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(71) Applicants:
• **SK Innovation Co., Ltd.**
Seoul 03188 (KR)
• **SK Geo Centric Co., Ltd.**
Jongno-gu
Seoul 03188 (KR)

(72) Inventors:
• **KIM, Dokyoung**
Daejeon 34124 (KR)

- **JEON, Heejung**
Daejeon 34124 (KR)
- **CHOI, Jaesuk**
Daejeon 34124 (KR)
- **KIM, Kayoung**
Daejeon 34124 (KR)
- **LEE, Howon**
Daejeon 34124 (KR)
- **KIM, Taejin**
Daejeon 34124 (KR)
- **CHOO, Daehyun**
Daejeon 34124 (KR)

(74) Representative: **Frick, Robert**
Lorenz Seidler Gossel
Rechtsanwälte Patentanwälte
Partnerschaft mbB
Widenmayerstraße 23
80538 München (DE)

(54) **METHOD FOR REMOVING CHLORINE FROM HIGH CHLORINE CONTENT WASTE OIL USING SOLID ACID SUBSTANCES**

(57) The present embodiment pertains to a technique for removing at least 90% of the chlorine in high Cl content oil by performing a high-temperature treatment using solid acid substances. The oil removed Cl from a waste oil can be incorporated in a refinery process and thereby converted into fuel or a chemical product.

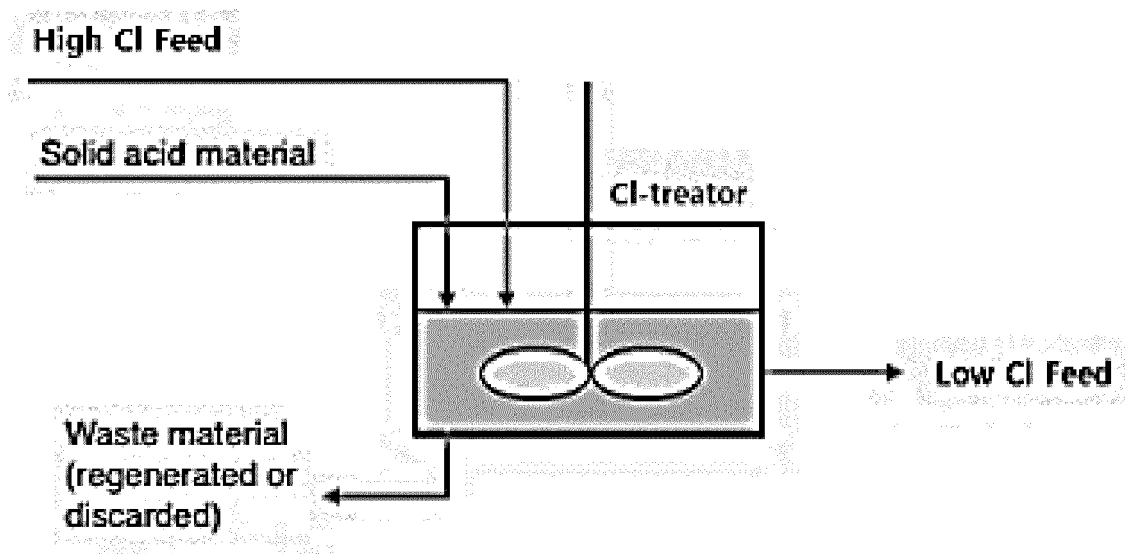
According to the present embodiment, chlorine can be removed through a high-temperature heat treatment after mixing high Cl content oil with a solid acid material. In the process of removing Cl, major impurities, such as S, N, and O, as well as Na, Ca, and Fe, which can act as catalyst poisons in the catalytic reactions of a refinery

process, are also removed at the same time.

In the process of removing Cl from the high Cl content oil through the solid acid substances, abnormal reactions, deterioration of product properties, and yield loss can be prevented by slightly increasing the average molecular weight of the oil composition through oligomerization and alkylation reactions.

This method is environmentally appropriate in that waste solid acid substances (waste zeolite, waste clay, etc.), which are discharged after use in petrochemical processes, can be used as solid acid substances for Cl removal after undergoing a simple treatment.

【FIG. 1】



Description

[Technical Field]

- 5 **[0001]** The present invention relates to a method for removing chlorine from a waste oil having a high chlorine content using a solid acid material.

[Background Art]

- 10 **[0002]** Since a large amount of impurities resulting from a waste material are included in an oil (waste oil) produced by a cracking or pyrolysis reaction of the waste material such as a waste plastic pyrolysis oil, when the oil is used as a fuel, air pollutants such as SO_x and NO_x may be released, and in particular, a Cl component may be converted into HCl which may cause device corrosion in a high-temperature treatment process and released.

- 15 **[0003]** Conventionally, Cl was removed by converting Cl into HCl by a hydrotreating (HDT) process using a refinery technique, but since the waste oil such as a waste plastic pyrolysis oil has a high Cl content, problems of equipment corrosion, reaction abnormality, and deterioration of product properties have been reported, and it is difficult to introduce the waste oil which has not been pretreated to the HDT process. In order to remove a Cl oil by using a convention refinery process, there is a need of a treatment technology of reducing Cl in a waste oil in which a Cl content (several ppm of Cl) is reduced to a level to allow introduction of the refinery process.

- 20 **[0004]** Related Art Document 1 (Japanese Patent Laid-Open Publication No. 1999-504672 A) relates to a method of producing gasoline, diesel engine oil, and carbon black from waste rubber and/or waste plastic materials. Specifically, it includes: removing Cl, N, S, and the like by bonds using a base material such as KOH or NaOH by a primary impurity removal process from a pyrolysis oil obtained from pyrolysis of waste rubber and waste plastic, and removing Cl, N, and S simultaneously with cracking of the pyrolysis oil in a secondary catalytic cracking process, wherein a cracked oil is then separated to produce a final product. However, in the primary impurity removal process, Cl is reduced by neutralization (using a base material such as KOH and NaOH), and in a neutralization bond removal reaction, Cl removal efficiency per unit weight of the base material is not high, and thus, it is difficult to produce a low Cl content oil to be introduced into a refinery process (several ppm of Cl). In addition, since a catalyst use cycle is short and a process of recycling a used material (neutralization catalyst) is complicated, it is not preferred in terms of process simplification.

- 30 **[0005]** Related Art Document 2 (Japanese Patent Registration No. 4218857 B2) relates to a chlorine compound remover. Specifically, it removes Cl from a fluid including a chlorine compound by adsorption using a clay chlorine remover such as zinc oxide and talc, and the adsorption removal is Cl removal by bonding and it is characterized in that Cl bonded to a Cl remover is not released. However, Related Art Document 2 uses a low-Cl content oil having a Cl content of less than 10 ppm as a raw material, as described in the evaluation test of a chlorine compound removal performance in a liquid hydrocarbon, and the Cl removal technology using an adsorbent as such is generally appropriate for adsorbing a trace amount of Cl for a long time. Therefore, applying the adsorption technology to the waste oil having a high Cl content is not effective.

- 35 **[0006]** Related Art Document 3 (Japanese Patent Laid-Open Publication No. 2019-532118 A) relates to a dechlorination method of a mixed plastic pyrolysis oil using devolatilization extrusion and a chloride scavenger. Specifically, it is characterized by converting plastic or a plastic pyrolysis oil into a mild oil having bp < 370°C by a pyrolysis reaction using a fluidized bed catalyst to remove Cl. However, when Cl is removed simultaneously with a pyrolysis reaction, it is removed in the form of organic Cl in which an olefin and Cl are bonded, and moisture simultaneously occurs to cause problems of equipment corrosion, reaction abnormality, deterioration of product properties, and product loss.

- 40 **[0007]** Therefore, a treatment technology of reducing Cl in a waste oil which reduces a Cl content in a waste oil having a high Cl content to a level (several ppm of Cl) to allow introduction to a refinery process is required, and in the process of applying the technology, problems of equipment corrosion, reaction abnormality, and deterioration of product properties should be minimized.

[Disclosure]

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[Technical Problem]

- [0008]** An object of the present invention is to provide a technology of reducing Cl in a waste oil having a high Cl content by using a solid acid material, for high value added (fuel, chemical conversion) of a waste oil having a high Cl content by application of a refinery process.

- 55 **[0009]** Specifically, the object of the present invention is to provide a technology of conversion into a Cl oil at a level to allow introduction to a refinery process, by removing 90 wt% or more of Cl from a pyrolysis oil having a high Cl content recovered by waste plastic pyrolysis by a Cl catalytic conversion reaction using a solid acid material.

[Technical Solution]

[0010] In one general aspect, a method for removing chlorine from a waste oil includes: a) preparing a mixture of a chlorine-containing waste oil and a solid acid material; b) reacting the mixture to remove chlorine; and c) separating a dechlorinated oil fraction and the solid acid material from the mixture to recover the dechlorinated oil fraction, wherein the following Relation 1 is satisfied:

[Relation 1]

$$1 \leq B/A \leq 3$$

wherein A is a wt% of components having a boiling point (bp) of 150°C or higher with respect to a total weight of the waste oil, and B is a wt% of components having bp of 150°C or higher with respect to a total weight of the dechlorinated oil fraction.

[0011] According to the exemplary embodiment, the waste oil having a high chlorine content provided in step a) may include a waste plastic pyrolysis oil, a biomass pyrolysis oil, a regenerated lubricant, a crude oil having a high chlorine content, or a combination thereof.

[0012] According to the exemplary embodiment, the solid acid material in step a) has a Bronsted acid point or a Lewis acid point, and may include zeolite, clay, silica-alumina-phosphate (SAPO), aluminum phosphate (ALPO), metal organic framework (MOF), silica alumina, or a mixture thereof.

[0013] According to the exemplary embodiment, impurities may be selectively reduced without a decrease in a molecular weight distribution of the waste oil, and the impurities may include sulfur, nitrogen, oxygen, and metals such as Na, Ca, Fe, Al, and As in addition to chlorine.

[0014] According to the exemplary embodiment, in step b), a method of carrying out an impurity reduction reaction may be implemented using a batch reactor, a semi-batch reactor, a continuous stirred-tank reactor (CSTR), and a fixed bed reactor.

[0015] According to the exemplary embodiment, separating the oil from which impurities have been removed and the solid acid material in step c) may use a separation method using filtering, centrifugation, decanting, and the like.

[0016] According to the exemplary embodiment, the dechlorinated oil fraction having a chlorine content of less than 10 ppm may be prepared by steps a) to c).

[Advantageous Effects]

[0017] 90 wt% or more of Cl is removed from an oil having a high Cl content, thereby converting the oil into a Cl oil at a level to allow introduction to a refinery process.

[0018] Not only Cl may be removed from the oil, but also impurities causing air pollutants such as N and S, and metal components which adversely affect a refinery process catalytic activity, such as Fe, As, Na, and Ca may be simultaneously removed.

[0019] When Cl is removed from the oil, the average molecular weight of the pyrolysis oil composition is slightly increased by an oligomerization reaction of an olefin and an alkylation reaction between the olefin and a branched paraffin in the pyrolysis oil, thereby preventing reaction abnormality, deterioration of product properties, and product loss.

[0020] Since a waste solid acid material (waste zeolite, waste clay, and the like) which is discarded after use in a petrochemical process may be used as a solid acid material for Cl removal as it is or after being simply treated, it is preferred from an environmental point of view.

[Description of Drawings]

[0021]

FIGS. 1 and 2 are schematic diagrams of a method for removing chlorine according to an exemplary embodiment of the present invention.

FIG. 3 is a graph showing a composition of a waste oil having a high Cl content.

FIG. 4 is a graph showing a composition change of an oil recovered after a Cl reduction reaction.

FIGS. 5 and 6 are graphs showing a residual N content and a residual S content by reaction temperature.

FIG. 7 is a graph showing an oil composition change by reaction temperature.

FIGS. 8 and 9 are graphs showing a residual Cl content and a Cl reduction rate by reaction time.

FIGS. 10 and 11 are graphs showing a residual N content and a residual S content by reaction time.
 FIG. 12 is a graph showing an oil composition change by reaction time.
 FIG. 13 is a graph showing an apparent reaction rate equation of a reaction according to an exemplary embodiment.
 FIGS. 14 and 15 are graphs showing a residual Cl content and a Cl reduction rate by catalytic amount.
 FIGS. 16 and 17 are graphs showing a residual N content and a residual S content by catalytic amount.
 FIG. 18 is a graph showing an oil composition change by catalytic amount.

[Best Mode]

[0022] Unless otherwise defined herein, all terms used in the specification (including technical and scientific terms) may have the meaning that is commonly understood by those skilled in the art. Throughout the present specification, unless explicitly described to the contrary, "comprising" any elements will be understood to imply further inclusion of other elements rather than the exclusion of any other elements. In addition, unless explicitly described to the contrary, a singular form includes a plural form herein.

[0023] In the present specification, "A to B" refers to "A or more and B or less", unless otherwise particularly defined.

[0024] In addition, "A and/or B" refers to at least one selected from the group consisting of A and B, unless otherwise particularly defined.

[0025] In the present specification, a boiling point (bp) of a waste oil and a dechlorinated oil fraction refers to that measured at a normal pressure (1 atm), unless otherwise defined.

[0026] According to an exemplary embodiment of the present invention, a method for removing chlorine from a waste oil is provided. The method includes: a) preparing a mixture of a chlorine-containing waste oil and a solid acid material; b) reacting the mixture to remove chlorine; and c) separating a dechlorinated oil fraction and the solid acid material from the mixture to recover the dechlorinated oil fraction, wherein the following Relation 1 is satisfied:

[Relation 1]

$$1 \leq B/A \leq 3$$

wherein A is a wt% of components having a boiling point (bp) of 150°C or higher with respect to a total weight of the waste oil, and B is a wt% of components having bp of 150°C or higher with respect to a total weight of the dechlorinated oil fraction.

[0027] In the present invention, a technology of reducing Cl in a waste oil having a high Cl content by using a solid acid material, for high value added (fuel, chemical conversion) of a waste oil having a high Cl content by application of a refinery process may be provided.

[0028] In the method for removing chlorine from a waste oil, first, a) a mixture of a chlorine-containing waste oil and a solid acid material is prepared.

[0029] The waste oil may include a waste plastic pyrolysis oil, a biomass pyrolysis oil, a regenerated lubricant, a crude oil having a high chlorine content, or a mixture thereof. Since a large amount of impurities produced from a waste material are included in the waste oil produced by a cracking or pyrolysis reaction of the waste material such as a waste plastic pyrolysis oil, when the waste oil is used, air pollutants may be released, and in particular, a Cl component may be converted into HCl and released in a high temperature treatment process, and thus, it is necessary to pretreat the waste oil to remove impurities.

[0030] Chlorine in the waste oil may be inorganic Cl, organic Cl, or a combination thereof, and a chlorine content in the waste oil may be 10 ppm or more or 20 ppm or more. Meanwhile, the upper limit of the content of chlorine in the waste oil is not particularly limited, but may be 600 ppm or less, preferably 500 ppm or less. A treatment technology of reducing Cl in a waste oil in which a Cl content (several ppm of Cl) is reduced to a level to allow introduction of the refinery process by treating the waste oil having a high Cl content is required.

[0031] Meanwhile, impurities in the waste oil may include N, S, and O which may be released as air pollutants such as SO_x and NO_x, and Fe, Na, Ca, Al, and the like as a metal component which adversely affects a refinery process catalytic activity. Specifically, N, S, and O may be included at a N content of 100 wppm or more or 500 to 8,000 wppm, a S content of 10 wppm or more or 20 to 1,000 wppm, and an O content of 2,000 wppm or more or 3,000 wppm to 3 wt% with respect to the total weight of the waste oil, and Fe, Na, Ca, and Al may be included at a Fe content of 1 wppm or more or 1 to 10 wppm, a Na content of 1 wppm or more or 1 to 10 wppm, a Ca content of 0.1 wppm or more or 0.1 to 5 wppm, and an Al content of 0.1 wppm or more or 0.1 to 5 wppm with respect to the total weight of the waste oil.

[0032] The waste oil may have a ratio (A₂/A₁) of 1 to 19, the ratio being a weight (A₂) of components having bp of

150°C or higher to a weight (A_1) of components having bp of lower than 150°C. Specifically, the weight ratio (A_2/A_1) of the waste oil components may be 1 to 16, preferably 3 to 15, and more preferably 9 to 13.

[0033] In addition, in the waste oil, a weight ratio of components having bp of 265°C or higher to components having bp of lower than 265°C may be 1.1 to 2.5, preferably 1.1 to 2.3 or 1.1 to 2.1, and more preferably 1.1 to 2.0, 1.1 to 1.8, or 1.1 to 1.7.

[0034] In addition, in the waste oil, a weight ratio of a C9+ component to a C4-C9 component may be 1 to 19, for example, 1 to 16, preferably 3 to 15, and more preferably 9 to 13.

[0035] In addition, in the waste oil, a weight ratio of a C18+ component to a C4-C17 component may be 1.1 to 2.5, preferably 1.1 to 2.3 or 1.1 to 2.1, and more preferably 1.1 to 2.0, 1.1 to 1.8, or 1.1 to 1.7.

[0036] The waste oil may include 0.1 to 80 wt% of C4-C7 L-Naph, 0.1 to 80 wt% of C6-C8 H-Naph, 0.1 to 70 wt% of C9-C17 Kero, 0.1 to 80 wt% of C18-C20 LGO, 0.1 to 80 wt% of C21-C25 VGO, and 0.1 to 99 wt% of C26+ AR, but the present invention is not limited thereto.

[0037] In addition, the waste oil may include 30 to 70 wt%, preferably 40 to 60 wt% of an olefin with respect to the total weight. As described later, by removing Cl in the pyrolysis oil under specific process conditions using the solid acid material of the present invention, production of an organic-Cl bond by a bond of olefin and Cl may be suppressed, and the average molecular weight of the pyrolysis oil composition may be slightly increased by the alkylation reaction between the oligomerization reaction of the olefin in the pyrolysis oil and the alkylation reaction between the olefin and the branched paraffin, and thus, reaction abnormality, deterioration of product properties, and product loss may be prevented.

[0038] The solid acid material includes a Bronsted acid, a Lewis acid, or a mixture thereof, and specifically, a solid material in which a Bronsted acid or a Lewis acid site is present, and the solid acid material may be zeolite, clay, silica-alumina-phosphate (SAPO), aluminum phosphate (ALPO), metal organic framework (MOF), silica alumina, or a mixture thereof.

[0039] The solid acid material is a solid material having a site capable of donating H^+ (Bronsted acid) or accepting a lone pair of electrons (Lewis acid), and allows derivation of various reactions such as cracking, alkylation, and neutralization depending on energy at an acid site. In the present invention, the solid acid material is activated in specific process conditions, thereby carrying out a catalytic conversion reaction to convert Cl into HCl. As a result, a high Cl content in the waste oil may be reduced to a several ppm level, and product abnormality (for example, cracking) and a yield loss (in the case in which Cl is removed as organic Cl, the case in which the oil is cracked and removed as gas, and the like) may be minimized.

[0040] As the solid acid material, waste zeolite, waste clay, and the like which are discarded after use in a petrochemical process are used as they are or used after a simple treatment for further activity improvement.

[0041] For example, a fluidized bed catalyst is used in a RFCC process in which a residual oil is converted into a light/middle distillate, and in order to maintain the entire activity of the RFCC process constant, a certain amount of catalyst in operation is exchanged with a fresh catalyst every day, and the exchanged catalyst herein is named RFCC equilibrium catalyst (E-Cat) and discarded entirely. RFCC E-Cat may be used as the solid acid material of the present invention, and RFCC E-Cat may be formed of 30 to 50 wt% of zeolite, 40 to 60 wt% of clay, and 0 to 30 wt% of other materials (alumina gel, silica gel, functional material, and the like). By using RFCC E-Cat as the solid acid material for reducing Cl in the Cl waste oil, a difference in cracking activity is small as compared with the fresh catalyst, and costs are reduced through environmental protection and reuse.

[0042] A simple treatment may be needed in order to use the waste zeolite, the waste clay, and the like as the solid acid material of the process of the present invention, and when a material such as coke or oil physically blocks the active site of the solid acid material, the material may be removed. In order to remove coke, air burning may be performed or a treatment with a solvent may be performed for oil removal. If necessary, when the metal component affects the active site of the solid acid material and deactivates the active site, a DeMet process in which a weak acid or dilute hydrogen peroxide is treated at a medium temperature to remove the metal component may be applied.

[0043] The solid acid material may further include a carrier or a binder including carbon, alkali earth metal oxides, alkali metal oxides, alumina, silica, silica-alumina, zirconia, titania, silicon carbide, niobia, aluminum phosphate, or a mixture thereof.

[0044] In step a), the solid acid material may be included at 5 to 10 wt%, preferably 7 to 10 wt%, and more preferably 8 to 10 wt% with respect to the total weight of the mixture. Within the range, as the amount of the solid acid material introduced is increased, a Cl removal effect is improved, and when the amount is 10 wt% or less, a cracking reaction in the oil may be suppressed, which is thus preferred.

b) After the mixture of the waste oil and the solid acid material of the present invention is prepared, the mixture is reacted to remove chlorine.

[0045] The reaction of removing chlorine from an oil having a high chlorine content is largely expected as the following two types: one in which chlorine in a hydrocarbon structure is converted into HCl by a reaction by an active site of a solid acid catalyst and then is released as HCl or partially converted into organic Cl and then released, and the other one in which Cl is removed by a reaction of a direct bond to the active site of the solid acid material. In a conventional

technology of removing Cl by H₂ feeding in a hydrotreating (HDT) process, the waste oil is cracked, so that Cl is likely to be removed in the form of organic-Cl. In particular, since gas occurrence is increased, product loss is large and an olefin component content in the waste oil may be increased, which is thus not preferred. The Cl removal reaction of the present invention may prevent the problems described above.

[0046] The reaction conditions may be a pressure of 1 bar or more and 100 bar or less under an inert gas atmosphere and a temperature of 200°C or higher and lower than 300°C. Specifically, the process conditions may be performed under pressure conditions of 1 to 100 bar of N₂, 1 to 60 bar of N₂, or 1 to 40 bar of N₂. When the reaction is performed under high vacuum or low vacuum conditions of less than 1 bar, a catalytic pyrolysis reaction occurs to decrease the viscosity and the molecular weight of the pyrolysis oil and change the composition of the oil product. In particular, Cl is bonded to an olefin to form organic Cl to be removed, thereby causing product loss. However, when the pressure is more than 100 bar, reactor operation is difficult and process costs are increased, which is thus not preferred.

[0047] Though the process conditions do not necessarily proceed under inert conditions such as N₂, a Cl reduction operation under inert conditions is advantageous in terms of operation safety and economic feasibility. Though similar Cl reduction performance is shown even under air conditions, when leak occurs under high temperature operating conditions at 230°C or higher, there is a risk of fire, and though Cl reduction efficiency is increased under H₂ conditions, economic feasibility is lowered by the use of H₂ as compared with a N₂ operation.

[0048] The process conditions may be performed at a temperature of, specifically 200 to 300°C, 230 to 300°C, 240 to 300°C, preferably 250 to 290°C or 255 to 285°C, and most preferably 260~280°C. As the temperature is raised in the temperature range described above, the Cl reduction effect is increased, and in particular, when a low temperature of lower than 200°C is applied, a conversion catalytic reaction in which chlorine (Cl) contained in the waste oil is converted into a hydrochloric acid (HCl) is greatly decreased. Due to the low Cl reduction performance, it is necessary to increase a catalyst content, reaction temperature/time, and the like for complementing the performance, which is disadvantageous from an economic point of view, and thus, is inappropriate for treating the waste oil having a high Cl content.

[0049] In addition, when the reaction temperature is excessively raised, a yield loss of a gas component occurs due to the cracking reaction, which may not be preferred.

[0050] Meanwhile, as the reaction temperature is raised, a removal rate of N and S may be increased, and in particular, when the reaction proceeds at a temperature of 260°C or higher, a reaction of removing N and S may proceed separately.

[0051] Meanwhile, the reaction of step b) may be carried out in a fixed bed catalytic reactor or a batch reactor, but the present invention is not limited thereto.

[0052] Though a regenerated oil may be prepared using a fluidized bed reactor, a contact time between the catalyst and the oil should be long for removing Cl in the regenerated oil, but the reduction efficiency of impurities such as Cl is low in the fluidized bed reactor having a very short contact time of several seconds or less as compared with the batch reactor having an infinite contact time between the catalyst and the oil. Though impurity reduction efficiency may be increased by raising the reaction temperature, a cracking side reaction occurs at a high temperature to cause a composition change, and fluidized bed equipment investments and operation costs are high, and thus, it is relatively disadvantageous to secure economic feasibility.

[0053] The fixed bed reactor and a continuous reactor are also advantageous in terms of a catalyst contact time as compared with the fluidized bed reactor and in terms of easy operation and securing safety as compared with the batch reactor, but have low long-term stability and low Cl reduction efficiency for the Cl removal reaction.

[0054] For example, when the Cl reduction reaction is carried out in a batch reactor, a stirring operation may be performed at 30 to 2000 rpm, preferably 200 to 1000 rpm, and more preferably 300 to 700 rpm, and/or for a reaction time of 0.1 to 48 hrs or 0.5 to 24 hrs, preferably 1 to 12 hrs or 2 to 12 hrs, and more preferably 3 to 5 hrs.

[0055] In addition, when the reaction is carried out in the fixed bed catalytic reactor, the operation is performed at LHSV of 0.1 to 10 hr⁻¹, preferably 0.3 to 5 hr⁻¹, more preferably 1 to 3 hr⁻¹, and/or gas over oil ratio (GOR) of 50 to 2000, preferably 200 to 1000, and more preferably 350 to 700.

c) Subsequently, a dechlorinated oil fraction and the solid acid material in the mixture are separated to recover the dechlorinated oil fraction.

[0056] The separation of the mixture may be performed by applying any known filtering or filtration method, but the present invention is not limited thereto.

[0057] The step of regenerating the separated waste solid acid material may be further performed, and for example, the used solid acid material may be placed in a calcination furnace and heat-treated at a temperature of 400 to 700°C, preferably 500 to 600°C under an air atmosphere for 2 to 4 hrs, but the present invention is not limited thereto.

d) Subsequently, a step of repeating steps a), b), and c) at least once may be further performed. By the repeated treatment, the Cl content of strict standards (at a level of 1 wppm) accepted in a subsequent refinery process may be met, and the average molecular weight and/or the viscosity of the waste oil composition may be slightly increased, thereby preventing reaction abnormality, deterioration of product properties, and product loss.

[0058] The dechlorinated oil fraction according to an exemplary embodiment of the present invention is characterized by satisfying the following Relation 1:

[Relation 1]

5

$$1 \leq B/A \leq 3$$

wherein A is a wt% of components having a boiling point (bp) of 150°C or higher with respect to a total weight of the waste oil, and B is a wt% of components having bp of 150°C or higher with respect to a total weight of the dechlorinated oil fraction.

[0059] Specifically, B/A may be 1 to 2, preferably 1 to 1.8, more preferably 1 to 1.5, and most preferably 1 to 1.3 or 1 to 1.2. In addition, the chlorine content in the dechlorinated oil fraction may be less than 10 ppm, specifically 9 ppm or less, 8 ppm or less, or 1 to 7 ppm. When Cl is removed from the waste oil, the average molecular weight and/or the viscosity of the waste oil composition is slightly increased by an oligomerization reaction of an olefin and an alkylation reaction between the olefin and a branched paraffin in the waste oil, thereby preventing reaction abnormality, deterioration of product properties, and product loss.

[0060] The dechlorinated oil fraction may have a ratio (B_2/B_1) of 1 to 20, the ratio being a weight (B_2) of components having bp of 150°C or higher to a weight (B_1) of components having bp of lower than 150°C. Specifically, the weight ratio (B_2/B_1) of the waste oil components may be 1 to 17, preferably 3 to 16, and more preferably 5 to 14.

[0061] In addition, in the dechlorinated oil fraction, a weight ratio of components having bp of 265°C or higher to components having bp of lower than 265°C may be 1.8 to 3.0, specifically 1.8 to 2.8, and preferably 1.8 to 2.6 or 1.9 to 2.5.

[0062] In addition, in the dechlorinated oil fraction, a weight ratio of a C9+ component to a C4-C8 component may be 1 to 20, for example, 1 to 17, preferably 3 to 16, and more preferably 5 to 14.

[0063] In addition, in the dechlorinated oil fraction, a weight ratio of a C18+ component to a C4-C17 component may be 1.8 to 3.0, for example, 1.8 to 2.8, and preferably 1.8 to 2.6 or 1.9 to 2.5. Thus, the effects described above may be further improved within the above range.

[0064] In addition, a weight ratio of chlorine in the dechlorinated oil fraction to chlorine in the waste oil may be 0.01 to 0.25, for example, 0.01 to 0.20, 0.01 to 0.10, and preferably 0.01 to 0.08.

[0065] Meanwhile, the method of removing chlorine from a waste oil according to an exemplary embodiment has an effect of removing impurities such as Fe, Na, Ca, and Al in addition to chlorine contained in the waste oil, which has not been expected before. For example, a Fe content may be less than 10 ppm, preferably 7 ppm or less or 5 ppm or less, and more preferably 3 ppm or less, a Na content may be less than 10 ppm, preferably 7 ppm or less or 5 ppm or less, and more preferably 3 ppm or less, and a Ca content may be less than 5 ppm, preferably 3 ppm or less or 1 ppm or less, and more preferably 0.5 ppm or less or 0.3 ppm or less, with respect to the total weight of the dechlorinated oil fraction.

[0066] In addition, a weight ratio of Fe in the dechlorinated oil fraction to Fe in the waste oil may be 0.1 to 0.7, for example, 0.1 to 0.6, and preferably 0.5 or less, a weight ratio of Na in the dechlorinated oil fraction to Na in the waste oil may be 0.1 to 0.7, for example, 0.1 to 0.5, and preferably 0.4 or less, a weight ratio of Ca in the dechlorinated oil fraction to Ca in the waste oil may be 0.1 to 0.7, for example, 0.1 to 0.6, and preferably 0.5 or less, and a weight ratio of Al in the dechlorinated oil fraction to Al in the waste oil may be 0.1 to 0.7, for example, 0.1 to 0.5, and preferably 0.4 or less.

[0067] Meanwhile, the method of removing chlorine from a waste oil according to an exemplary embodiment expresses an effect of removing impurities such as N, Ca, and O in addition to chlorine contained in the waste oil, which has not been expected before. For example, a N content may be less than 300 ppm, preferably 250 ppm or less or 200 ppm or less, and more preferably 170 ppm or less, a S content may be less than 20 ppm, preferably 19 ppm or less or 18 ppm or less, and more preferably 17 ppm or less, and an O content may be less than 0.2 wt%, preferably 0.15 wt% or less or 0.1 wt% or less, and more preferably less than 0.1 wt%, with respect to the total weight of the dechlorinated oil fraction.

[0068] In addition, a weight ratio of N in the dechlorinated oil fraction to N in the waste oil may be 0.1 to 0.7, for example, 0.1 to 0.6, and preferably 0.5 or less, a weight ratio of S in the dechlorinated oil fraction to S in the waste oil may be less than 1, for example, 0.1 to 0.9, and preferably 0.8 or less, and a weight ratio of O in the dechlorinated oil fraction to O in the waste oil may be less than 1, for example, 0.1 to 0.9, preferably 0.8 or less, 0.7 or less, 0.6 or less, or 0.5 or less.

[0069] Hereinafter, the preferred Examples and Comparative Examples of the present invention will be described. However, the following Examples are only a preferred exemplary embodiment of the present invention, and the present invention is not limited thereto.

Example 1. Analysis of composition of waste oil having high Cl content (waste plastic pyrolysis oil)

[0070] A waste oil (waste plastic pyrolysis oil) converted by pyrolysis of a plastic waste was recovered and used as a raw material of a Cl removal reaction. In order to confirm the effect of impurity removal by the reaction and a molecular weight change, the following analysis was performed. In order to confirm a molecular weight distribution in the waste

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plastic pyrolysis oil, GC-Simdis analysis (HT-750) was performed. Analysis for impurities such as Cl, S, N, O, Fe, Ca, Na, Al, Si, and P was performed, and ICP, TNS, EA-O, and XRF analyses were performed for this. In addition, GC-MSD analysis was performed for olefin content analysis. Compositions and impurity properties of the pyrolysis oils used as the raw material are shown in the following Tables 1 and 2 and FIG. 3 by the analysis results.

[Table 1]

Cut Name	Expected carbon range	Range, °C	Expected yield (By Simdis.)	Cutting yield (wt%)
L-Naph.	C4~C7	IBP~80	1.7	3.04
H-Naph.	C6~C8	80~150	14.2	15.92
KERO	C9~C17	150~265	23.0	27.85
LGO	C18~C20	265~340	16.8	16.08
VGO	C21~C25	340~380	10	13.19
AR	C26+	380+	34.3	23.31
SUM	-	-	100	99.39

[0071] Referring to Table 1 and FIG. 3, it was confirmed that the pyrolysis oil used as a raw material had a composition of 18.96 wt% of naphtha, 43.93 wt% of Kero/LGO, and a VGO/AR oil content of 36.50 wt%.

[Table 2]

mg/Kg	Inorganic Cl	Organic Cl	N	s	O	Fe	Ca	Na	Al	Si	P
Pyrolysis oil A	28	490	966	75	7,600	0.5	0.5	1.5	N/D	N/D	N/D

Example 2. Cl reduction reaction in oil by treating solid acid material at high temperature

Example 2-1.

[0072] Pyrolysis oil which was solid at room temperature and an oil having a high Cl content of Example 1 was allowed to stand in an oven at 70°C for 3 hours, and was converted into a liquid phase. 120 g of the liquid pyrolysis oil of Example 1 and 4.2 g of RFCC E-cat were sequentially introduced to an autoclave having a reactor internal volume of 300 cc. The physical properties of the RFCC E-cat used were confirmed as shown in the following Table 3.

[Table 3]

Type	TSA (m ² /g)	ZSA (m ² /g)	MSA (m ² /g)	Z/M Ratio	PV (cc/g)	APD (Å)
RFCC E-cat	122	36	86	0.42	0.20	67

(In Table 3, TSA is a total specific surface area, ZSA is a zeolite specific surface area, MSA is a specific surface area of mesopores or larger pores, Z/M is a ratio of the zeolite specific surface area (ZSA) to the specific surface area of mesopores or larger pores (MSA), PV is a pore volume, and APD is an average pore size.)

[Table 4]

wt%	Na	Ni	V	Fe	Mg	P	La ₂ O ₃	CeO ₂	TiO ₂	SiO ₂	Al ₂ O ₃
RFCC	0.13	0.53	1.21	0.65	0.07	0.56	0.69	0.10	0.78	40	53
E-cat											

[0073] The RFCC E-cat used was a catalyst having a total specific surface area of 112 m²/g, a pore volume of 0.20 cc/g, and an average particle size of 79 μm.

[0074] Certain amounts of pyrolysis oil and E-cat were introduced to a reactor, the reactor was fastened, and N₂ purge was performed. Thereafter, stirring was performed at 500 rpm under the conditions of N₂ and 1 bar, and the reactor temperature was raised up to 180°C at a rate of 1°C/min. Then, the reaction was maintained for 3 hours and then

completed.

[0075] After completion of the reaction, autoclave coupling was released while the temperature was maintained at 80°C, and the treated pyrolysis oil and E-cat in the mixture in the reactor were separated by a filter paper. The treated pyrolysis oil recovered was analyzed for a composition change and an impurity content change, and the results are shown in Tables 8 to 10 and FIG. 4.

Example 2-2.

[0076] The experiment was carried out in the same manner as in Example 2-1, except that zeolite was used as the solid acid material. The treated pyrolysis oil recovered was analyzed for a composition change and an impurity content change, and the results are shown in the following Tables 8 to 10 and FIG. 4.

[0077] The physical properties of zeolite used in the experiment were analyzed and are shown in the following Tables 5 and 6.

[Table 5]

Solid acid material	BET (m ² /g)		Pore volume (cc/g)	Average pore diameter (Å)
	Micro	External		
Zeolite	948.9		0.549	23.1
	867.2	81.7		

[Table 6]

SAR (SiO ₂ /Al ₂ O ₃ Mole Ratio)	Nominal Cation Form	Na ₂ O (wt %)	Unit Cell Size (Å)
60	Hydrogen	0.03	24.24

Example 2-3.

[0078] The experiment was carried out in the same manner as in Example 2-1, except that clay was used as the solid acid material. The treated pyrolysis oil recovered was analyzed for a composition change and an impurity content change, and the results are shown in Tables 8 to 10 and FIG. 4.

[0079] The physical properties of clay used in the experiment were analyzed and are shown in the following Table 7.

[Table 7]

Solid acid material	BET (m ² /g)		Pore volume (cc/g)	Average pore diameter (Å)
	Micro	External		
Clay	278.7		0.30	44.2
	58.7	220.0		

[0080] The results of analyzing the samples which were recovered after being subjected to a Cl reduction treatment using the solid acid materials of Examples 2-1, 2-2, and 2-3 are shown in Table 8.

[Table 8]

	Unit	Feed	RFCC E-cat	Zeolite	Clay
S	ppm	75	67	78	61
N	ppm	966	639	604	412
Organic Cl	ppm	490	212	224	197
Inorganic Cl	ppm	28	12	11	11
Fe	ppm	0.5	0.9	0.3	0.4
Na	ppm	1.5	0.5	0.6	0.6

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(continued)

	Unit	Feed	RFCC E-cat	Zeolite	Clay
Ca	ppm	0.5	0.5	0.6	0.6
O	wt%	0.76	0.56	0.50	0.46

[0081] Referring to Table 8, a reduction of 50 wt% or more based on Cl was possible even in the operating conditions of a small catalytic amount of 3.5 wt% and an operation temperature of 180°C, and in particular, in the case of the clay catalyst, a high impurity removal effect of 60 wt% of Cl (organic, inorganic), 57 wt% of N, 59 wt% of O, and the like and a good removal effect of 19 wt% of S were confirmed. In the case of RFCC E-cat, a VGO/AR yield increase effect was similar to that of clay, which was 7.4 wt%, but the impurity removal effect of 57 wt% of Cl, 34 wt% of N, 27 wt% of O, 11 wt% of S, and the like was inferior to that of the clay. However, a S adsorption effect by the solid acid catalyst was at a level of 0-19 wt%, which was lower than that of N, Cl, and the like. It was confirmed that impurities other than Cl, such as Fe, Na, Ca, and O were removed together.

[Table 9]

	BP (°C)	Raw material (wt%)	RFCC E-cat (wt%)	Zeolite (wt%)	Clay (wt%)
L-Naph	<80	0.9	0	0	0
H-Naph	80~150	13.9	8.9	11.4	8.8
Kero	150~265	23.4	20.2	22.1	20.3
LGO	265~340	17.6	19.3	19.5	19.5
VGO	340~380	10.4	11.7	11.4	11.3
AR	>380	33.8	39.9	35.6	40.1
Relation 1 (B/A)	-	-	1.07	1.04	1.07

[Table 10]

	BP (°C)	Zeolite	Clay	RFCC E-cat
		Increase/decrease rate*, %	Increase/decrease rate, %	Increase/decrease rate, %
H-Naph	80~150	-18.0	-36.7	-36.0
Kero	150~265	-5.6	-13.2	-13.7
LGO	265~340	10.8	10.8	9.7
VGO	340~380	9.6	8.7	12.5
AR	>380	5.3	18.6	18.0
(Increase/decrease rate*: increase/decrease rate as compared with raw material composition, (selectivity - raw material selectivity) / raw material selectivity X 100)				

[0082] Referring to Tables 9 and 10, as a result of analyzing the composition after the reaction, it was confirmed that the composition of naphtha oil (bp < 150°C) was slightly decreased and the composition of LGO or higher was slightly increased, and in particular, when the clay catalyst having the highest reduction efficiency for Cl, S, and N was applied, it was confirmed that the oil average molecular weight increase was the highest.

Example 3. Review of Cl reduction reaction characteristics using RFCC E-cat.

Example 3-1. Review of temperature effect

[0083] Since the Cl reduction characteristics of the solid acid catalyst were confirmed, a Cl reduction tendency by reaction variable was confirmed therefrom, for deriving optimal Cl reduction operating conditions.

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[0084] Pyrolysis oil B used as the raw material was waste plastic pyrolysis oil having a Cl content level of 67 wppm. The molecular weight distribution and the impurity content were analyzed by the same analysis as Example 1, and the results are shown in the following Tables 11 and 12.

[Table 11]

Cut Name	Expected carbon range	Boiling point (°C)	Yield (wt%)
H-Naph	~C8	<150	8.1
KERO	C9~C17	150~265	24.4
LGO	C18~C20	265~340	22.7
VGO/AR	C21~	>340	44.8
SUM	-	-	100

[Table 12]

mg/Kg	Cl	N	s	O
Pyrolysis oil B	67	348	20	0.2

[0085] Since the pyrolysis oil was also solid, it was maintained in an oven at 70°C for 3 hours or more, and then was converted into a liquid phase and used. 120 g of the liquid pyrolysis oil and 12 g of RFCC E-cat were sequentially introduced to an autoclave having a reactor internal volume of 300 cc. The same materials as those used in Example 2-1 of RFCC E-cat used were used.

[0086] Certain amounts of pyrolysis oil and E-cat were introduced to the reactor, and the weight was measured. The reactor was fastened, and N₂ purge was performed. Thereafter, stirring was performed at 500 rpm under the conditions of 1 bar of N₂, and the reactor temperature was raised up to a target temperature at a rate of 1°C/min. The reaction was maintained for 3 hours and then terminated.

[0087] After the completion of the reaction, the reactor temperature was maintained at 80°C, autoclave coupling was released, and the weight of the reactor including the mixture of the treated pyrolysis oil and E-cat was measured to calculate a recovery rate.

[0088] The treated pyrolysis oil and E-cat in the mixture in the reactor were separated by a filter paper. The treated pyrolysis oil recovered was analyzed for a composition change and an impurity content change, and the results are shown in the following Tables 13 to 15 and FIGS. 4 to 10.

[Table 13]

Classification	Feed	E-cat	Recovery	Recovery rate	Reaction temperature	Cl	N	s	O
	(g)	(g)	(g)	(%)	(°C)	wppm	wppm	wppm	wt %
Feed						67	348	20	0.2
Example 3-1	119.8	11.8	116	96.8	170	45	184	16.8	<0.1
	119.4	12	115.2	96.5	203	40	184	16.9	<0.1
	119.5	12.1	115	96.2	237	30	184	16.6	<0.1
	119.8	11.7	117.1	97.7	260	15	167	17.4	<0.1
	120.2	12	116.9	97.3	280	7	162	15.6	<0.1

[Table 14]

Reaction temperature (°C)	Cl, wppm	Cl reduction rate (%)
170	45	32.84
203	40	40.30

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(continued)

Reaction temperature (°C)	Cl, wppm	Cl reduction rate (%)
237	30	55.22
260	15	77.61
280	7	89.55

[0089] The recovery rate was 96.2 to 97.7%, and the loss occurring during the experiment was 2.3 to 2.8% which was very low. It was confirmed that as the reaction temperature was raised, the Cl reduction rate (Cl reduction amount per unit E-cat) was increased, and as the reaction temperature was raised in the experimental temperature range, Cl removal performance was improved.

[0090] It was also confirmed that removal ratios of N and S were increased as not only the Cl content but also the reaction temperature was increased. In the case of N, a difference in the reduction rate was not large under the conditions of 240°C or lower, but the reduction rate was increased under the conditions of 260°C or higher, and thus, it was inferred that the N reduction reaction was separately carried out based on 260°C (see FIGS. 5 and 6).

[Table 15]

Class ification	Reaction tem perature	Naph (bp <150°C)	Kero (bp 150~265°C)	LGO (bp 265~340°C)	VGO (bp>340°C)	Relation 1 (B/A)
	(°C)	wt%	wt%	wt%	wt%	(wt%/wt%)
Feed		8.1	24.4	22.7	44.8	-
Exam ple 3-1	170	7.5	22.5	23	47	1.00
	203	7.9	22.9	22.6	46.6	1.00
	237	7.8	22.2	22.4	47.6	1.01
	260	7	21.9	22.6	48.5	1.00
	280	7.9	22.9	22.2	47	1.00

(In Relation 1 of Table 15, A is wt% of components having a boiling point (bp) of 150°C or higher with respect to the total weight of the raw material (waste oil), and B is wt% of components having bp of 150°C or higher with respect to the total weight of each oil treated with RFCC E-Cat, Zeolite, and clay.)

[0091] Referring to Table 15 and FIG. 7, the composition was hardly changed at a reaction temperature of 170 to 240°C, and at 260°C or higher, an oligomerization phenomenon in which the contents of naphtha and kerosene were slightly decreased and the contents of LGO and VGO were slightly increased was confirmed. When high temperature stirring operation was performed at a reaction temperature of 275 to 295°C, product abnormality and yield loss were minimized, and the Cl content to be desired of < 10 ppm was satisfied.

Example 3-2. Review of time effect

[0092] In order to confirm the Cl reduction characteristics of the solid acid catalyst, the Cl reduction tendency over time under the operating conditions at 280°C in which a difference in composition derived in Example 3-1 was small and the Cl reduction efficiency was high was confirmed. Other reaction variables such as a catalytic amount and a stirring speed and the analysis method were performed under the same conditions as Example 3-1. Further, the analysis results are shown in the following Tables 16 and 17 and FIGS. 8 to 12.

[Table 16]

Classification	Feed	E-cat	Recovery	Recovery rate	Time	Cl	N	S	O
	(g)	(g)	(g)	(%)	(h)	wppm	wppm	wppm	wt%
Feed						67	348	20	0.2

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(continued)

Classification	Feed	E-cat	Recovery	Recovery rate	Time	Cl	N	S	O
	(g)	(g)	(g)	(%)	(h)	wppm	wppm	wppm	wt%
Example 3-2	119.2	12	114.7	96.2	0.08	32	174	16	0.2
	119.5	11.9	116.6	97.6	0.5	21	161	16	0.1
	119.5	11.9	115.1	96.3	1	15	171	15	<0.1
	120.2	12	116.9	97.3	3	7	162	15.6	<0.1
	119.8	11.9	117.3	97.9	5	4	153	15	<0.1

[Table 17]

Time (h)	Cl, wppm	Cl reduction rate (%)
0.08	32	52.24
0.5	21	68.66
1	15	77.61
2	10	85.07
3	7	89.55
5	4	94.03

[0093] Referring to Tables 16 and 17 and FIGS. 8 to 11, it was confirmed that S, N, and O including Cl were decreased over time. There was no significant difference in the recovery rate over time. For the raw material having a Cl content of 67 wppm, a treatment time was increased to increase the Cl reduction efficiency, and in a treatment of 24 hours, a Cl content of 1.6 wppm which was reduced by 97.6% of total Cl was confirmed.

[0094] It was confirmed that for a Cl reduction tendency, the Cl reduction rate was gradually lowered after initial rapid Cl reduction, and the Cl reduction rate tended to decrease over time, but the reduction rates of N and S were almost constant over time.

[Table 18]

Classification	Time	Naph (bp <150°C)	Kero (bp 150~265°C)	LGO (bp 265~340°C)	VGO (bp>340°C)	Relation 1 (B/A)
	(h)	wt%	wt%	wt%	wt%	(wt%/wt%)
Feed		8.1	24.4	22.7	44.8	-
Example 3-2	0.08	5.7	23.6	21.7	49	1.03
	0.5	6.5	24	21.5	48	1.02
	1	7.5	23.5	22	47	1.01
	2	6.4	23.8	21.7	48.1	1.02
	3	7.9	22.9	22.2	47	1.00
	5	7.5	23.5	22	47	1.01

[0095] Referring to Table 18 and FIG. 12, a tendency in which Naphtha and Kero ratios were increased and LGO and VGO were decreased over time was confirmed. Thus, it may be inferred that as the cracking reactivity was increased, the reduction rate of impurities including the Cl reduction rate was increased.

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[Table 19]

t (h)	C	0th (C ₀ /C)	1 st (ln (C ₀ /C))	2 nd (1/C)
0.08	32	2.09	0.74	0.03
0.5	21	3.19	1.16	0.05
1	15	4.47	1.50	0.07
2	10	6.70	1.90	0.10
3	7	9.57	2.26	0.14
5	4	16.75	2.82	0.25

[0096] Referring to Table 18 and FIG. 13, a reaction order of the Cl reduction reaction was calculated by interpreting the Cl reduction performance over a reaction time. When a reciprocal (1/C) of the reaction time (t) and the Cl weight was shown, it was confirmed that the Cl reduction rate approximated the second order reaction rate equation to the reaction time. In summary, since the slope of the Cl removal amount was rapidly decreased in more or less than 3 hours and the Cl content to be desired of < 10 ppm was satisfied, it was found that it is most preferred that the stirring operation at a high temperature is performed for 3 hours.

Example 3-3. Review of amount of catalyst introduced

[0097] In order to confirm the Cl reduction characteristics of the solid acid catalyst, the Cl reduction tendency depending on an amount of catalyst introduced under the operating conditions at 280°C for 3 hours in which a difference in composition compared with the raw material derived in Examples 3-1 and 3-2 was small and the Cl reduction efficiency was high was confirmed. Other reaction variables such as a stirring speed and the analysis method were performed under the same conditions as Example 3-1. The analysis results are shown in the following Tables 21 to 23 and FIGS. 14 to 18.

[Table 20]

Classification	Feed (g)	E-cat (g)	Recovery (g)	Recovery rate (%)	Catalytic amount (%)	Cl wppm	N wppm	s wppm	O wt%
Feed						67	348	20	0.2
Example 3-3	120	0	117.3	97.8	0	45	328	18	0.2
	119.5	1.2	116.5	97.5	1	29	310	22	0.2
	120	3	117.4	97.8	2.5	28	282	20	0.2
	119.6	5.9	113.4	94.8	5	16	233	17	0.1
	119.5	9	115.1	96.3	7.5	11	200	16	<0.1
	120.2	12	116.9	97.3	10	7	162	15.6	<0.1

[0098] Referring to Table 20 and FIGS. 14 to 17, it was confirmed that when the catalytic amount introduced was gradually increased to 10 wt%, the Cl reduction rate was increased as the catalytic amount was increased. Like the results in Examples 3-1 and 3-2, the contents of N, S, and O were removed together, in addition to Cl.

[0099] N showed a tendency of being removed in proportion to the increase in the catalytic amount introduced. S had the same tendency of being removed in proportion to the increase in the catalytic amount introduced, but the slope of S reduction to the catalytic amount introduced of 10 wt% was very low.

[Table 21]

Classification	Catalytic amount	Naph (bp <150°C)	Kero (bp 150~265°C)	LGO (bp 265~340°C)	VGO (bp >340°C)	Relation 1 (B/A)
	(%)	wt%	wt%	wt%	wt%	(wt%/wt %)
Feed		8.1	24.4	22.7	44.8	-

(continued)

Classification	Catalytic amount	Naph (bp <150°C)	Kero (bp 150~265°C)	LGO (bp 265~340°C)	VGO (bp >340°C)	Relation 1 (B/A)
	(%)	wt%	wt%	wt%	wt%	(wt%/wt %)
Example 3~3	0	5.8	22	21.2	51	1.03
	1	5.8	22.7	20	51.5	1.03
	2.5	5.7	23.0	21.7	49.4	1.02
	5	6.3	22.3	21.1	50.4	1.02
	7.5	5.8	22.7	21.5	50	1.03
	10	7.9	22.9	22.2	47	1.00

[0100] Referring to Table 21 and FIG. 18, it was confirmed that the composition was not changed much under the conditions of an increase in the introduced amount up to 10 wt% of E-cat, even with the increase in the catalytic amount introduced.

[Table 22]

mg/Kg	Fe	Na	Ca	Al
Pyrolysis oil B	2.9	5.7	0.5	0.3
Example 3-1 280°C	1.3	2.1	0.2	0.1

[0101] In order to confirm whether metal impurities such as Fe, Na, and Ca may be removed in addition to impurities such as Cl, N, S, and O, analysis of metal impurities for the sample recovered under the operating conditions of 280°C of Example 3-1 in which no composition was changed and Cl reduction efficiency was high was performed. The Results of comparing the contents of metal impurities for the samples recovered under the operating conditions of 280°C of Example 3-1 with the contents of metal impurities of the raw material sample are shown in Table 22. It was confirmed that 60% or more of Fe, Na, Ca, and Al was all removed at the same time.

Example 3-4. Review of experiment of high pressure N₂ influence

[0102] In order to confirm the Cl reduction characteristics under the conditions of N₂ high pressure operation, the Cl reduction characteristics under the conditions of 35 bar of N₂ were confirmed in the operating conditions of 280°C, 3 hrs, 10 wt% of E-cat which was derived from Examples 3-1, 3-2, and 3-3. Other reaction variables such as a stirring speed and the analysis method were performed under the same conditions as Example 3-1. The analysis results are shown in the following Tables 23 and 24.

[Table 23]

Classification	Feed	E-cat	Recovery	Recovery rate	N ₂	Cl	N	s	O
	(g)	(g)	(g)	(%)	(bar)	wppm	wppm	wppm	wt%
Feed						67	348	20	0.2
Example 3-4	120.2	12	116.9	97.3	1	7	162	15.6	<0.1
	119.2	119.2	115.9	97.2	35	6	152	17.5	<0.1

[Table 24]

Classification	N ₂	Naph (bp <150°C)	Kero (bp 150~265°C)	LGO (bp 265~340°C)	VGO (bp >340°C)	Relation 1 (B/A)
	(bar)	wt%	wt%	wt%	wt%	(wt%/wt%)
Feed		8.1	24.4	22.7	44.8	-
실시예 3-4	1	7.9	22.9	22.2	47	1.00
	35	6.5	24.8	21.3	47.4	1.02

[0103] Referring to Tables 23 and 24, by applying high pressure N₂ of 35 bar, it was confirmed that there was no significant difference in the Cl reduction efficiency and the N, S, O reduction efficiency and the composition was not changed much, even when the catalytic reaction was performed in a liquid phase under the operating conditions of 280°C, and there was no significant difference in the impurity reduction activity resulting from a difference in catalyst/raw material reaction depending on a N₂ pressure change.

[0104] From the experiment of Example 3, it was confirmed that the waste oil having a high Cl content of 67 wppm had almost no change in the composition by the high-temperature treatment, and 95% or more of the Cl content may be removed, after 10 wt% of RFCC E-cat which was the solid acid catalyst was introduced. At the same time, it was confirmed that S, N, and O may be removed in addition to Cl, and the metal impurities such as Fe, Al, Na, and Ca may be removed.

Example 3-5. Review of influence of low-rate stirring treatment

[0105] Since the solid acid catalyst and the raw material had different phases under the reaction conditions, the raw material/catalyst ratio by position may vary, unless the stirring speed was not maintained to a certain level or higher. The raw material/catalyst non-uniformity as such may decrease the Cl reduction reaction activity, and in order to confirm the Cl reduction efficacy in the phenomenon, a low-speed stirring experiment was carried out.

[0106] After a mixture of the raw material and the catalyst was introduced, the experiment was carried out under the conditions of a stirring speed of 40 rpm at which the solid acid catalyst sinking to the bottom of the reactor was not uniformly mixed with the raw material. The Cl reduction characteristics under the conditions of the stirring speed of 40 rpm, not 500 rpm were confirmed in the operating conditions of 1 bar of N₂, 280°C, 3 hrs, and 10 wt% of E-cat. The analysis method was performed under the same conditions as in Example 3-1. The analysis results are shown in the following Tables 25 and 26.

[Table 25]

Classification	Feed	E-cat	Recovery	Recovery rate	Stirring speed	Cl	N	s	O
	(g)	(g)	(g)	(%)	(rpm)	wppm	wppm	wppm	wt%
Feed						67	348	20	0.2
Example 3-5	120.2	12	116.9	97.3	500	7	162	15.6	<0.1
	119.5	12	116.5	97.5	40	15	205	16	0.1

[Table 26]

Classification	Stirring speed	Naph (bp <150°C)	Kero (bp 150~265°C)	LGO (bp 265~340°C)	VGO (bp >340°C)	Relation 1 (B/A)
	(rpm)	wt%	wt%	wt%	wt%	(wt%/wt%)
Feed		8.1	24.4	22.7	44.8	-
Example 3-5	500	7.9	22.9	22.2	47	1.00
	40	7.4	26.5	22.9	43.2	1.01

[0107] Referring to Tables 25 and 26, the Cl reduction effect of 75% or more was confirmed even under the stirring speed of 40 rpm, and it was confirmed that N, S, O, and the like were also reduced. As a result of confirming the

composition change, it was confirmed that the material of the composition in a VGO range was at a similar level before and after the reaction, and there was no significant difference but only a small amount of naphtha was converted into Kero. Unlike the general experimental results in which general LGO and VGO ranges were increased, it was confirmed that only a small amount of light olefin in naphtha was converted into Kero under the conditions of a low stirring speed, and VGO conversion by oligomerization of a heavy olefin was limited.

Example 4. Review of CI reduction reaction characteristics using waste clay

[0108] Since the CI reduction reaction characteristics for the oil having a high CI content of RFCC E-cat in Example 3 were confirmed, the CI reduction reaction activity was also reviewed for the clay which was the solid acid material.

[0109] The pyrolysis oil used as the raw material was a pyrolysis oil at a level of a CI content of 67 wppm used in Example 3-1. The waste clay was a clay catalyst discarded after being used for removing an olefin during the petrochemical process. The waste clay catalyst was a catalyst discarded in the petrochemical process, and was used after removing the oil included on the surface and in the inside by drying. The physical properties of the waste clay catalyst are shown in the following Table 27.

[Table 27]

Sample	Surface area, m ² /g		Pore volume (cc/g)	Average pore diameter (Å)	Apparent Bulk Density (g/cc)
	Micro	external			
Clay	281.1		0.32	45.6	0.7147
	21.7	259.4			
Particle size			2.0 mm or more	2.0-0.3mm	0.3 mm or less
Content (wt%)			15.7781	83.8070	0.4149

[0110] 53 g of the pyrolysis oil which was maintained in an oven at 70°C for 3 hours or more to be converted into a liquid phase and 5.3 g of the spent clay were introduced to a 130 cc autoclave reactor. Thereafter, the reactor was fastened, and purging was performed three times at 10 bar of N₂. After a leak test was performed under the conditions of 30 bar of N₂, no leak was confirmed and the reactor was vented, in a state of being stabilized in 1 bar of N₂, stirring was performed at 500 rpm, and the temperature was raised up to a target temperature. After reaching the target temperature, the temperature was maintained for 3 hours and the reaction was completed. After the completion of the reaction, the temperature was lowered to 80°C, the reactor was disassembled, and filtration was performed to separate the oil having reduced impurities and spent clay.

[0111] Analysis for confirming an impurity content and a composition change was performed in the same manner as in Example 2. The results of clay experiment are shown in Table 28.

[Table 28]

Classification	Temperature/time	Clay waste catalyst	RFCC E-cat
	(°C/hr)	CI, wppm	CI, wppm
Feed	-	67	67
Example 4	200/3	30	40
	280/1	14	15
	280/3	11	7

[0112] Referring to Table 28, the CI reduction performance was superior to that of RFCC E-cat in the conditions of a temperature of 200°C, but in a high temperature/long term treatment, the CI reduction performance was inferior to that of RFCC E-cat. In addition, it was confirmed that the oligomerization reactivity was higher than that of RFCC E-cat in the conditions of high temperature/long term treatment, and thus, a LGO/VGO composition increase phenomenon was higher.

Example 5. Application of fixed bed reactor

[0113] Pyrolysis oil which was solid at room temperature and an oil having a high Cl content of Example 1 was allowed to stand in an oven at 70°C for 3 hours, and was converted into a liquid phase. The fixed bed reactor was filled with 8.1 g of the same material as RFCC E-cat of Examples 2 and 3, dried by N₂ purge at 280°C, and pressed at 37 bar, and then the pyrolysis oil was supplied using a liquid pump. The diameter of the reactor used was 7 mm, and the filling amount and the feed supply rate were varied depending on the experimental conditions. The sample discharged to the rear end of the reactor with varied space velocity per catalyst was collected and a residual Cl content was measured, and the results are shown in the following Table 29.

[Table 29]

	WHSV(/hr)	Throughput/g_cat	Cl (ppm)
Case 1	0.42	2.3	2
		5.0	11
		6.5	26
		6.9	25
		10.1	23
		11.7	41
		13.4	42
		14.6	44
Case 2	1.40	15.5	48
		2.8	3
		7.2	17
		9.4	35
Case 3	2.44	12.2	35
		3.4	8
		8.7	32
		13.3	26
Case 4	5.90	24.8	35
		4.3	9
		7.7	42
		24.5	47
		67.7	56

[0114] Referring to Table 29, as the reaction time was increased, removal performance deteriorated, and thus, a discharged Cl concentration was increased. A feed throughput per catalyst satisfying Cl content < 10 ppm in a range of an appropriate space velocity of 0.1/hr to 10/hr was ~5 g_{feed}/g_{cat}.

[Table 30]

WHSV /hr	Temperature, °C	Pressure, bar	Feed g/g_cat	Cl ppm	N ppm	S ppm
1.6	289.0	37.91	1.4	2	2.8	5.1
	292.8	35.35	2.7	24	34	17.8
	296.4	35.94	4.3	42	156	19.3
	293.9	37.58	5.4	49	185	20.6
	293.1	35.5	6.4	48	219	20.7

[0115] Referring to Table 30, as a result of measuring the contents of Cl and other impurities in the conditions of a space velocity of 1.6/hr as in the following examples, a N and S removal effect was confirmed like Example 3. As the reaction time was increased, it was confirmed that N and S removal ability was deteriorated together with the deterioration of Cl removal performance.

Example 6. Review of further Cl reduction by repeated treatment

[0116] A further Cl reduction possibility was reviewed by a repeated treatment, for the sample from which impurities including Cl were removed by the solid acid material.

[0117] The raw material and the catalyst were the same as the pyrolysis oil and E-cat which were used in Example 3. The experiment was performed under the same operating conditions as the treatment conditions at 280°C of Example 3-1 having a Cl reduction rate of 90% or more, with little change in the composition as compared with the raw material, thereby recovering the oil of Example 6-1. The analysis of the recovered oil was performed in the same manner as in Example 3, and the results are shown in the following Table 31.

[Table 31]

Classification	Raw material	Reaction temperature	Time	Cl	N	s	O
		(°C)	(hr)	wppm	wppm	wppm	wt%
Feed	-	-	-	67	348	20	0.2
Example 3_280°C	Feed	280	3	7	162	15.6	<0.1
Example 6-1	Feed	280	3	6	158	15.5	<0.1
Example 6-2	6-1	280	24	1	19	7.8	<0.1

[0118] Referring to Table 31, as a result of analyzing the composition and the impurities, it was confirmed that the Cl content, the S, N, and O content, the composition, and the like of the oil of Example 3 (treated at 280°C) and the oil of Example 6-1, which were treated in the same operating conditions and recovered, were all similar, and thus, the method is reproducible.

[0119] The treatment was repeated once again under the same reaction temperature conditions, using the recovered oil of Example 6-1 as the raw material, and the oil of Example 6-2 was recovered. The impurity content and the composition of the recovered oil of Example 6-2 were obtained in the same manner as in Example 3, and the analysis results are shown in the following Table 32.

[Table 32]

Classification	Reaction temperature	Time	Naph (bp <150°C)	Kero (bp 150~265°C)	LGO (bp 265~340°C)	VGO (bp>340°C)	Relation 1 (B/A)
	(°C)	(hr)	wt%	wt%	wt%	wt%	(wt%/wt%)
Feed	-	-	8.1	24.4	22.7	44.8	-
Example 3	280	3	7.9	22.9	22.2	47.0	1.00
Example 6-1	280	3	7.4	25.1	22.1	45.5	1.01
Example 6-2	280	24	6.5	24.6	21.7	47.3	1.02

[0120] Referring to Table 32, the sample of Example 6-2 obtained by retreating and recovering the sample of Example 6-1 had a Cl content of 1 wppm and N and S contents of 19 wppm and 7.8 wppm, respectively, and thus, a very large impurity reduction effect was confirmed. The Cl content acceptable in the most refinery processes is limited to a level of 1 wppm in the raw material for preventing device corrosion, and it was confirmed that the oil of Example 6-2 satisfied the standard of the impurity content. Thus, it was confirmed that a very low impurity standard process may be also applied as a technology for manufacturing a raw material by the repeated treatment.

[0121] Though oligomerization effect such as a decreased ratio of a naphtha region and a slightly increased ratio of

heavy hydrocarbons such as VGO was observed, there was no significant difference overall in the composition.

[0122] When the results of the examples were combined, it was confirmed that the impurities may be selectively removed with little change in the composition of the oil, by treating the waste oil with the solid acid material, according to the present invention. In addition, it was confirmed from Example 6 that the impurities may be extremely decreased with little change in the composition of the oil by repeatedly applying the solid acid material.

[0123] Although the exemplary embodiments of the present invention have been described above, the present invention is not limited to the exemplary embodiments but may be made in various forms different from each other, and those skilled in the art will understand that the present invention may be implemented in other specific forms without departing from the spirit or essential feature of the present invention. Therefore, it should be understood that the exemplary embodiments described above are not restrictive, but illustrative in all aspects.

Claims

1. A method for removing chlorine from a waste oil, the method comprising:

- a) preparing a mixture of a chlorine-containing waste oil and a solid acid material;
- b) reacting the mixture to remove chlorine; and
- c) separating a dechlorinated oil fraction and the solid acid material from the mixture to recover the dechlorinated oil fraction,

wherein the following Relation 1 is satisfied:

[Relation 1]

$$1 \leq B/A \leq 3$$

wherein A is a wt% of components having a boiling point (bp) of 150°C or higher with respect to a total weight of the waste oil, and B is a wt% of components having bp of 150°C or higher with respect to a total weight of the dechlorinated oil fraction.

2. The method for removing chlorine from a waste oil of claim 1, wherein the waste oil includes a waste plastic pyrolysis oil, a biomass pyrolysis oil, a regenerated lubricant, a crude oil having a high chlorine content, or a mixture thereof.

3. The method for removing chlorine from a waste oil of claim 1, wherein the waste oil has a ratio (A_2/A_1) of 1 to 19, the ratio being a weight (A_2) of components having bp of 150°C or higher to a weight (A_1) of components having bp of lower than 150°C.

4. The method for removing chlorine from a waste oil of claim 1, wherein the waste oil has a chlorine content of 10 ppm or more.

5. The method for removing chlorine from a waste oil of claim 1, wherein the solid acid material is zeolite, clay, silica-alumina-phosphate (SAPO), aluminum phosphate (ALPO), metal organic framework (MOF), silica alumina, or a mixture thereof.

6. The method for removing chlorine from a waste oil of claim 1, wherein the solid acid material in a) is included at 5 to 10 wt% with respect to a total weight of the mixture.

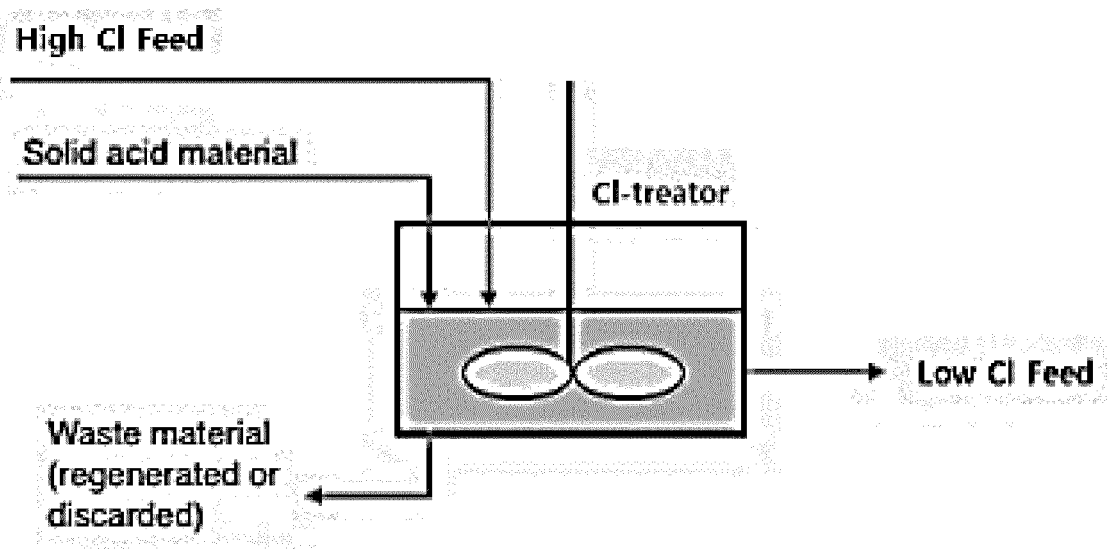
7. The method for removing chlorine from a waste oil of claim 1, wherein the reaction in b) is the catalytic conversion reactions that the chlorine contained in the waste oil is removed by a reaction of a direct bond to an active site of the solid acid material and/or is converted into a hydrochloric acid (HCl) at the active site of the solid acid material.

8. The method for removing chlorine from a waste oil of claim 1, wherein the reaction of b) is performed at a pressure of 1 bar or more and 100 bar or less under an inert gas atmosphere and at a temperature of 200°C or higher and lower than 300°C.

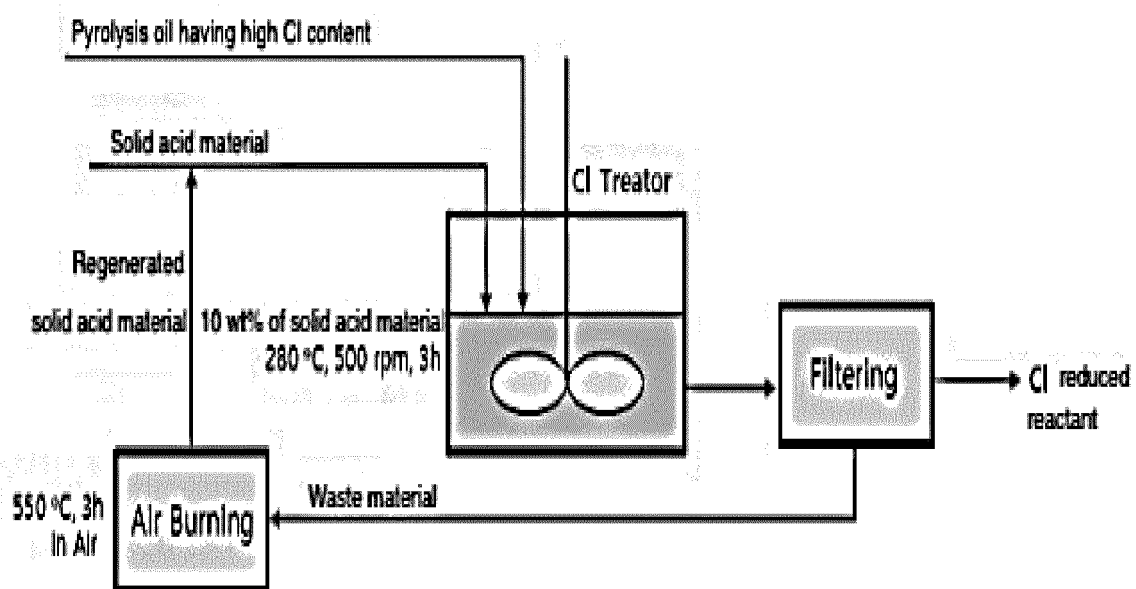
EP 4 105 298 A1

9. The method for removing chlorine from a waste oil of claim 1, wherein the reaction of b) is performed for 0.1 to 48 hours.
10. The method for removing chlorine from a waste oil of claim 1, wherein the reaction of b) is performed at a stirring speed of 30 to 2000 rpm.
11. The method for removing chlorine from a waste oil of claim 1, further comprising: d) repeating a), b), and c) once or more.
12. The method for removing chlorine from a waste oil of claim 1, wherein the dechlorinated oil fraction has a ratio (B_2/B_1) of 1 to 20, the ratio being a weight (B_2) of components having bp of 150°C or higher to a weight (B_1) of components having bp of lower than 150°C.
13. The method for removing chlorine from a waste oil of claim 1, wherein the dechlorinated oil fraction has a chlorine content of less than 10 ppm.
14. The method for removing chlorine from a waste oil of claim 1, wherein a weight ratio of chlorine in the dechlorinated oil fraction to chlorine in the waste oil is 0.01 to 0.25.
15. The method for removing chlorine from a waste oil of claim 1, wherein Fe, Na, Ca, and Al contained in the waste oil are further removed.
16. The method for removing chlorine from a waste oil of claim 1, wherein N, S, and O contained in the waste oil are further removed.

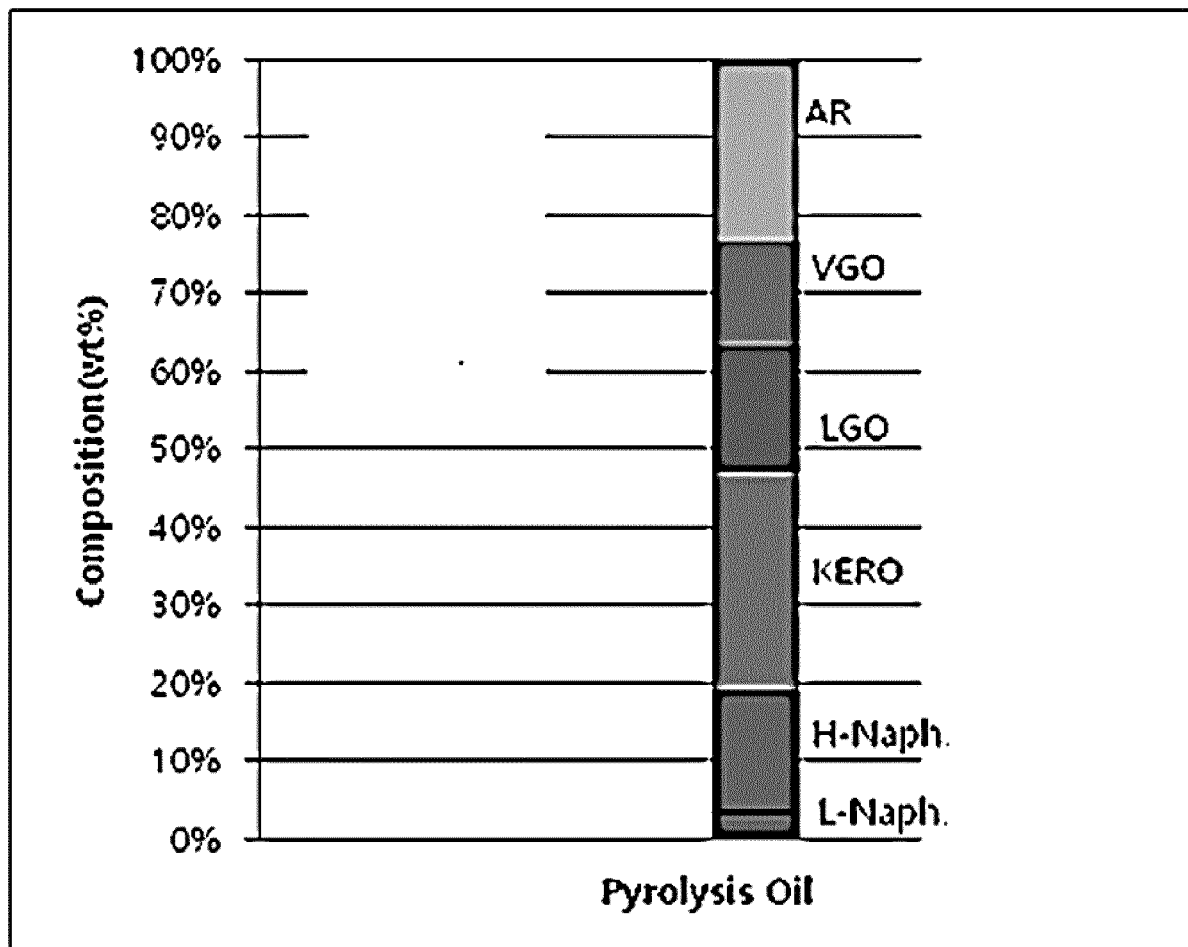
【FIG. 1】



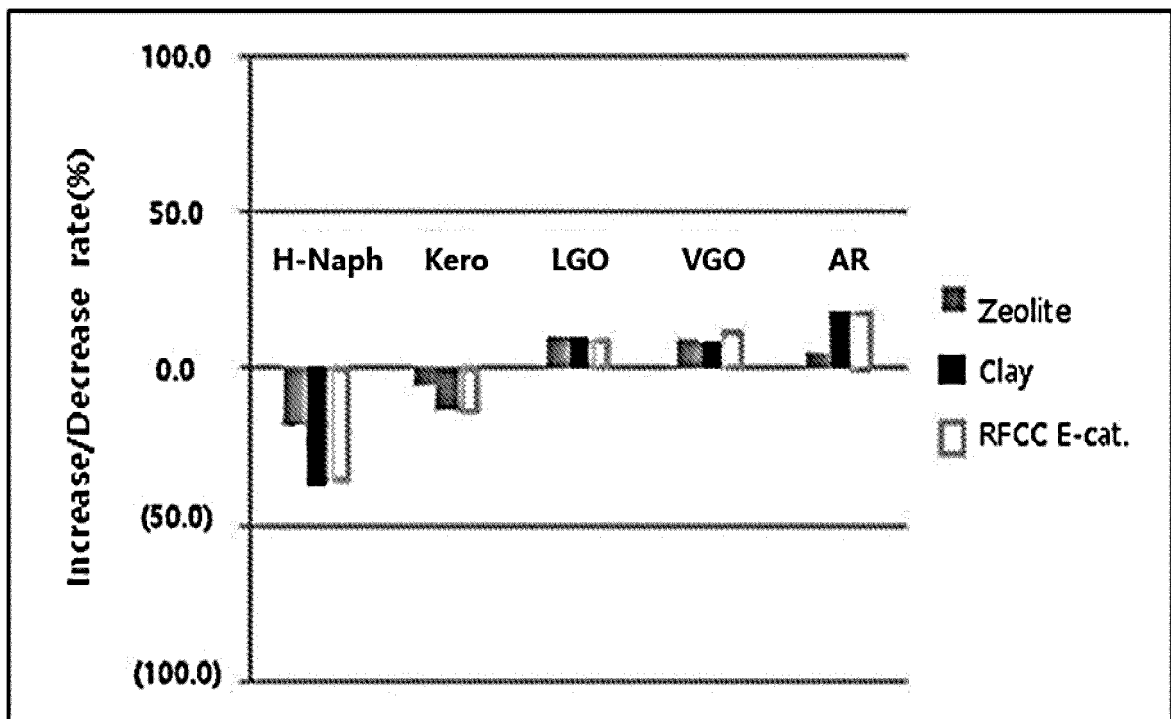
【FIG. 2】



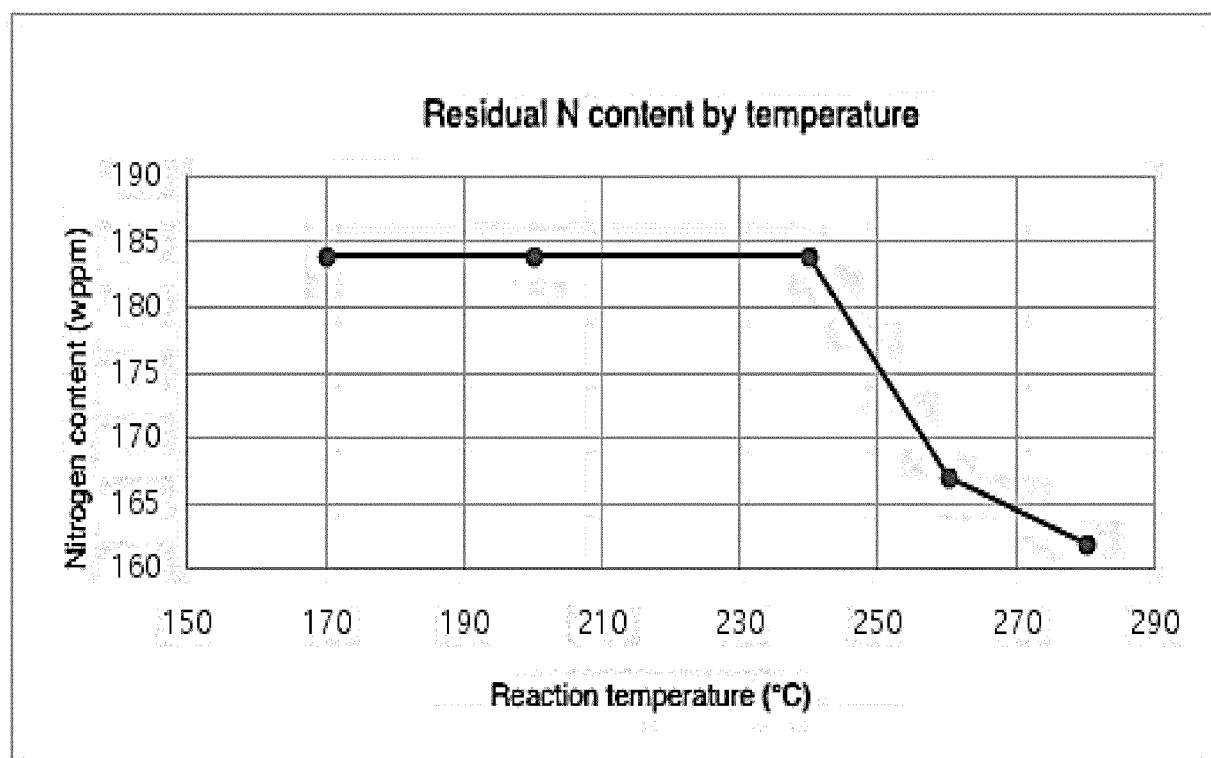
【FIG. 3】



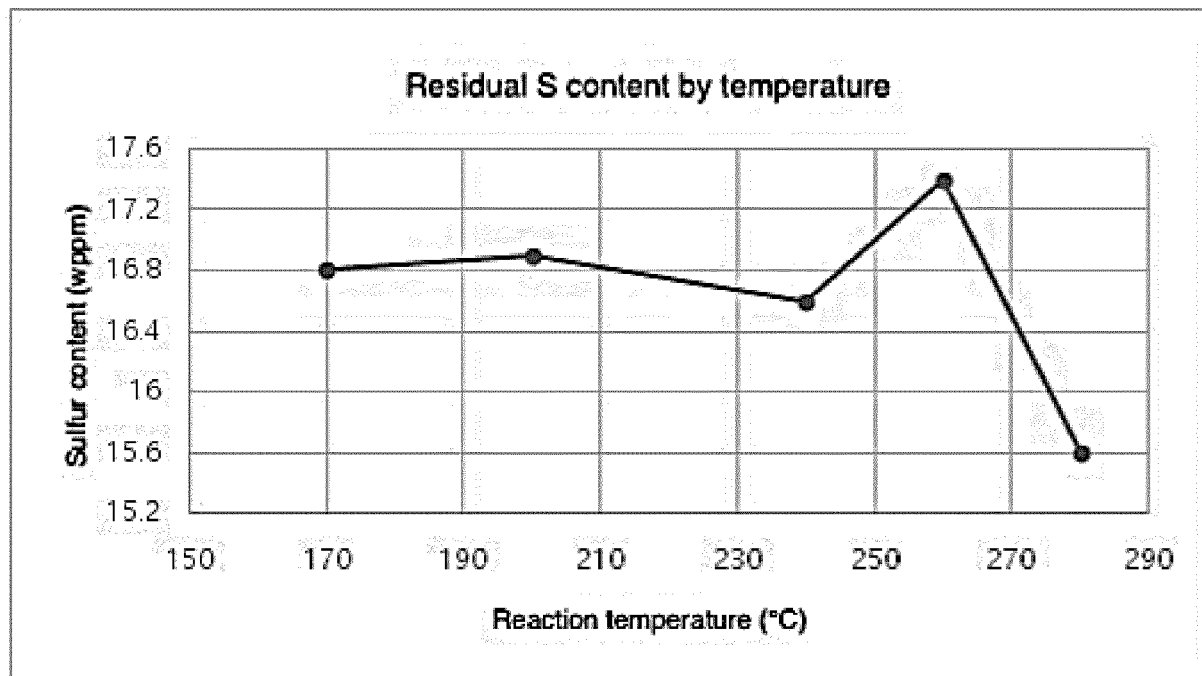
【FIG. 4】



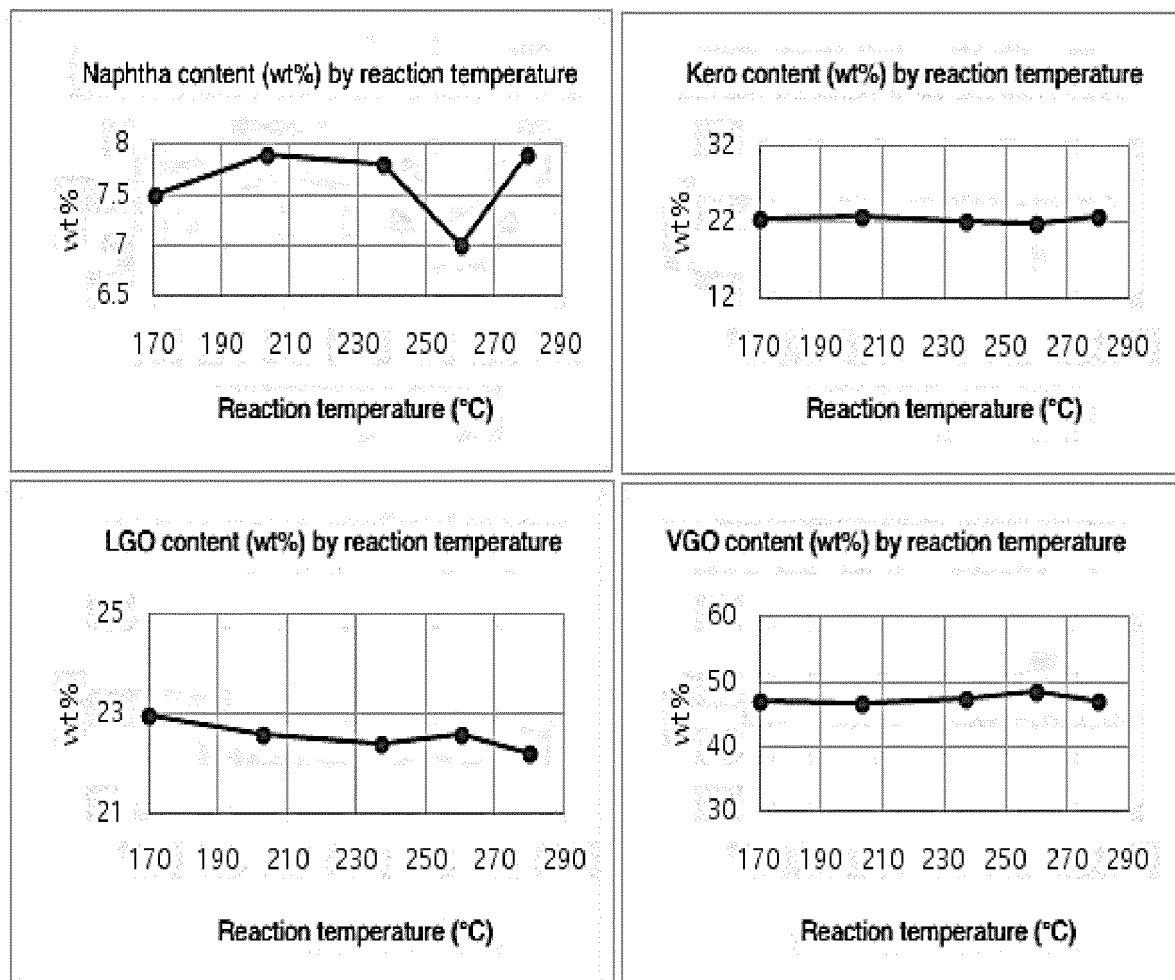
【FIG. 5】



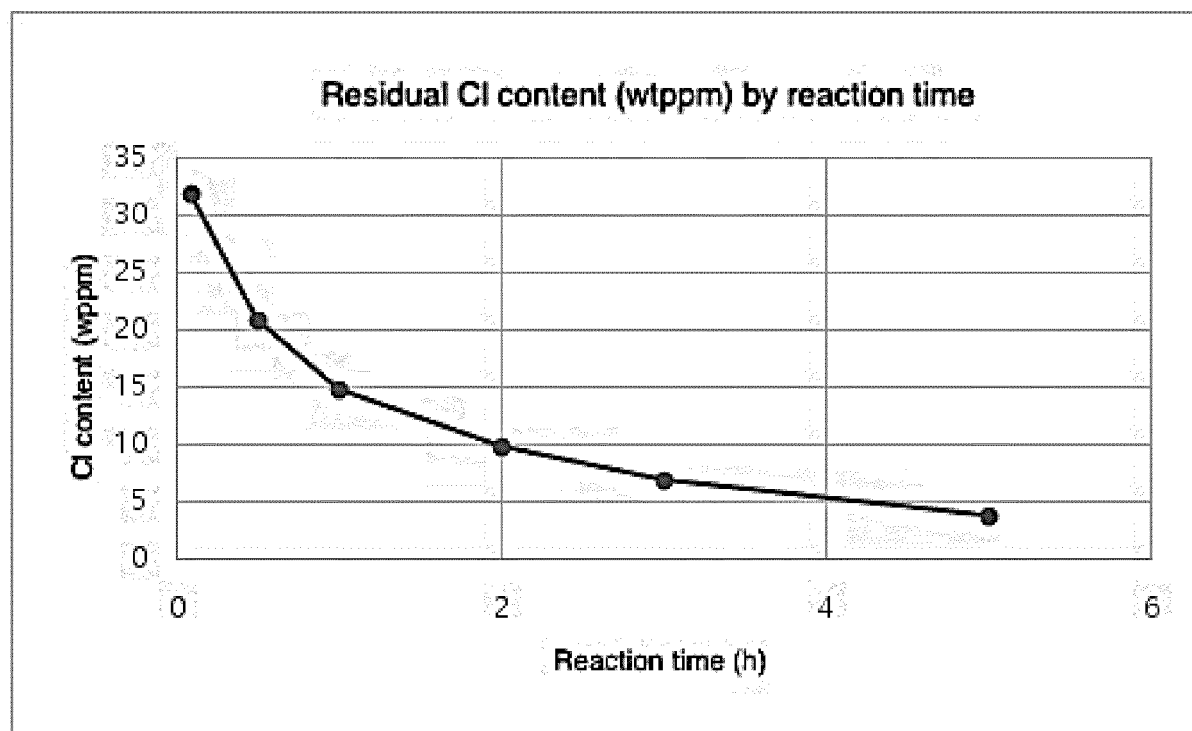
【FIG. 6】



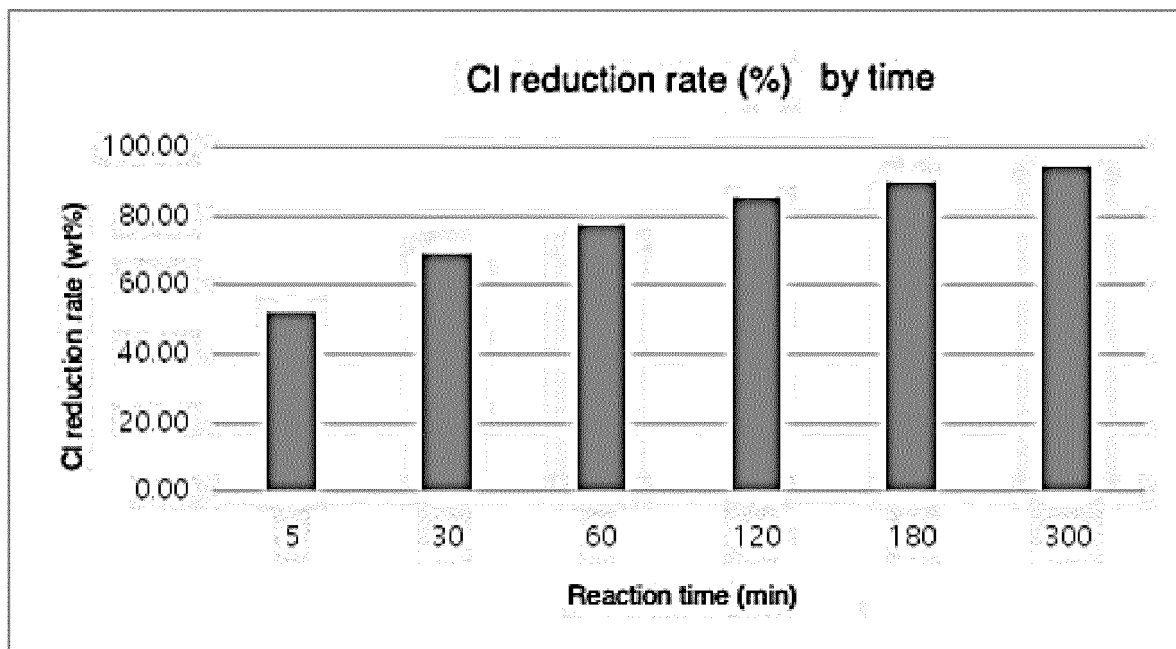
【FIG. 7】



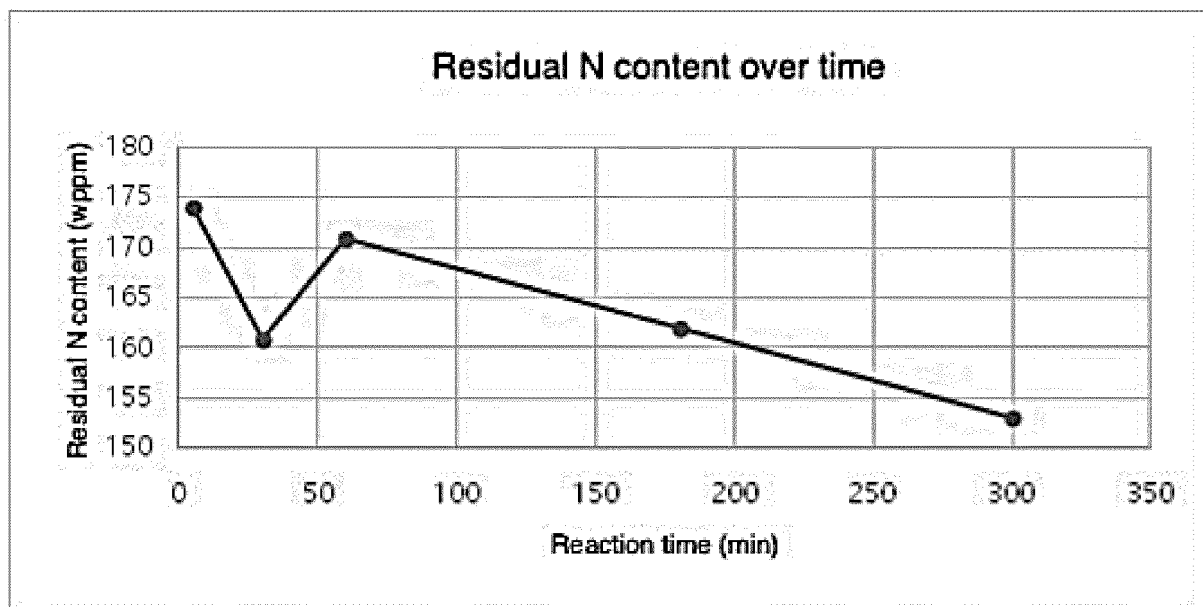
【FIG. 8】



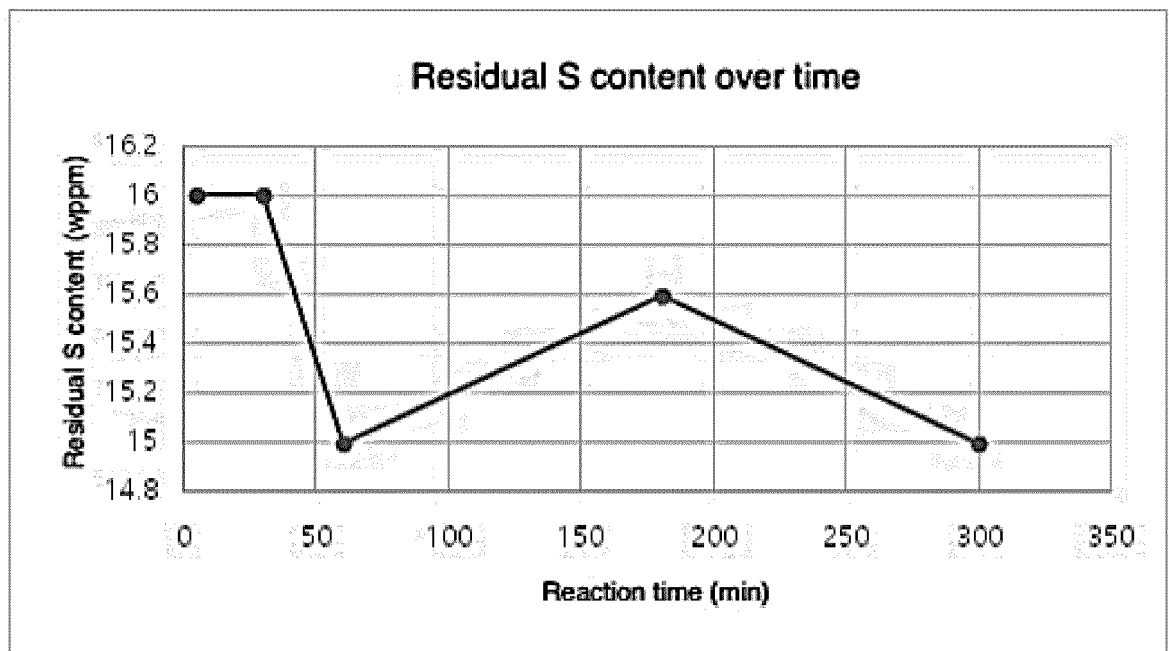
【FIG. 9】



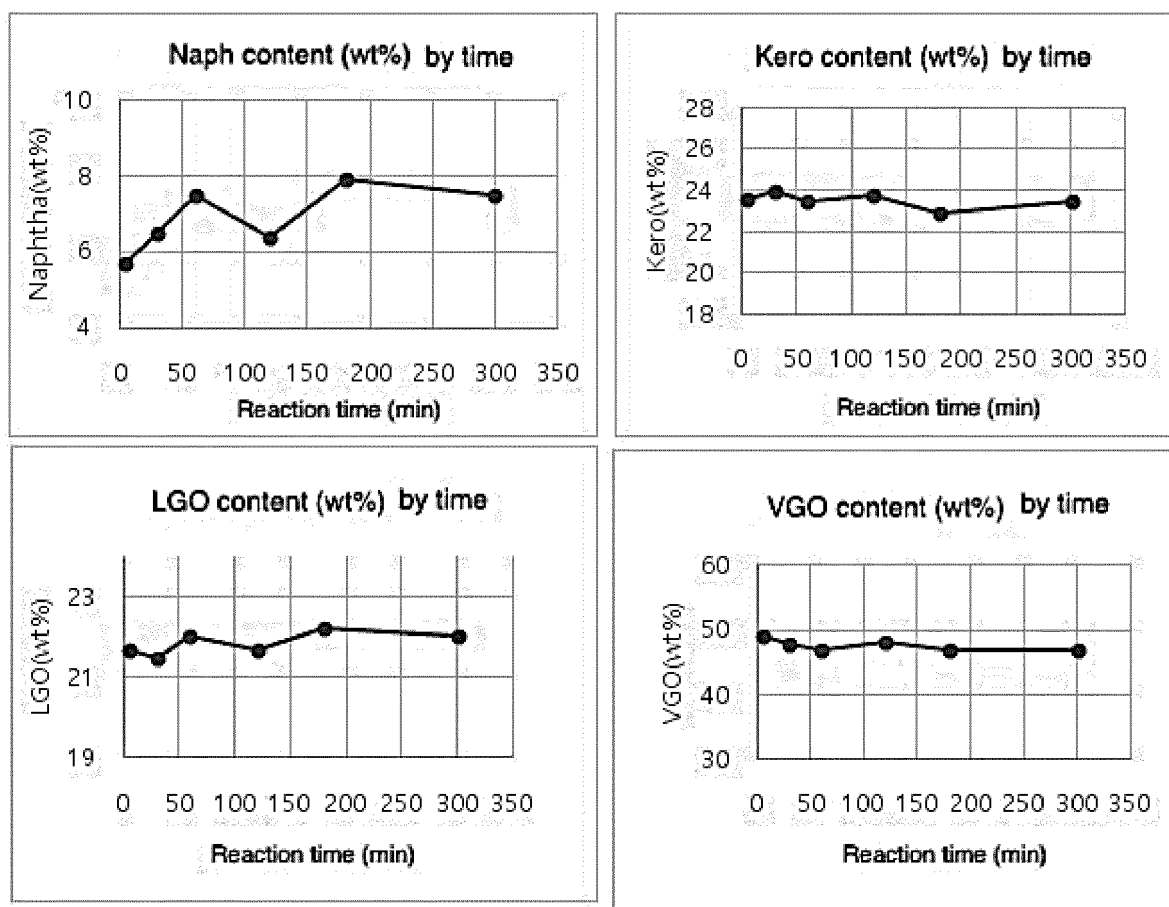
【FIG. 10】



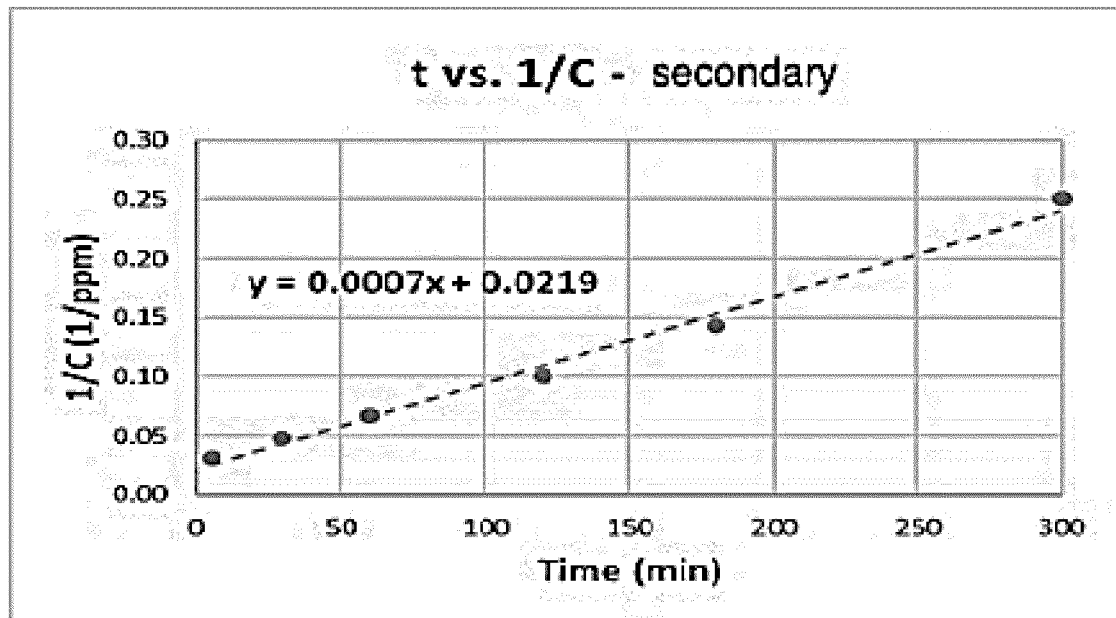
【FIG. 11】



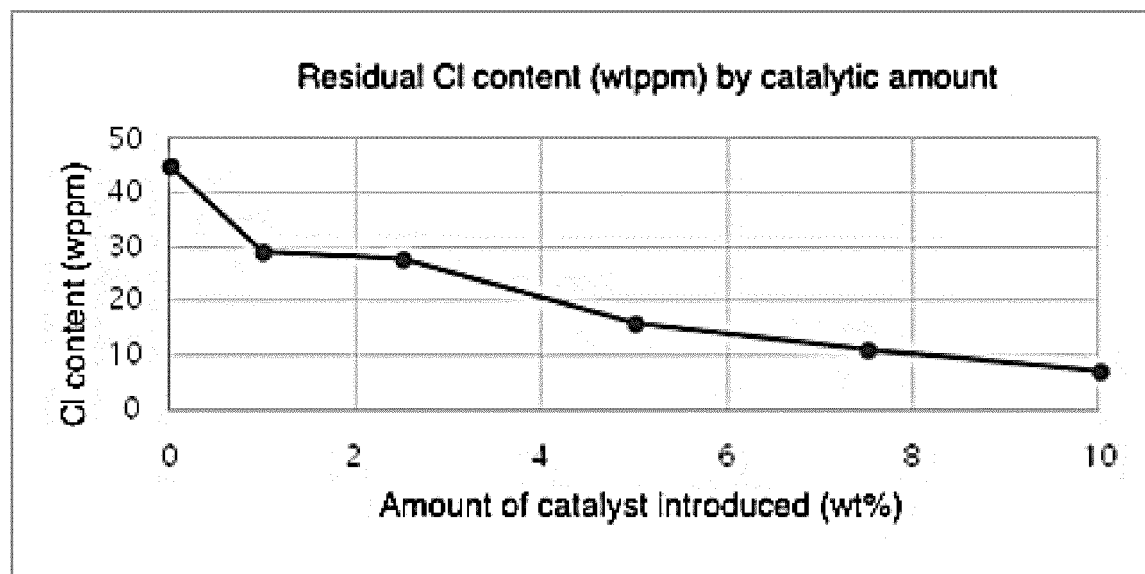
【FIG. 12】



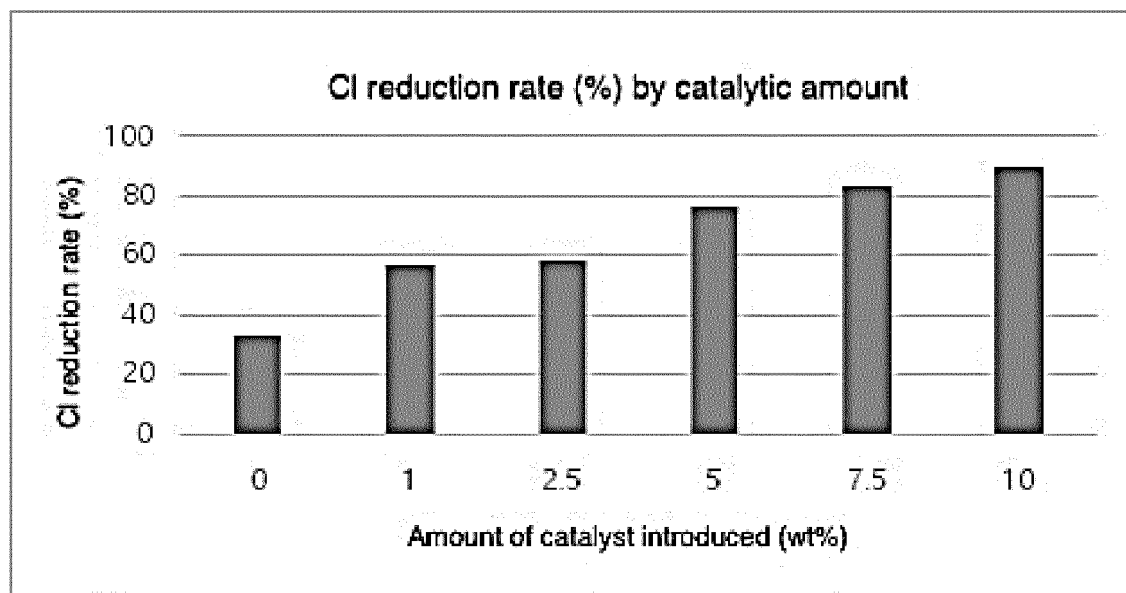
【FIG. 13】



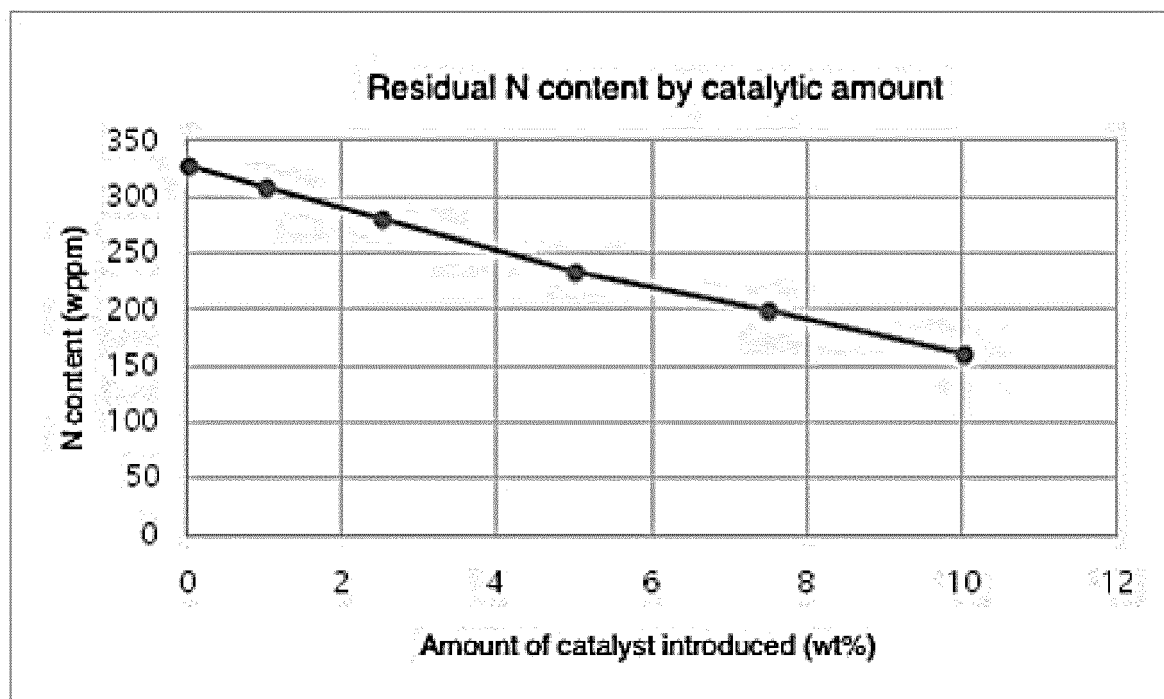
【FIG. 14】



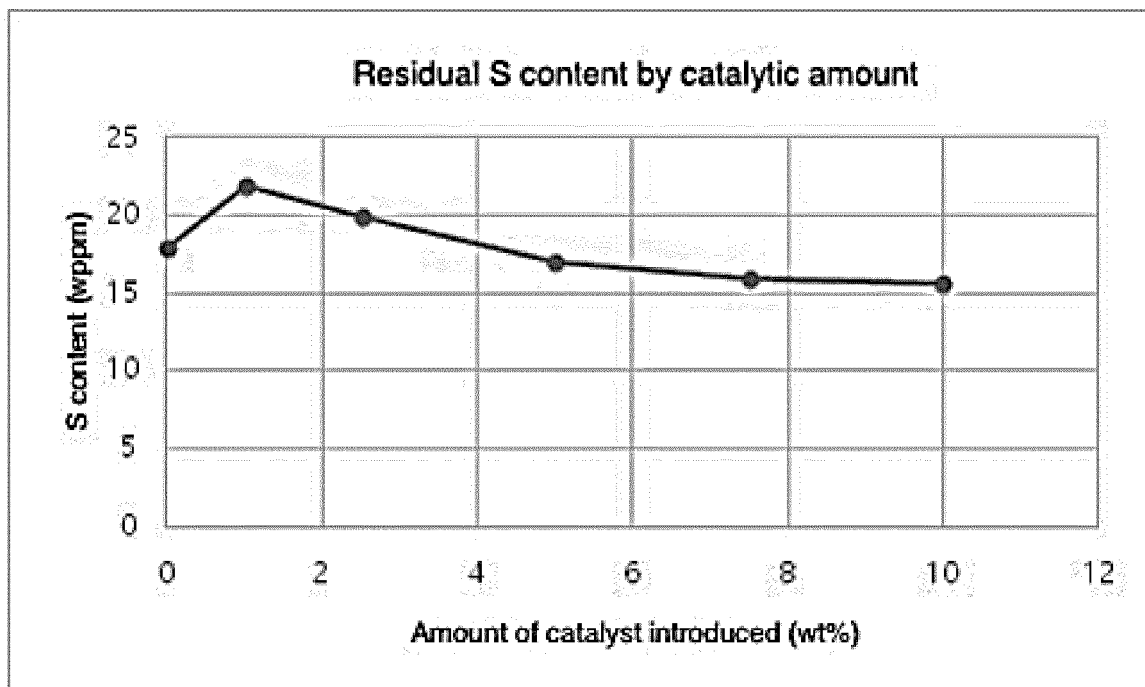
【FIG. 15】



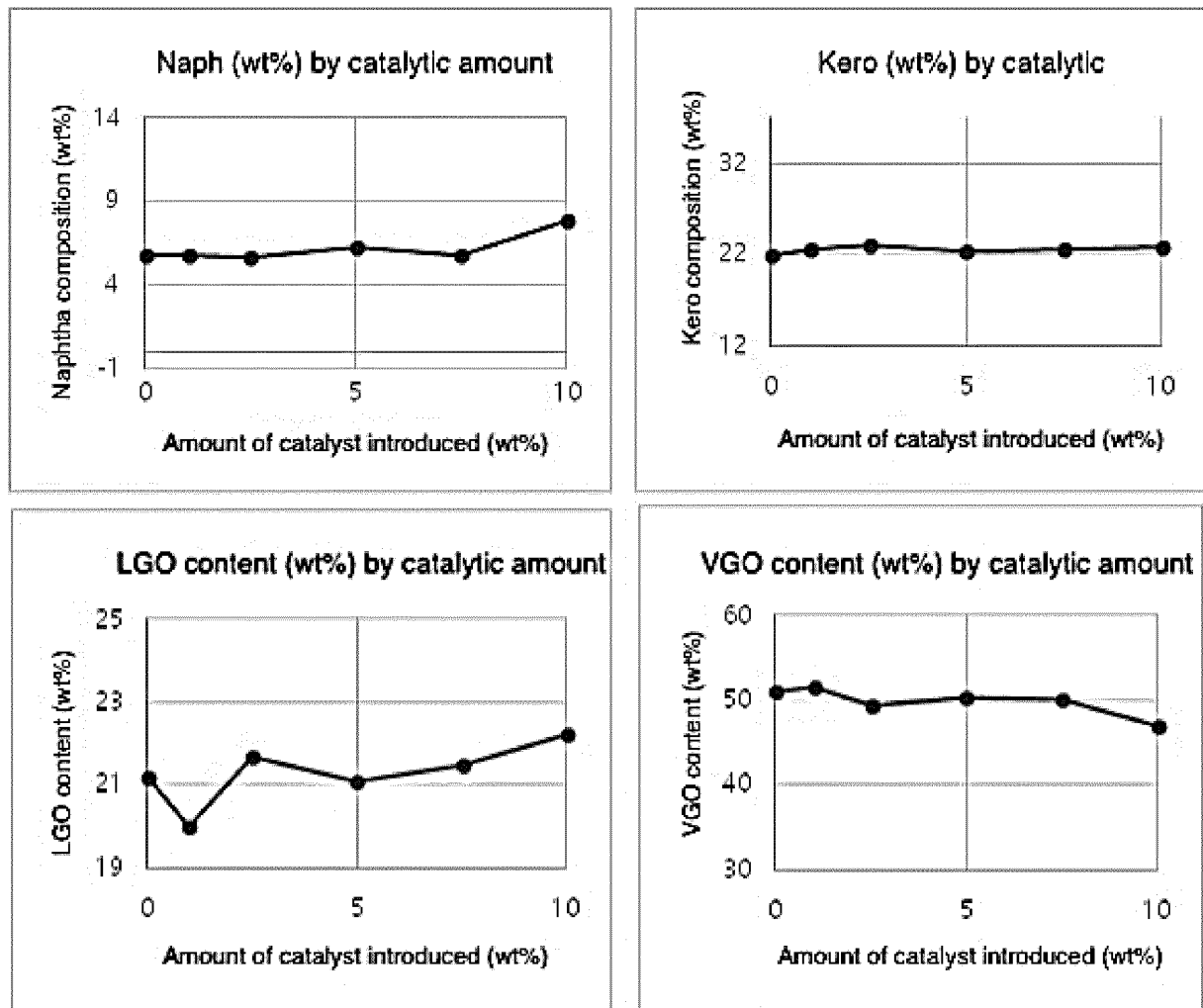
【FIG. 16】



【FIG. 17】



【FIG. 18】



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2020/015788

A. CLASSIFICATION OF SUBJECT MATTER C10G 17/095(2006.01)i; C10G 1/10(2006.01)i; C10G 7/00(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC																		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C10G 17/095(2006.01); C07C 2/08(2006.01); C07C 2/56(2006.01); C08J 11/12(2006.01); C08J 11/16(2006.01); C10G 1/10(2006.01); C10G 29/00(2006.01); C10G 29/02(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: IPC as above Japanese utility models and applications for utility models: IPC as above Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS (KIPO internal) & keywords: 고체산(solid acid), 염소(chlorine), 폐유(waste oil), 제올라이트(zeolite), 클레이(clay), 실리카(silica)																		
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>CN 105368486 A (CHINA PETROLEUM & CHEMICAL CORPORATION et al.) 02 March 2016 (2016-03-02) See claims 1 and 16; and paragraph [0056].</td> <td>1-16</td> </tr> <tr> <td>A</td> <td>KR 10-2014-0041809 A (CHEVRON U.S.A. INC.) 04 April 2014 (2014-04-04) See entire document.</td> <td>1-16</td> </tr> <tr> <td>A</td> <td>JP 2019-532118 A (SABIC GLOBAL TECHNOLOGIES B.V.) 07 November 2019 (2019-11-07) See entire document.</td> <td>1-16</td> </tr> <tr> <td>A</td> <td>JP 2019-527758 A (SABIC GLOBAL TECHNOLOGIES B.V.) 03 October 2019 (2019-10-03) See entire document.</td> <td>1-16</td> </tr> <tr> <td>A</td> <td>JP 2014-037518 A (OKAWA TEKKO KK) 27 February 2014 (2014-02-27) See entire document.</td> <td>1-16</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	CN 105368486 A (CHINA PETROLEUM & CHEMICAL CORPORATION et al.) 02 March 2016 (2016-03-02) See claims 1 and 16; and paragraph [0056].	1-16	A	KR 10-2014-0041809 A (CHEVRON U.S.A. INC.) 04 April 2014 (2014-04-04) See entire document.	1-16	A	JP 2019-532118 A (SABIC GLOBAL TECHNOLOGIES B.V.) 07 November 2019 (2019-11-07) See entire document.	1-16	A	JP 2019-527758 A (SABIC GLOBAL TECHNOLOGIES B.V.) 03 October 2019 (2019-10-03) See entire document.	1-16	A	JP 2014-037518 A (OKAWA TEKKO KK) 27 February 2014 (2014-02-27) See entire document.	1-16
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A	JP 2014-037518 A (OKAWA TEKKO KK) 27 February 2014 (2014-02-27) See entire document.	1-16																
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Date of the actual completion of the international search 03 March 2021	Date of mailing of the international search report 03 March 2021																	
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2020/015788

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 105368486 A	02 March 2016	CN 105368486 B	30 June 2017
KR 10-2014-0041809 A	04 April 2014	AU 2012-276045 A1	28 March 2013
		AU 2012-276045 B2	12 February 2015
		BR 112013010521 A2	02 August 2016
		CA 2819152 A1	03 January 2013
		CA 2819152 C	14 August 2018
		CN 103270007 A	28 August 2013
		DE 112012002730 T5	17 April 2014
		GB 2505544 A	05 March 2014
		SG 194435 A1	30 December 2013
		US 2013-0001133 A1	03 January 2013
		US 8795515 B2	05 August 2014
		WO 2013-002887 A1	03 January 2013
JP 2019-532118 A	07 November 2019	CN 109563414 A	02 April 2019
		EP 3491102 A1	05 June 2019
		EP 3491102 B1	15 July 2020
		US 10829696 B2	10 November 2020
		US 2019-0270939 A1	05 September 2019
		WO 2018-025103 A1	08 February 2018
JP 2019-527758 A	03 October 2019	CN 109563413 A	02 April 2019
		EP 3491103 A1	05 June 2019
		US 10717936 B2	21 July 2020
		US 2019-0299491 A1	03 October 2019
		WO 2018-025104 A1	08 February 2018
JP 2014-037518 A	27 February 2014	None	

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 1999504672 A [0004]
- JP 4218857 B [0005]
- JP 2019532118 A [0006]