sufficient pyrolysis may be performed.

[0065] In an exemplary embodiment, the pyrolysis reactor 400 may include a rotary kiln reactor 100. The step (S0) may be performed using a pyrolysis reactor 400 known in the related art, for example, a rotary kiln reactor 100, an autoclave reactor, a continuous reactor, an auger reactor, or a fluidized bed reactor, and in particular, it may be advantageous to perform the step (S0) using the rotary kiln reactor 100 in terms of improving the process efficiency.

[0066] The step (S4) is a step of recovering the refined oil 10 from the gas component from which the high boiling point wax component 3 is removed, and in the step (S4), the refined oil 10 may be recovered by condensing the gas component from which the high boiling point wax component 3 is removed through a cooling and liquefaction process. Specifically, the condensed component may include an oil layer in which pyrolysis gas is liquefied, and a water layer formed by liquefaction of a byproduct containing water vapor generated during the heat treatment process, and finally, the refined oil 10 may be obtained through oil-water separation. The oil layer (refined oil) may be recovered directly by separating the oil layer and the water layer through the oil-water separation, or the oil layer (refined oil) may be recovered by adsorbing the water layer and then recovering the water layer. An electric field may be applied to effectively separate the oil layer and the water layer, and the oil layer and the water layer may be separated in a short time by electrostatic adhesion due to application of the electric field. In addition, an additive may be added as necessary to increase the oil-water separation efficiency, and the additive may be a common demulsifier known in the art. As an exemplary embodiment, as illustrated in FIG. 4, the refined oil 10 recovered in the step (S4) may be re-treated by being re-supplied to the rotary kiln reactor 100 in the step (S1). Through this, the impurity removal efficiency and lightening efficiency may be further improved. The re-supply process may be repeated one or more times.

[0067] In an exemplary embodiment, the refined oil 10 recovered in the step (S4) may have a content of chlorine reduced by 50% or more compared to the waste plastic pyrolysis oil feedstock 1 in the step (S1). The refined oil 10 having such reduced content of chlorine is obtained through a series of processes including the steps (S1) to (S4). Specifically, the refined oil 10 having a content of chlorine reduced by 60% or more may be obtained, more specifically, the refined oil 10 having a content of chlorine reduced by 70% or more may be obtained, the refined oil 10 having a content of chlorine reduced by 90% or less may be obtained.

[0068] In an exemplary embodiment, the refined oil 10 recovered in the step (S4) may have a content of each of nitrogen, sulfur, and oxygen reduced by 20% or more compared to the waste plastic pyrolysis oil feedstock 1 in the step (S1). The refined oil 10 having a reduced content of each of nitrogen, sulfur, and oxygen as well as a reduced content of chlorine may be obtained through a series of processes including the steps (S1) to (S4). Specifically, the refined oil 10 having a content of each of nitrogen, sulfur, and oxygen reduced by 30% or more may be obtained, more specifically, the refined oil 10 having a content of each of nitrogen, sulfur, and oxygen reduced by 40% or more may be obtained, and the refined oil 10 having a content of each of nitrogen, sulfur, and oxygen reduced by 70% or less may be obtained.

[0069] In an exemplary embodiment, a weight ratio of the refined oil 10 recovered in the step (S4) to light oil in the waste plastic pyrolysis oil feedstock 1 in the step (S1) may be 1.3 or more. Typically, the waste plastic pyrolysis oil feedstock 1 contains an excessive amount of heavy oil such as LGO or VGO/AR compared to light oil such as H-Naphtha or KERO. However, the refined oil 10 having an improved degree of lightening may be obtained through a series of processes including the steps (S1) to (S4). Specifically, a weight ratio of the refined oil 10 to the light oil in the waste plastic pyrolysis oil feedstock 1 may be 1.5 or more, more specifically, 1.7 or more, and 3 or less.

[0070] In addition, the present invention provides a device for refining waste plastic pyrolysis oil, the device including: a rotary kiln reactor 100 into which a waste plastic pyrolysis oil feedstock 1 is introduced; a gas separator 200 into which a gas component is introduced from the rotary kiln reactor 100; a condenser 300 into which a light gas component 4 is introduced from the gas separator 200; and a re-supply line in which a high boiling point wax component 3 is separated in the gas separator 200 and the separated high boiling point wax component 3 is re-supplied to the rotary kiln reactor 100. The rotary kiln reactor 100 has an advantage of high heat treatment efficiency because it applies heat uniformly while rotating. As described above, since the liquid waste plastic pyrolysis oil is introduced into the rotary kiln reactor 100 as a feedstock rather than solid waste plastics, the impurity removal efficiency and lightening efficiency may be significantly improved.

[0071] In an exemplary embodiment, the rotary kiln reactor 100 may sequentially include a first zone, a second zone, and a third zone in a direction from a feedstock inlet to an outlet. As described above, the rotary kiln reactor 100 including the first zone, the second zone, and the third zone may perform a multi-stage temperature increase process. Specifically, a step (S1-1), a step (S1-2), and a step (S1) may be performed in the first zone, the second zone, and the third zone, respectively. In this case, an optimal temperature gradient may be formed, and the impurity removal efficiency and

lightening efficiency may be further improved. As another exemplary embodiment, a multi-stage temperature increase process may be performed by increasing a temperature of the entire rotary kiln reactor 100, and specific details are described in the section regarding the multi-stage temperature increase process including the steps (S1-1), (S1-2), and (S1).

[0072] In an exemplary embodiment, the rotary kiln reactor 100 may include a batch reactor. The batch reactor may prevent a disadvantage of a continuous reactor in which the entire process is stopped when a problem with feedstock input occurs during pyrolysis, and may achieve excellent overall process stability. As an example, a continuous type rotary kiln reactor 100 may also be used.

[0073] The rotary kiln reactor 100 is connected to the gas separator 200, and at an outlet of the rotary kiln reactor 100, char or carbide, which is a solid component 5, and a pyrolysis gas component are separated from pyrolysis products, and only the pyrolysis gas component may be introduced into the top of the gas separator 200.

[0074] As the gas separator 200, a gas separator 200 known in the related art may be used, and the gas separator 200 may be designed, for example, in a distillation manner. A low boiling point pyrolysis gas and the high boiling point wax component 3 may be separated from the pyrolysis gas component by controlling a flow direction, a temperature gradient, and the like in a direction of a wall of the gas separator 200. However, this is merely an example, and the gas separator 200 may be designed in a manner known in the related art. The high boiling point wax component 3 may be discharged through the bottom of the gas separator 200, and an external cooling unit may be provided at the bottom of the gas separator 200 for efficient discharge. The separated high boiling point wax component 3 may be re-supplied to the rotary kiln reactor 100 through a re-supply line connected from the bottom of the gas separator 200 to the inlet of the rotary kiln reactor 100.

[0075] The pyrolysis gas component from which the high boiling point wax component 3 is removed in the gas separator 200 may be cooled and liquefied in the condenser 300, and refined oil 10 may be recovered in a recovery tank. The condenser 300 may include a zone through which a coolant flows, and the pyrolysis gas introduced into the condenser 300 may be liquefied by the coolant and converted into pyrolysis oil. When the pyrolysis oil produced in the condenser 300 rises to a predetermined level, the pyrolysis oil may be transferred to and recovered in the recovery tank. The liquid pyrolysis oil recovered in the recovery tank may include an oil layer and a water layer, and oil-water separation may proceed in an oil-water separator to form an oil layer and a water layer in the liquid pyrolysis oil. When the oil layer and the water layer are separated, the oil layer may be immediately recovered or may be recovered after adsorbing the water layer, such that an oil layer (refined oil) in which a content of chlorine is minimized may be recovered. An electric field application device may be provided to effectively separate the oil layer and the water layer. In a case where the water layer is discharged and adsorbed, a density is detected using a density profiler, such that it is possible to prevent the oil layer from being adsorbed together with the water layer when the water layer is adsorbed, and only the water layer may be effectively adsorbed.

[0076] As for the contents not further described in the device for refining waste plastic pyrolysis oil, the description of the method for refining waste plastic pyrolysis oil described above may be used as reference.

[0077] Hereinafter, the present invention will be described in detail with reference to Examples.

Example 1

[0078] A refining process of waste plastic pyrolysis oil was performed using a refining device including a rotary kiln reactor, a gas separator, and a condenser. As a feedstock charged into the rotary kiln reactor, liquid pyrolysis oil produced by pyrolyzing domestic waste plastics was used.

[0079] First, domestic mixed plastics containing 3 wt% or more of PVC together with PE and PP were extruded at 250°C to prepare 500 g of domestic waste plastic pellets. The domestic waste plastic pellets were put into a pyrolysis reactor, and then pyrolysis was performed at 400°C in a non-oxidizing atmosphere for 250 minutes, thereby obtaining a waste plastic pyrolysis oil feedstock.

[0080] A content of impurities such as chlorine, nitrogen, sulfur, and oxygen contained in the waste plastic pyrolysis oil feedstock was measured by ICP and XRF analysis, and it was measured that the content of chlorine was 564 ppm, the content of nitrogen was 1,083 ppm, the content of sulfur was 105 ppm, and the content of oxygen was 0.9 wt%.

[0081] The obtained waste plastic pyrolysis oil feedstock was put into the rotary kiln reactor, and then a heat treatment process was performed, thereby obtaining refined oil. Specifically, the rotary kiln reactor was operated under conditions of an inclination angle of 1.48 degrees, a rotation speed of 0.9 Nrpm, and an oxygen concentration of 0.5% or less, and the heat treatment process was performed by increasing the temperature of the rotary kiln reactor to 500°C at a temperature increase rate of 0.75°C/min for 200 minutes.

[0082] Only a pyrolysis gas component was recovered from the heat treatment process product, and the recovered pyrolysis gas component was supplied to a gas separator. In the gas separator, a high boiling point wax component contained in the pyrolysis gas component was separated through the bottom of the gas separator, the separated high boiling point wax component was re-supplied once to the rotary kiln reactor through a re-supply line connected from the

bottom of the gas separator to an inlet of the rotary kiln reactor, and the heat treatment process was repeated.

[0083] Finally, pyrolysis gas from which the high boiling point wax component was removed was recovered at the top of the gas separator, the recovered pyrolysis gas was passed through a condenser, and refined oil (waste plastic pyrolysis oil) was recovered in a recovery tank.

Example 2

[0084] A reaction was performed under the same conditions as those in Example 1, except that a heat treatment process was performed by additionally putting an additive into the rotary kiln reactor. Specifically, as the additive, a Cu/CaO additive having a size (D50) of 48.9 μm and a BET specific surface area of 6.4 m^2/g was used.

Example 3

[0085] A reaction was performed under the same conditions as those in Example 1, except that a heat treatment process was performed by increasing the temperature of the rotary kiln reactor to 500°C at a temperature increase rate of 6°C/min for 200 minutes.

Example 4

[0086] A reaction was performed under the same conditions as those in Example 1, except that a heat treatment process was performed by applying a multi-stage temperature increase process to the rotary kiln reactor. Specifically, a first heat treatment process was performed by increasing the temperature of the rotary kiln reactor to 100°C at a temperature increase rate of 1°C/min and then maintaining the temperature for 50 minutes. Thereafter, a second heat treatment process was performed by increasing the temperature of the rotary kiln reactor to 250°C at a temperature increase rate of 0.9°C/min and then maintaining the temperature for 150 minutes. Thereafter, a heat treatment process was performed by increasing the temperature of the rotary kiln reactor to 500°C at a temperature increase rate of 0.75°C/min for 200 minutes.

Comparative Example 1

[0087] A reaction was performed under the same conditions as those in Example 1, except that refined oil was recovered in a recovery tank directly through a condenser without going through the process of separating the high boiling point wax component of the pyrolysis gas produced in the rotary kiln reactor and re-supplying the separated high boiling point wax component.

Comparative Example 2

[0088] A reaction was performed under the same conditions as those in Example 1, except that domestic waste plastic pellets, rather than waste plastic pyrolysis oil, were applied as a feedstock to be put into the rotary kiln reactor. Specifically, 500 g of the domestic waste plastic pellets of Example 1 were put into the rotary kiln reactor, and then a heat treatment process was performed. The rotary kiln reactor was operated under conditions of an inclination angle of 1.48 degrees, a rotation speed of 0.9 Nrpm, and an oxygen concentration of 0.5% or less, and the heat treatment process was performed by increasing the temperature of the rotary kiln reactor to 500°C at a temperature increase rate of 0.75°C/min for 200 minutes. Only a pyrolysis gas component was recovered from the heat treatment process product, and the recovered pyrolysis gas component was supplied to a gas separator. In the gas separator, a high boiling point wax component contained in the pyrolysis gas component was separated through the bottom of the gas separator, the separated high boiling point wax component was re-supplied once to the rotary kiln reactor through a re-supply line connected from the bottom of the gas separator to an inlet of the rotary kiln reactor, and the heat treatment process was repeated. Finally, pyrolysis gas from which the high boiling point wax component was removed was recovered at the top of the gas separator, the recovered pyrolysis gas was passed through a condenser, and waste plastic pyrolysis oil was recovered in a recovery tank.

Evaluation Examples

Impurity Removal Effect

[0089] The contents of chlorine, nitrogen, sulfur, and oxygen contained in each of the feedstock and the obtained refined oil were measured by ICP and XRF analysis, and the impurity removal effect was evaluated.

Lightening Effect

[0090] Naphtha and KERO components contained in each of the feedstock and the refined oil were quantified through a gas chromatography method (ASTM D86), the combined weight was measured, and then a degree of lightening was evaluated.

[0091] The analysis results are shown in Table 1.

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2 (waste plastic pellets)
Reactor temperature (temperature increase rate)		500°C (0.75°C/min)	500°C (0.75°C/min)	500°C (6°C/min)	100°C (1°C/min) 250°C (0.9°C/min) 500°C (0.75°C/min)	500°C (0.75°C/min)	500°C (0.75°C/min)
Whether high boiling point wax is separated and re-supplied or not		○	○	○	○	X	○
Additive		X	○ (Cu/CaO)	X	X	X	X
Chlorine (ppm)	Feedstock	564					807
	Refined oil	215	143	258	148	337	605
Nitrogen (ppm)	Feedstock	1,083					1,509
	Refined oil	709	573	821	592	1,002	1,325
Sulfur (ppm)	Feedstock	105					306
	Refined oil	72	62	81	55	97	265
Oxygen (wt%)	Feedstock	0.9					2.3
	Refined oil	0.42	0.25	0.61	0.27	0.78	2.1
Naphtha + KERO (wt%)	Feedstock	42.5					37.1
	Refined oil	66.6	78.1	59.2	77.2	44.7	40.5

Result Analysis

[0092] As shown in Table 1, in all Examples 1 to 4 according to the present invention, it could be confirmed that impurities such as chlorine, nitrogen, sulfur, and oxygen in the waste plastic pyrolysis oil feedstock were effectively reduced and refined oil in which a content of light oil (Naphtha and KERO) was increased was obtained.

[0093] Specifically, in Example 2 in which the heat treatment process was performed by adding the Cu/CaO additive to the rotary kiln reactor, it could be confirmed that the reduction effect of impurities such as chlorine, nitrogen, sulfur, and oxygen and the lightening effect were the best.

[0094] In Example 3 in which the heat treatment process was performed by setting the temperature increase rate of the rotary kiln reactor to 6°C/min, it could be confirmed that the reduction effect of the impurities such as chlorine, nitrogen, sulfur, and oxygen and the lightening effect were somewhat lower than those in Example 1, but were excellent compared to those in Comparative Examples 1 and 2.

[0095] In Example 4 in which the heat treatment process was performed by applying a multi-stage temperature increase process to the rotary kiln reactor, it could be confirmed that the reduction effect of impurities such as chlorine, nitrogen, sulfur, and oxygen and the lightening effect were more excellent than those in Example 1.

[0096] In Comparative Example 1 in which the process of separating the high boiling point wax component of the pyrolysis gas produced in the rotary kiln reactor and re-supplying the separated high boiling point wax component was not performed, it could be confirmed that the reduction effect of impurities such as chlorine, nitrogen, sulfur, and oxygen and the lightening effect were significantly reduced.

[0097] In Comparative Example 2 in which the domestic waste plastic pellets rather than waste plastic pyrolysis oil were applied as a reaction feedstock, it could be confirmed that the reduction effect of impurities such as chlorine, nitrogen, sulfur, and oxygen and the lightening effect were significantly reduced.

[0098] As set forth above, the method and device for refining waste plastic pyrolysis oil according to the present invention may effectively reduce impurities in waste plastic pyrolysis oil.

[0099] Further, the method and device for refining waste plastic pyrolysis oil according to the present invention may improve the lightening efficiency of waste plastic pyrolysis oil.

[0100] Further, the method and device for refining waste plastic pyrolysis oil according to the present invention may realize a stable process without corrosion or blockage of a reactor.

Claims

1. A method for refining waste plastic pyrolysis oil, the method comprising:

(S1) subjecting a waste plastic pyrolysis oil feedstock to a heat treatment by charging the waste plastic pyrolysis oil feedstock into a rotary kiln reactor and increasing a temperature of the rotary kiln reactor;
(S2) recovering a gas component from a product in the step (S1);
(S3) separating a high boiling point wax component from the recovered gas component and re-supplying the separated high boiling point wax component to the rotary kiln reactor in the step (S1); and
(S4) recovering refined oil from the gas component from which the high boiling point wax component is removed.

2. The method of claim 1, wherein the waste plastic pyrolysis oil feedstock is liquid pyrolysis oil containing 10 to 30 wt% of Naphtha, 20 to 30 wt% of KERO, 10 to 30 wt% of LGO, and 30 to 50 wt% of VGO.

3. The method of claim 1 or 2, wherein in the step (S1), the heat treatment is performed by increasing the temperature of the rotary kiln reactor to a third temperature.

4. The method of claim 3, wherein the third temperature is 400 to 600°C.

5. The method of claim 3, wherein when the temperature of the rotary kiln reactor is increased to the third temperature in the step (S1), a temperature increase rate is 0.5°C/min to 5°C/min.

6. The method of any one of claims 3 to 5, further comprising, before the step (S1):

(S1-1) subjecting the waste plastic pyrolysis oil feedstock to a first heat treatment by increasing a temperature of the rotary kiln reactor to a first temperature; and
(S1-2) subjecting the waste plastic pyrolysis oil feedstock to a second heat treatment by increasing a temperature of the rotary kiln reactor to a second temperature,

wherein the temperature of the rotary kiln reactor is increased by sequentially heating the rotary kiln reactor from the first temperature to the third temperature.

7. The method of any one of claims 1 to 6, wherein the first temperature is 50 to 150°C.

8. The method of any one of claims 1 to 7, wherein the second temperature is 220 to 300°C.

9. The method of any one of claims 1 to 8, wherein in the step (S1), the heat treatment is performed by adding an additive.

10. The method of claim 9, wherein the additive includes a metal oxide catalyst or a composite catalyst in which an active metal is supported on a metal oxide carrier.

11. The method of any one of claims 1 to 10, further comprising, before the step (S1), (S0) charging waste plastics into a pyrolysis reactor and pyrolyzing the waste plastics at a temperature of 300 to 600°C in a non-oxidizing atmosphere to produce a waste plastic pyrolysis oil feedstock.

12. The method of claim 11, wherein the pyrolysis reactor in the step (S0) includes a rotary kiln reactor.

13. A device for refining waste plastic pyrolysis oil, preferably during a method of any one of claims 1 to 12, the device comprising:

a rotary kiln reactor configured to receive a waste plastic pyrolysis oil feedstock;
a gas separator into configured to receive a gas component from the rotary kiln reactor;
a condenser configured to receive a light gas component from the gas separator; and
a re-supply line configured to re-supply a high boiling point wax component separated in the gas separator to the rotary kiln reactor.

14. The device of claim 13, wherein the rotary kiln reactor sequentially includes a first zone, a second zone, and a third zone in a direction from a feedstock inlet to an outlet.

15. The device of claim 13 or 14, wherein the rotary kiln reactor includes a batch reactor.

FIG. 1

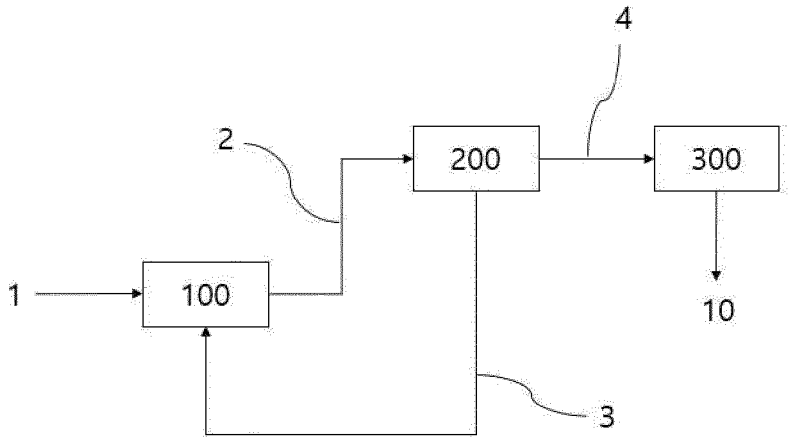


FIG. 2

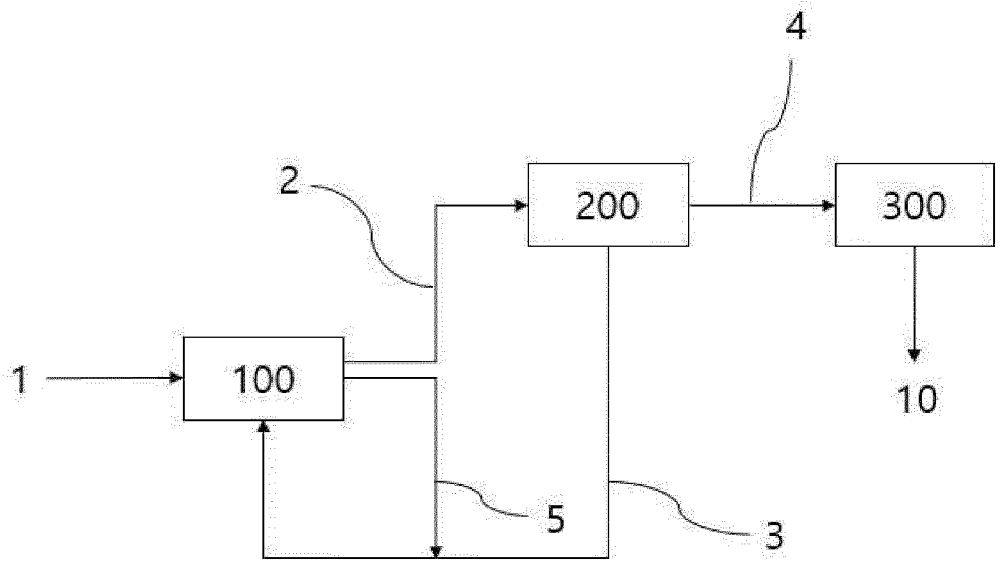


FIG. 3

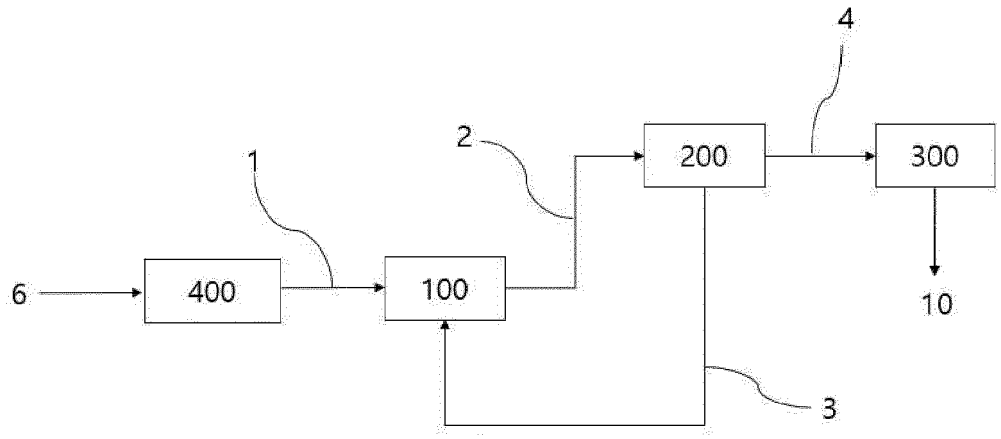


FIG. 4

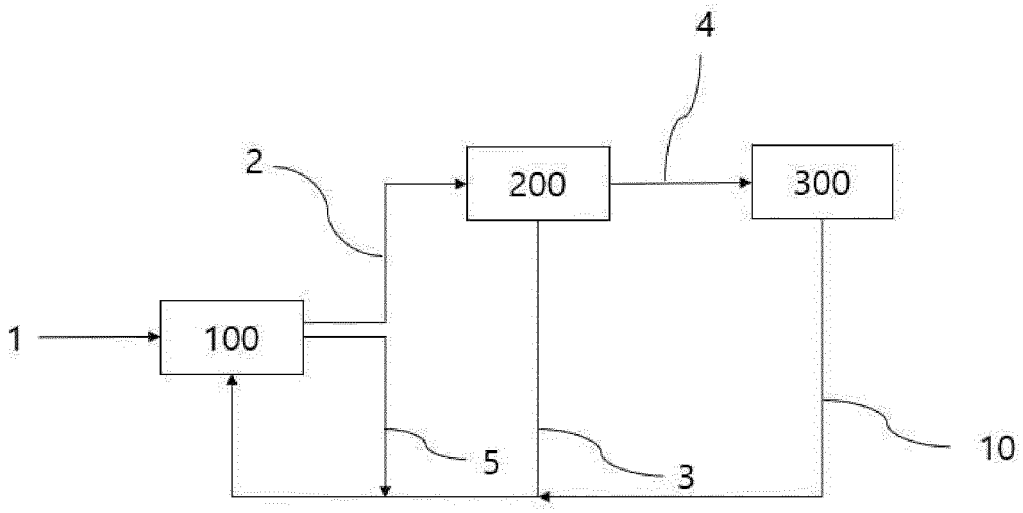
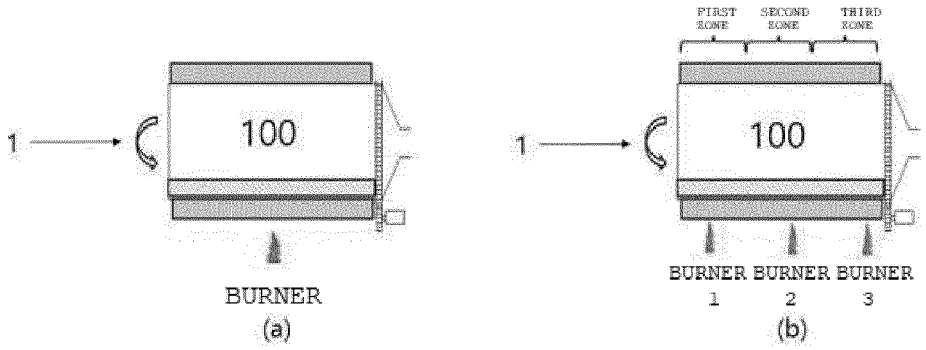


FIG. 5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EUROPEAN SEARCH REPORT

Application Number
EP 23 20 7945

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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			C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	12 March 2024	Chau, Thoi Dai

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12-03-2024

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