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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 WASTE OIL FRACTIONS CONTAINING HIGH CONTENT OF CHLORINE USING SOLID ACID MATERIAL**

(57) Provided is a technology of removing 90% or more chlorine by treating an oil fraction having a high Cl content at a high temperature using a solid acid catalyst. The dechlorinated oil fraction may be introduced to a refinery process and converted into a fuel or a chemical product.

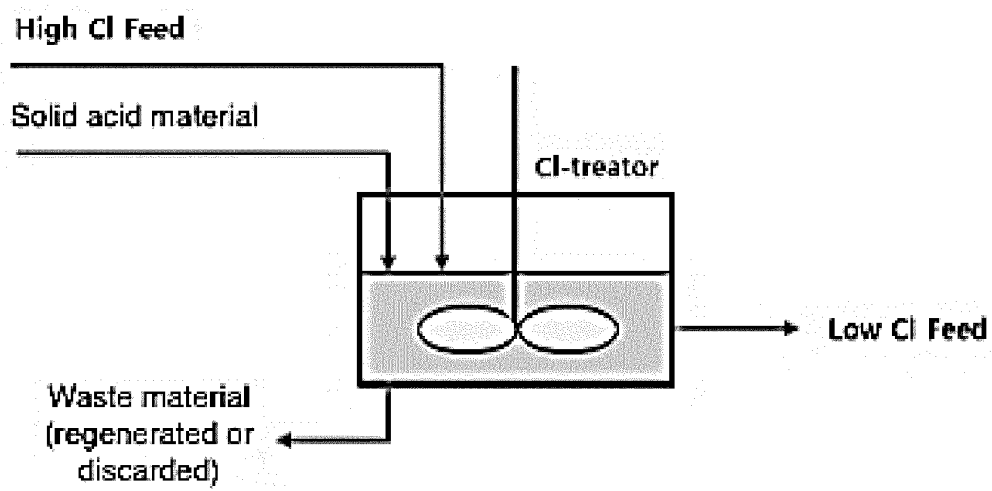
In the present embodiment, the solid acid catalyst and the oil fraction having a high Cl content are mixed and then chlorine is removed by a heat treatment at a high temperature. Main impurities such as S, N, and O and Na, Ca, Fe, and the like which may act as a catalyst

poison in the catalyst reactions of a refinery process are removed simultaneously with the process of removing Cl.

By the treatment at a high temperature in a process of removing Cl in an oil fraction having a high Cl content by the solid acid material, a reduction effect of Cl and N, S, O, and metal impurities may be increased.

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 by a simple treatment, it is preferred from an environmental point of view.

【FIG. 1】



Description

[Technical Field]

- 5 **[0001]** The present invention relates to a method for removing chlorine from waste oil fraction 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 fraction (waste oil fraction) produced by a cracking or pyrolysis reaction of the waste material such as a waste plastic pyrolysis oil, when the oil fraction 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 fraction 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 fraction which has not been pretreated to the HDT process. In order to remove a Cl oil fraction by using a convention refinery process, there is a need of a treatment technology of reducing Cl in a waste oil fraction 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 fraction is then separated to produce a final product. However, in the primary impurity removal process, Cl is reduced by neu-
25 tralization (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 fraction 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 fraction having a Cl content of less than 10 ppm as a raw material, as described in the evaluation test of a chlorine compound removal
35 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 fraction having a high Cl content is not effective.

- 40 **[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 fraction into a mild oil fraction 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, the oil fraction is mainly converted into an organic Cl form in which an olefin and Cl are bonded, which is then removed by bonding at a solid acid point or gas discharge, but it produces moisture simultaneously to cause problems of equipment corrosion, reaction abnormality, deterioration of product properties, and product loss.

- 45 **[0007]** Therefore, a treatment technology of reducing Cl in a waste oil fraction which reduces a Cl content in a waste oil fraction 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.

50 [Disclosure]

[Technical Problem]

- 55 **[0008]** An object of the present invention is to provide a technology of reducing Cl in a waste oil fraction having a high Cl content by using a solid acid material, for high value added (fuel, chemical conversion) of a waste oil fraction having a high Cl content by application of a refinery process.

[0009] Specifically, the object of the present invention is to provide a technology of conversion into a Cl oil fraction 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]

- 5 **[0010]** In one general aspect, a method for removing chlorine from a waste oil fraction includes: a) preparing a mixture of a chlorine-containing waste oil fraction and a solid acid material; b) reacting the mixture at a pressure of 1 bar or more and 100 bar or less under an inert gas atmosphere to remove chlorine; and c) separating a dechlorinated oil fraction and the solid acid material from the mixture and recovering the dechlorinated oil fraction, wherein the waste oil fraction includes 50 wt% or less of components having a boil fractioning point (bp) of 150°C or higher with respect to a total weight of the waste oil fraction and satisfies the following Relation 1 :

$$[\text{Relation 1}] \quad 0.85 < B/A < 1.15$$

15 wherein A is a wt% of components having bp of 150°C or higher with respect to the total weight of the waste oil fraction, 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] The waste oil fraction may include a waste plastic pyrolysis oil, a biomass pyrolysis oil, a regenerated lubricant, a high chlorine content crude oil fraction, or a mixture thereof.

[0012] The waste oil fraction may have a Cl content of 10 ppm or more.

20 **[0013]** 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.

[0014] The solid acid material in step a) may be included at 5 to 10 wt% with respect to the total weight of the mixture.

[0015] The reaction in step b) may be the catalytic conversion reactions that chlorine contained in the waste oil fraction 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.

25 **[0016]** The reaction in step b) may be performed at a temperature of higher than 280°C and lower than 380°C.

[0017] The method for removing chlorine from a waste oil fraction may further include d) repeating steps a), b), and c) once or more.

[0018] The dechlorinated oil fraction may have a chlorine content of less than 10 ppm.

30 **[0019]** A weight ratio of chlorine in the dechlorinated oil fraction to chlorine in the waste oil fraction may be 0.01 to 0.1.

[Advantageous Effects]

[0020] 90 wt% or more of Cl is removed from an oil fraction having a high Cl content, thereby converting the oil fraction into a Cl oil fraction at a level to allow introduction to a refinery process.

35 **[0021]** Not only Cl may be removed from the oil fraction, but also impurities causing air pollutants such as N and S, and metal components which adversely affect a refinery process catalytic activity, such as As, Na, and Ca, may be simultaneously removed.

[0022] 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.

40 **[0023]** Since chlorine is removed without a substantial change of oil fraction properties, deterioration of product properties due to oligomerization and product loss due to cracking may be prevented.

[Description of Drawings]

45 **[0024]**

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

50 FIGS. 3 and 4 are graphs showing a residual N content and a residual S content by reaction temperature.

FIG. 5 is a graph showing an oil fraction composition change by reaction temperature.

FIGS. 6 and 7 are graphs showing a residual Cl content and a Cl reduction rate by reaction time.

FIGS. 8 and 9 are graphs showing a residual N content and a residual S content by reaction time.

FIG. 10 is a graph showing an oil fraction composition change by reaction time.

55 FIGS. 11 and 12 are graphs showing a residual Cl content and a Cl reduction rate by catalytic amount.

FIGS. 13 and 14 are graphs showing a residual N content and a residual S content by catalytic amount.

FIG. 15 is a graph showing an oil fraction composition change by catalytic amount.

[Best Mode]

[0025] 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.

[0026] In the present specification, "A to B" refers to "A or more and B or less", unless otherwise particularly defined.

[0027] In addition, "A and/or B" refers to at least one selected from the group consisting of A and B, unless otherwise particularly defined.

[0028] In the present specification, a boil fractioning point (bp) of a waste oil fraction and a dechlorinated oil fraction refers to that measured at a normal pressure (1 atm), unless otherwise defined.

[0029] According to an exemplary embodiment of the present invention, a method for removing chlorine from a waste oil fraction is provided. The method includes: a) preparing a mixture of a chlorine-containing waste oil fraction and a solid acid material; b) reacting the mixture at a pressure of 1 bar or more and 100 bar or less under an inert gas atmosphere to remove chlorine; and c) separating a dechlorinated oil fraction and the solid acid material from the mixture and recovering the dechlorinated oil fraction, wherein the waste oil fraction includes 5 to 50 wt% of components having a boil fractioning point (bp) of lower than 150 °C with respect to a total weight of the waste oil fraction and satisfies the following Relation 1:

$$[\text{Relation 1}] \quad 0.85 < B/A < 1.15$$

wherein A is a wt% of components having bp of 150°C or higher with respect to the total weight of the waste oil fraction, 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.

[0030] In the present invention, a technology of reducing Cl in a waste oil fraction having a high Cl content by using a solid acid material, for high value added (fuel, chemical conversion) of a waste oil fraction having a high Cl content by application of a refinery process may be provided.

[0031] In the method for removing chlorine from a waste oil fraction, first, a) a mixture of a chlorine-containing waste oil fraction and a solid acid material is prepared.

[0032] The waste oil fraction may include a waste plastic pyrolysis oil, a biomass pyrolysis oil, a regenerated lubricant, a content crude oil fraction 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 fraction produced by a cracking or pyrolysis reaction of the waste material such as a waste plastic pyrolysis oil, when the waste oil fraction is used, air pollutants may be released, and in particular, a Cl component may be converted into HCl and released in an oxidation process at a high temperature, and thus, it is necessary to pretreat the waste oil fraction to remove impurities.

[0033] Chlorine in the waste oil fraction may be inorganic Cl, organic Cl, or a combination thereof, and a chlorine content in the waste oil fraction may be 10 ppm or more or 20 ppm or more. Meanwhile, the upper limit of the content of chlorine in the waste oil fraction 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 fraction 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 fraction having a high Cl content is required.

[0034] Meanwhile, impurities in the waste oil fraction 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 ppm or more or 500 to 8,000 ppm, a S content of 10 ppm or more or 20 to 1,000 ppm, and an O content of 2,000 ppm or more or 3,000 ppm to 3 wt% with respect to the total weight of the waste oil fraction, and Fe, Na, Ca, and Al may be included at a Fe content of 1 ppm or more or 1 to 10 ppm, a Na content of 1 ppm or more or 1 to 10 ppm, a Ca content of 0.1 ppm or more or 0.1 to 5 ppm, and an Al content of 0.1 ppm or more or 0.1 to 5 ppm with respect to the total weight of the waste oil fraction.

[0035] The waste oil fraction may include 5 to 50 wt%, for example, 5 to 45 wt%, 5 to 40 wt%, 5 to 35 wt%, 5 to 30 wt%, 5 to 25 wt%, 5 to 20 wt%, or 5 to 15 wt% of components having bp of lower than 150°C with respect to the total weight. In addition, the component may be included at 10 to 50 wt%, 15 to 50 wt%, 20 to 50 wt%, 25 to 50 wt%, 30 to 50 wt%, 35 to 50 wt%, or 40 to 50 wt%. Though the waste oil fraction of the present invention has a high content of light oil fraction, chlorine is removed without a substantial change in oil fraction properties, and thus, deterioration of product properties due to oligomerization and product loss due to excessive cracking may be prevented.

[0036] In addition, the waste oil fraction may include 10 to 35 wt%, for example, 10 to 30 wt%, 10 to 29 wt%, 11 to 28 wt%, 12 to 27 wt%, 13 to 26 wt%, 14 to 26 wt%, or 15 to 25 wt% of components having bp of 150 °C to 265°C with respect to the total weight.

[0037] In addition, the waste oil fraction may include 10 to 35 wt%, for example, 10 to 30 wt%, 10 to 29 wt%, 11 to 28 wt%, 12 to 27 wt%, 13 to 26 wt%, 14 to 26 wt%, or 15 to 25 wt% of components having bp of 265°C to 340°C with

respect to the total weight.

[0038] In addition, the waste oil fraction may include 20 to 65 wt%, for example, 25 to 60 wt%, 25 to 55 wt%, 25 to 50 wt%, 30 to 50 wt%, 32 to 48 wt%, or 35 to 45 wt% of components having bp of higher than 340°C with respect to the total weight.

[0039] In addition, the waste oil fraction may include 30 to 70 wt%, preferably 40 to 60 wt% of an olefin with respect to the total weight. As described above, by removing Cl in the pyrolysis oil in a high temperature operating process conditions using the solid acid material of the present invention, a phenomenon in which an average molecular weight is slightly lowered by occurrence of a cracking reaction is shown. An olefin, in particular, a light olefin having high reactivity is produced in a cracking process and bonded to Cl, which is converted into organic Cl and bonded to a solid acid or released to the outside as gas, or a Cl removal effect by breakage of a C-Cl bond in a cracking process may be increased, but due to the problems of product loss and deterioration of product properties, an excessive cracking reaction is not preferred.

[0040] 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.

[0041] 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.

[0042] 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.

[0043] For example, a fluidized bed catalyst is used in a RFCC process of conversion into a light/middle distillate of a residual oil, 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 E-Cat (equilibrium 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 fraction, a difference in cracking activity is small as compared with the fresh catalyst, and costs are reduced through environmental protection and reuse.

[0044] 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 fraction 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 fraction 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.

[0045] 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.

[0046] 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 fraction may be suppressed, which is thus preferred.

[0047] After preparing the mixture of the waste oil fraction and the solid acid material, b) the mixture is reacted at a pressure of 1 bar or more and 100 bar or less under an inert gas atmosphere to remove chlorine.

[0048] The reaction of removing chlorine from an oil fraction 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 fraction 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 fraction may be increased, which is thus not preferred. In the Cl removal reaction of the present invention also, a cracking reaction may be derived. However, in the present invention, the reaction proceeds at a low temperature of higher than 280°C and lower than 380°C as compared with common cracking conditions of 530°C or higher, and E-cat., which includes dealuminated zeolite as a main component and is a weak acid material, is applied. As a result, the cracking reaction itself may be suppressed, and also, middle unit cracking at a Naphtha/Kero level due to mild cracking is selectively produced rather than conversion into a subunit molecule such as gas, thereby preventing the problems described above.

[0049] 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 higher than 280°C and lower than 380°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 fraction 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.

[0050] 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. Similar Cl reduction performance is shown even under air conditions, when leak occurs under high temperature operation conditions at higher than 280°C, 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.

[0051] The process conditions may be, specifically, a temperature of higher than 280°C and lower than 380°C or a temperature of 290 to 360°C, and may be performed under temperature conditions of 290 to 340°C, most preferably 295 to 335°C. As the temperature is raised in the temperature range described above, the Cl reduction effect is increased, but in order to minimize a problem of a decreased liquid yield due to conversion of the waste oil fraction into gases by the increased cracking reaction, it is necessary to adjust a catalytic content and reaction temperature/time and the like. However, it is an appropriate treatment method for rapidly treating the waste oil fraction having a high Cl content. Further, since a removal rate of N, S, and metal impurities is increased by a reaction temperature rise in the numerical range, a sweetening effect for introduction of a refinery process may be expected.

[0052] 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.

[0053] Though a regenerated oil fraction may be prepared using a fluidized bed reactor, a contact time between the catalyst and the oil fraction should be long for removing Cl in the waste oil fraction, 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 fraction.

[0054] 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.

[0055] 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.

[0056] 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 fraction ratio (GOR) of 50 to 2000, preferably 200 to 1000, and more preferably 350 to 700.

[0057] c) Subsequently, a dechlorinated oil fraction and the solid acid material in the mixture are separated to recover the dechlorinated oil fraction.

[0058] The separation of the mixture may be performed by applying any known filtering method, but the present invention is not limited thereto.

[0059] 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.

[0060] d) Subsequently, a step of repeating steps a), b), and c) once or more 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 limited, and an excessive cracking reaction itself is suppressed to maintain the average molecular weight and/or the viscosity of the waste oil fraction composition, thereby preventing reaction abnormality, deterioration of product properties, and product loss.

[0061] The dechlorinated oil fraction according to an exemplary embodiment of the present invention is characterized by satisfying the following Relation 1:

$$\text{[Relation 1]} \quad 0.85 < B/A < 1.15$$

wherein A is a wt% of components having bp of 150°C or higher with respect to the total weight of the waste oil fraction, 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.

[0062] Specifically, B/A may be 0.9 to 1.1 or 0.95 to 1.05. In addition, for example, it may be 0.85 to 1.15, 0.85 to 1.1, or 0.85 to 1.05. In addition, for example, it may be 0.90 to 1.15 or 0.95 to 1.15.

[0063] The chlorine content in the dechlorinated oil fraction may be less than 10 ppm, specifically 8 ppm or less, 6 ppm or less, preferably 1 to 5 ppm, or 1 to 4 ppm. When Cl is removed from the waste oil fraction, the cracking reaction

is suppressed, not an excessive cracking reaction but a mild cracking reaction is derived, and organic Cl produced by a bond of the produced olefin to Cl resulting from the breakage of a C-Cl bond may be bonded at an acid point of the solid acid material and removed, or may be released as gas. In addition, Cl may be released to the outside in the form of HCl by conversion into HCl.

[0064] The dechlorinated oil fraction may include 5 to 60 wt%, for example, 5 to 55 wt%, 5 to 50 wt%, 5 to 45 wt%, 5 to 40 wt%, 5 to 35 wt%, 5 to 30 wt%, 5 to 25 wt%, 5 to 20 wt%, or 5 to 15 wt% of components having bp of lower than 150°C with respect to the total weight. In addition, it may be included at, for example, 10 to 60 wt%, 15 to 60 wt%, 20 to 60 wt%, 25 to 60 wt%, 30 to 60 wt%, 35 to 60 wt%, 40 to 60 wt%, 45 to 60 wt%, or 50 to 60 wt%. In the present invention, though the waste oil fraction has a high content of light oil fraction, chlorine is removed without a substantial change in oil fraction properties, and thus, deterioration of product properties due to oligomerization and product loss due to excessive cracking may be prevented in the dechlorinated oil fraction.

[0065] In addition, the dechlorinated oil fraction may include 10 to 45 wt%, for example, 10 to 40 wt%, or 10 to 35 wt% of components having bp of 150°C to 265°C with respect to the total weight.

[0066] In addition, the dechlorinated oil fraction may include 10 to 35 wt%, for example, 10 to 30 wt%, 10 to 29 wt%, 11 to 28 wt%, 12 to 27 wt%, 13 to 26 wt%, 14 to 26 wt%, or 15 to 25 wt% of components having bp of 265°C to 340°C with respect to the total weight.

[0067] In addition, the dechlorinated oil fraction may include 20 to 60 wt%, for example, 25 to 55 wt%, 20 to 50 wt%, 20 to 45 wt%, or 25 to 40 wt% of components having bp of higher than 340°C with respect to the total weight.

[0068] In an exemplary embodiment of the present invention, a weight ratio of chlorine in the dechlorinated oil fraction to chlorine in the waste oil fraction may be 0.01 to 0.5, for example, 0.01 to 0.4, 0.01 to 0.3, or 0.01 to 0.2, preferably 0.01 to 0.1, more preferably 0.01 to 0.09, 0.01 to 0.08, 0.01 to 0.07, 0.01 to 0.06, or 0.01 to 0.05.

[0069] Meanwhile, the method of removing chlorine from a waste oil fraction 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 fraction, 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 5 ppm, and more preferably 3 ppm or less, a Ca content may be less than 5 ppm, preferably 3 ppm or less, or 0.3 ppm or less, and an Al content may be less than 3 ppm, preferably 1 ppm or less or 0.5 ppm or less, and more preferably 0.3 ppm or less or 0.1 ppm or less, with respect to the total weight of the dechlorinated oil fraction.

[0070] In addition, a weight ratio of Fe in the dechlorinated oil fraction to Fe in the waste oil fraction 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 fraction may be 0.1 to 0.7, for example, 0.1 to 0.5, and preferably 0.45 or less, a weight ratio of Ca in the dechlorinated oil fraction to Ca in the waste oil fraction may be 0.1 to 0.8, for example, 0.2 to 0.7, and preferably 0.6 or less, and a weight ratio of Al in the dechlorinated oil fraction to Al in the waste oil fraction may be 0.1 to 0.7, for example, 0.1 to 0.5, and preferably 0.4 or less.

[0071] Meanwhile, the method of removing chlorine from a waste oil fraction 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 fraction, 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.

[0072] In addition, a weight ratio of N in the dechlorinated oil fraction to N in the waste oil fraction 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 fraction 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 fraction 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.

[0073] 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 Cl-containing waste oil fraction (plastic pyrolysis oil fraction) composition

[0074] A waste oil fraction (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 conform a molecular weight distribution in the 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, by the analysis results:

[Table 1]

Cut Name	Expected carbon range	Boil fractioning point (°C)	Yield (wt%)
H-Naph.	~C8	<150	8.1
KERO	C9~C17	150~265	24.4
LGO	C18~C26	265~340	22.7
LGO-2/UCO-1	C20~	340<	44.8
SUM	-	-	100

[Table 2]

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

Example 2. Review of Cl reduction reaction characteristics using RFCC E-cat.

Example 2-1. Review of temperature effect

[0075] 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 operation conditions.

[0076] Since the pyrolysis oil of Example 1 was also solid phase, it was used after being maintained in an oven at 70°C for 3 hours or more and then converted into a liquid phase.

[0077] The solid acid material used in reduction of impurities including Cl was RFCC E-cat. The physical properties of the RFCC E-cat. used are confirmed as shown in the following Tables 3 and 4.

[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

[0078] (In Table 3, TSA is a total specific surface area, ZSA is a zeolite specific surface area, MSA is a mesoporous specific surface area, Z/M is a ratio of the zeolite specific surface area (ZSA) to the mesoporous specific surface area (MSA), PV is a pore volume, and APD is an average pore size.)

[Table 4]

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

[0079] 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.

[0080] 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 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 at a rate of 1°C/min to raise the temperature to a target temperature. The reaction was maintained for 3 hours and then terminated.

[0081] 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 a mixture of a treated pyrolysis oil and E-cat. was measured and the recovery rate was calculated.

[0082] The mixture of the treated pyrolysis oil and E-cat. in the reactor was separated by a filter paper. The recovered treated pyrolysis oil was analyzed for a composition change and an impurity content change, and the results are shown in the following Tables 5 to 7 and FIGS. 3 to 5.

[Table 5]

Classification	Feed	E-cat.	Recovery	Recovery rate	Reaction temperature	Cl	N	S	O
	(g)	(g)	(g)	(%)	(°C)	wpp m	wpp m	wpp m	wt%
Feed						67	348	20	0.2
Example	119.6	11.8	115.5	96.6	300	4	148	13.7	<0.1
2-1	120.1	11.8	110.5	92.0	330	3	122	14	<0.1
	120.0	12.0	103.7	86.5	350	2	83	12	<0.1

[Table 6]

Reaction temperature (°C)	Cl, wppm	Cl reduction rate (%)
300	4	94.03
330	3	95.52
350	2	97.01

[0083] As the reaction temperature rose, the recovery rate was continuously decreased from 96.6% to 86.5%. However, the Cl reduction rate (reduction amount of Cl per unit E-cat.) was increased from 94.03% to 97.01 %, and it was confirmed that the Cl removal performance was improved as the reaction temperature rose.

[0084] 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, it was confirmed that the removal rate was rapidly increased as the reaction temperature was raised, but in the case of S, the reduction rate was increased as the temperature rose, but a rapid reduction effect like Cl and N was not observed.

[Table 7]

Classification	Reaction temperature	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	-
Example 2-1	300	10.7	26.9	23	39.4	0.97
	330	13.5	31.5	24	31.0	0.94
	350	19.9	37.7	22.1	20.3	0.87

[0085] Referring to Table 7 and FIG. 5, at a reaction temperature of 300°C, the composition change with the feed was not large, but as the temperature rose, VGO and LGO ratios were decreased by the cracking reaction, Naphtha and Kero ratios were increased, and in particular, at 350°C, a VGO content was very low at a 20% level, and it was shown that a light fraction ratio was greatly increased with the Kero content of 57.6%, and thus, it was confirmed that there may be operating stability and a possibility of danger during transport.

Example 2-2. Review of time effect

[0086] In order to confirm the Cl reduction characteristics of the solid acid catalyst, the Cl reduction tendency over time under operating conditions at 330°C in which a difference in composition derived in Example 2-1 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 2-1. Further, the analysis results are shown in the following Tables 8 to 10 and FIGS. 6 to 10.

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[Table 8]

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
Example 2-2	119.2	12.0	115	96.5	0.08	17	149	16	0.1
	119.2	11.9	114.8	96.3	0.5	10	141	15	<0.1
	119.3	11.9	113.2	94.9	1	6	130	15	<0.1
	120.1	11.8	110.5	92.0	3	3	122	14	<0.1
	119	12.0	106.5	89.5	5	1.7	109	13	<0.1

[Table 9]

Time (h)	Cl, wppm	Cl reduction rate (%)
0.08	17	74.6
0.5	10	85.1
1	6	91.0
3	3	95.5
5	1.7	97.5

[0087] Referring to Tables 8 and 9 and FIGS. 6 to 9, it was confirmed that S, N, and O including Cl were decreased over time. The recovery rate was gradually decreased due to the cracking reaction 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 it was confirmed that 97.5 wt% of total Cl was reduced only with the treatment of 5 hours.

[0088] N was removed by 50% or more at the beginning of the operation time, and the reduction rate was increased over time, but it was confirmed that the increase in the N reduction rate was decreased. However, it was confirmed that S had a very low reduction activity as compared with N and Cl, but was constantly reduced over time.

[Table 10]

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 2-2	0.08	9.3	25.2	24.2	41.3	0.99
	0.5	10.1	26.2	23.5	40.2	0.98
	1	10.7	28.3	23.7	37.3	0.97
	3	13.5	31.5	24	31	0.94
	5	15.9	33.5	25.1	25.5	0.92

[0089] Referring to Table 10 and FIG. 10, 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.

Example 2-3. Review of catalytic amount introduced

[0090] In order to confirm the Cl reduction characteristics of the solid acid catalyst, the Cl reduction tendency depending on a catalytic amount introduced under operating conditions at 330°C for 3 hours in which a difference in composition

compared with the raw material derived in Examples 2-1 and 2-2 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 2-1. The analysis results are shown in the following Tables 11 to 13 and FIGS. 11 to 15.

[Table 11]

Classification	Feed	E-cat.	Recovery	Recovery rate	Catalytic amount	Cl	N	S	O
	(g)	(g)	(g)	(%)	(%)	wpp m	wpp m	wpp m	wt%
Feed						67	348	20	0.2
Example 2-3	120.5	0	118.1	98.2	0	41	319	18	0.2
	119.2	1.2	116.8	98.0	1	23	297	18	0.2
	119.3	3.0	116.1	97.3	2.5	21	265	17	0.1
	119.5	6.0	113.9	95.3	5	15	220	16	0.1
	119.2	8.9	112.5	94.4	7.5	8	173	15	<0.1
	120.1	11.8	110.5	92.0	10	3	122	14	<0.1

[0091] Referring to Table 11 and FIGS. 11 to 14, 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. In addition, it was confirmed that the contents of N, S, and O were removed together. A tendency in which N and S were removed in proportion to the increase in the catalytic amount introduced was shown, and it was confirmed that N was greatly decreased to a 65% level of the total amount like Cl. However, it was confirmed that S has a relatively low reduction rate at a 30% level as compared with Cl and N and a small increase in the reduction rate due to the increase in the catalytic amount.

[Table 12]

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%/wt%)
Feed		8.1	24.4	22.7	44.8	-
Example 2-3	0	5.7	23.2	21.7	49.4	1.03
	1	6.1	24.1	22	47.8	1.02
	2.5	7.2	24.9	22.4	45.5	1.01
	5	9.7	26.8	22.8	40.7	0.98
	7.5	12.0	28.2	26.3	33.5	0.96
	10	13.5	31.5	24.0	31.0	0.94

[0092] Referring to Table 12 and FIG. 15, as the catalytic amount introduced was increased to 10 wt%, it was confirmed that the Naphtha ratio was gradually increased and the VGO ratio was decreased. Under the operating conditions in which the cracking reaction occurred, it was considered that the cracking side reaction was increased as the catalytic amount introduced was increased to cause a composition change.

[Table 13]

mg/Kg	Fe	Na	Ca	Al
Pyrolysis oil B	2.9	5.7	0.5	0.3
Example 2-1 (330°C)	1.2	2.5	0.3	0.1

[0093] 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 330°C

of Example 2-1 in which no composition was changed and Cl reduction efficiency was high was performed. It was confirmed that 60% or more of Fe, Na, Ca, and Al was all removed at the same time.

[0094] When the results of the examples are combined, it was confirmed that the impurities were selectively removed with little change in the composition of the oil fraction, by the treatment of the solid acid material according to the present invention.

[0095] 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 fraction, the method comprising:

- a) preparing a mixture of a chlorine-containing waste oil fraction and a solid acid material;
- b) reacting the mixture at a pressure of 1 bar or more and 100 bar or less under an inert gas atmosphere to remove chlorine; and
- c) separating a dechlorinated oil fraction and the solid acid material from the mixture and recovering the dechlorinated oil fraction,

wherein the waste oil fraction includes 5 to 50 wt% of components having a boil fractioning point (bp) of lower than 150°C with respect to a total weight of the waste oil fraction and satisfies the following Relation 1:

$$[\text{Relation 1}] \quad 0.85 < B/A < 1.15$$

wherein A is a wt% of components having bp of 150°C or higher with respect to the total weight of the waste oil fraction, 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 fraction of claim 1, wherein the waste oil fraction includes a waste plastic pyrolysis oil, a biomass pyrolysis oil, a regenerated lubricant, a crude oil fraction having a high chlorine content, or a mixture thereof.
- 3. The method for removing chlorine from a waste oil fraction of claim 1, wherein the waste oil fraction has a chlorine content of 10 ppm or more.
- 4. The method for removing chlorine from a waste oil fraction 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.
- 5. The method for removing chlorine from a waste oil fraction 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.
- 6. The method for removing chlorine from a waste oil fraction of claim 1, wherein the reaction in b) is the catalytic conversion reactions that chlorine contained in the waste oil fraction 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.
- 7. The method for removing chlorine from a waste oil fraction of claim 1, wherein the reaction in b) is performed at a temperature of higher than 280°C and lower than 380 °C.
- 8. The method for removing chlorine from a waste oil fraction of claim 1, further comprising: d) repeating a), b), and c) once or more.
- 9. The method for removing chlorine from a waste oil fraction of claim 1, wherein the dechlorinated oil fraction has a

chlorine content of less than 10 ppm.

10. The method for removing chlorine from a waste oil fraction of claim 1, wherein a weight ratio of chlorine in the dechlorinated oil fraction to chlorine in the waste oil fraction is 0.01 to 0.1.

5 11. The method for removing chlorine from a waste oil fraction of claim 1, wherein Fe, Na, Ca, and Al contained in the waste oil fraction are further removed.

10 12. The method for removing chlorine from a waste oil fraction of claim 1, wherein N, S, and O contained in the waste oil fraction are further removed.

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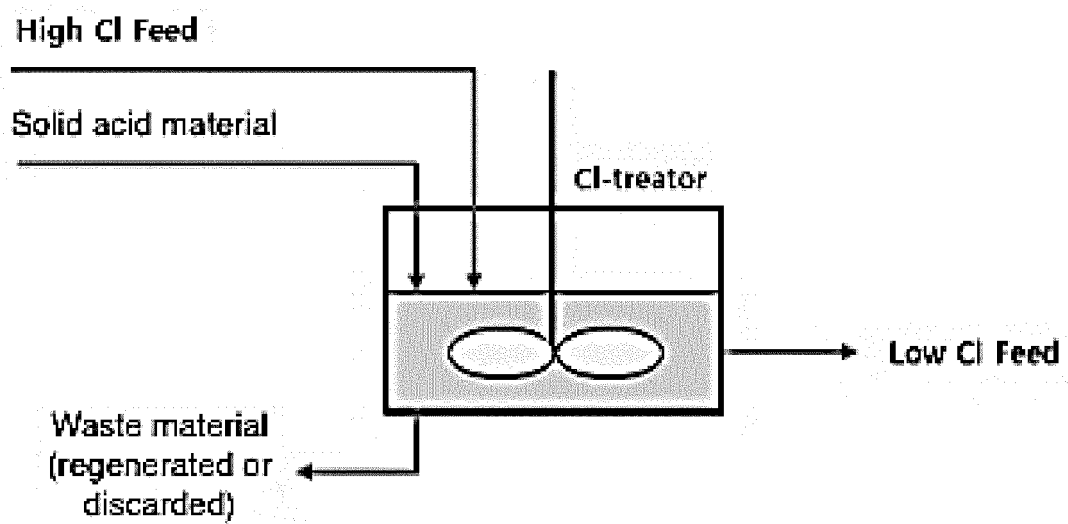
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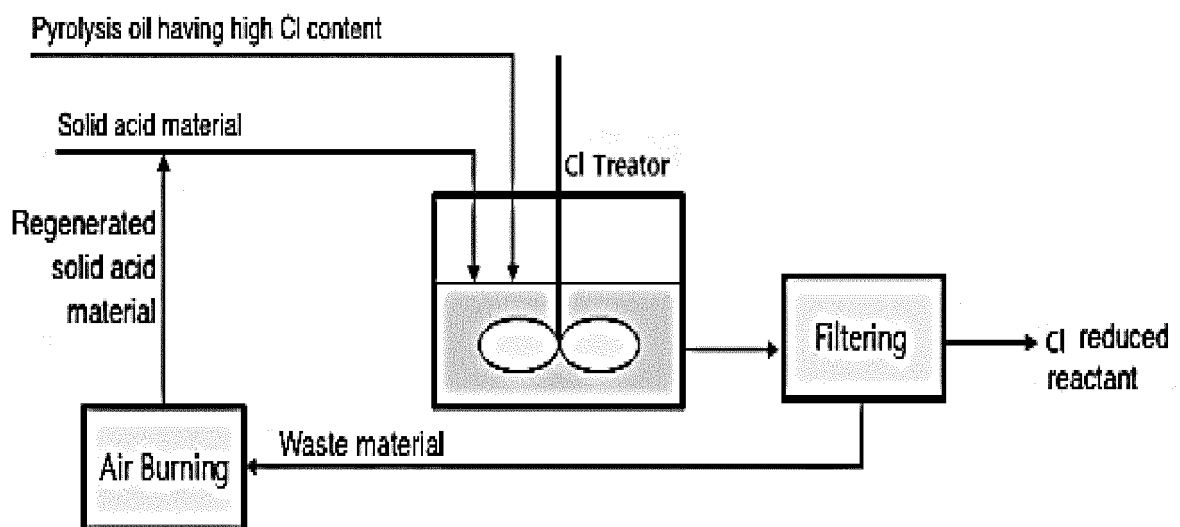
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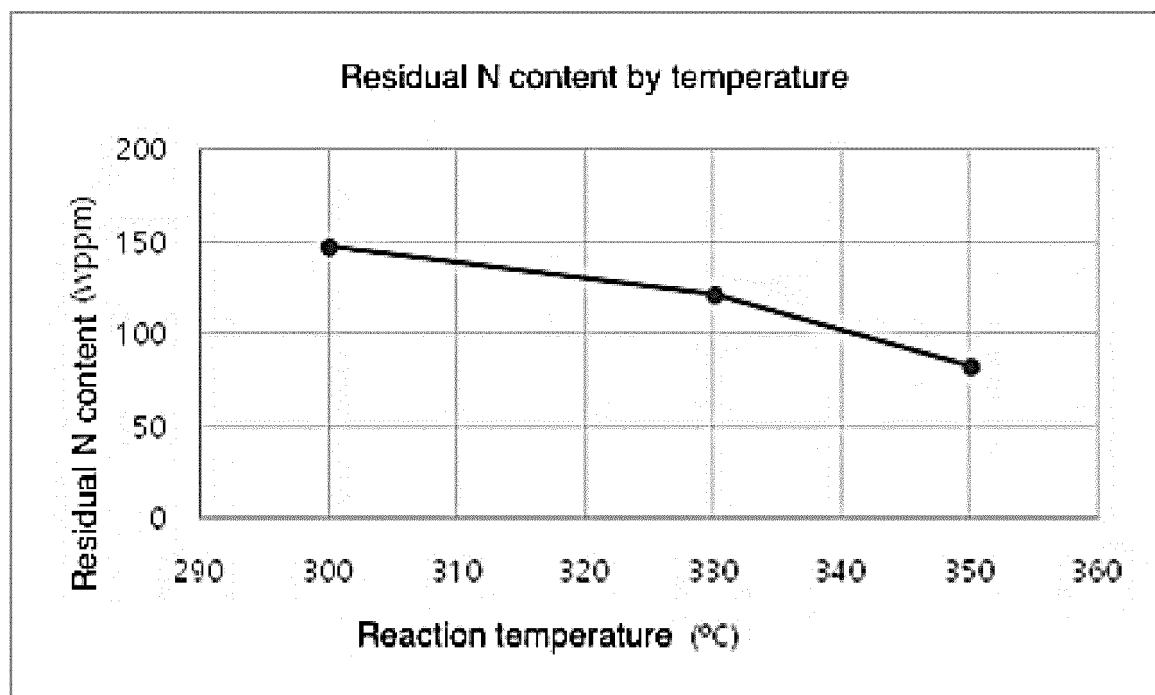
【FIG. 1】



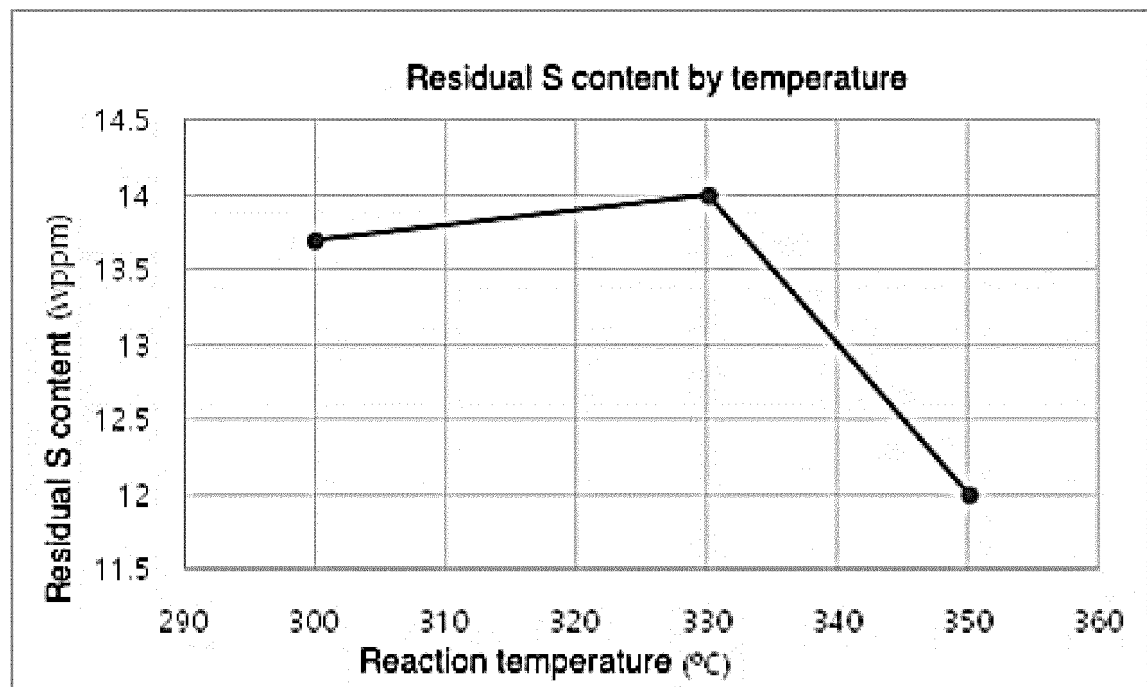
【FIG. 2】



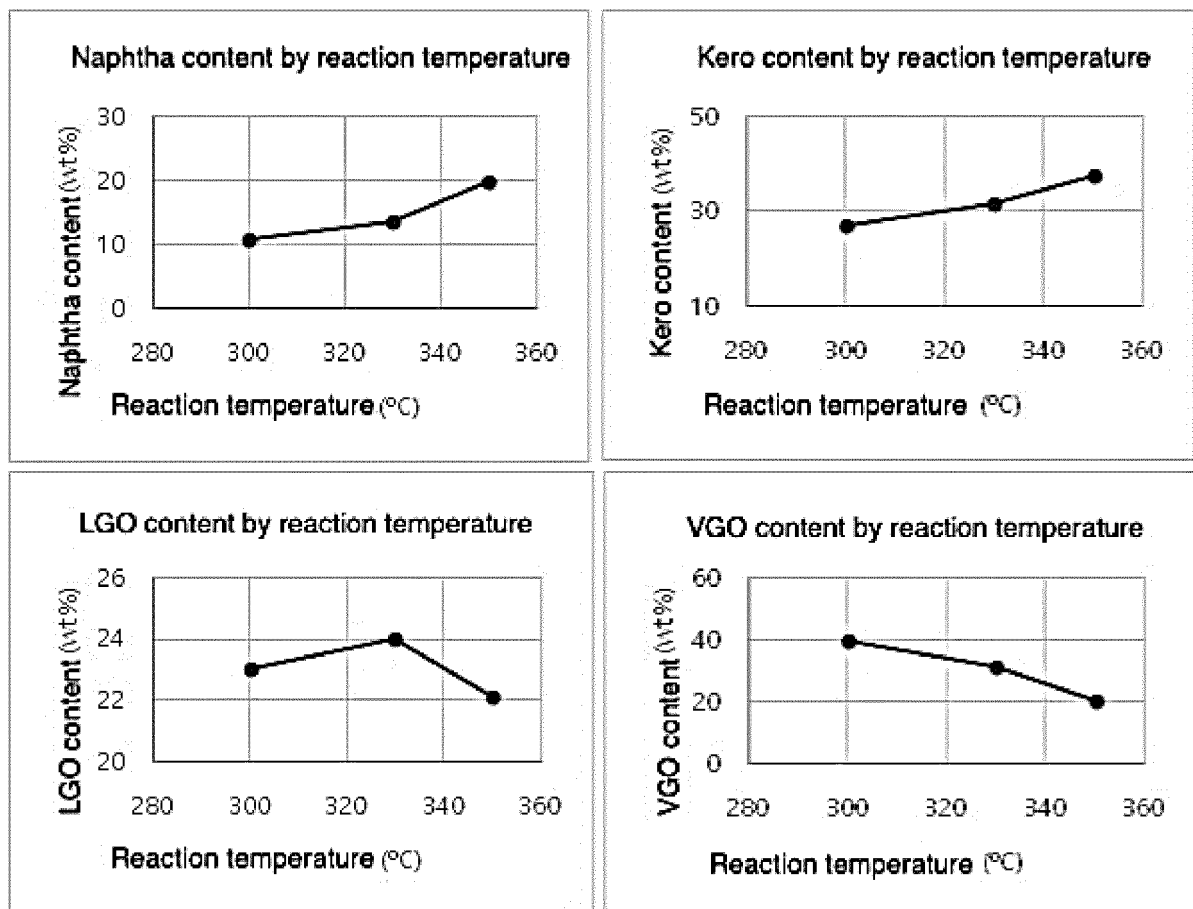
【FIG. 3】



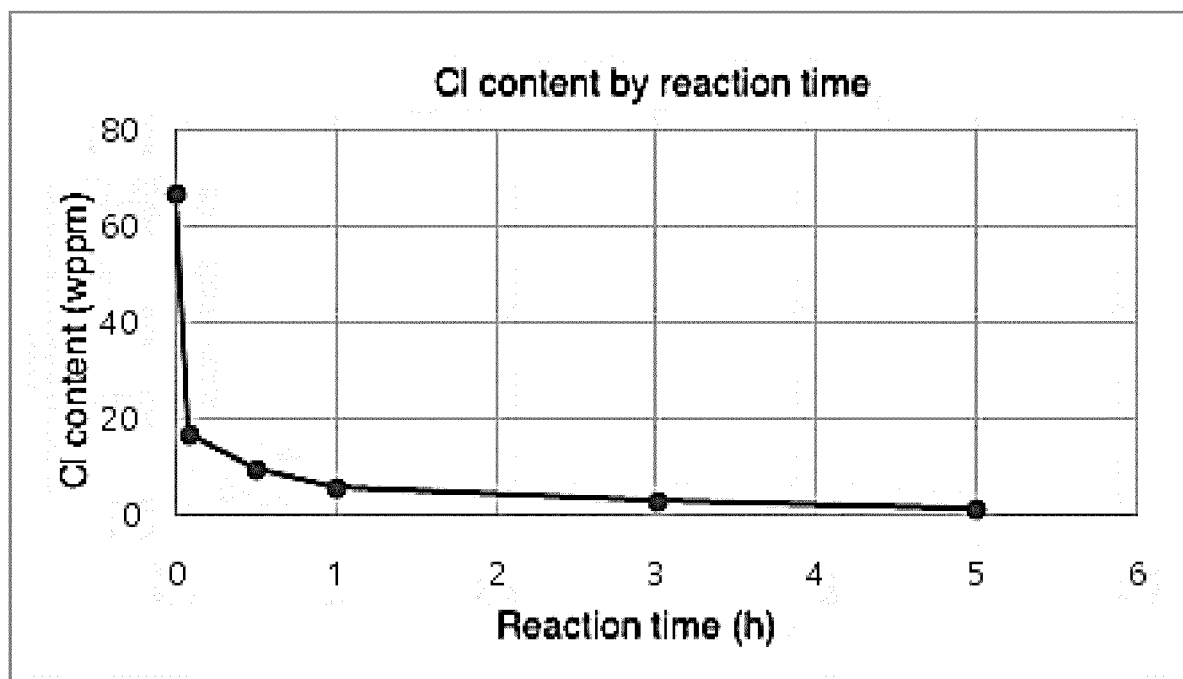
【FIG. 4】



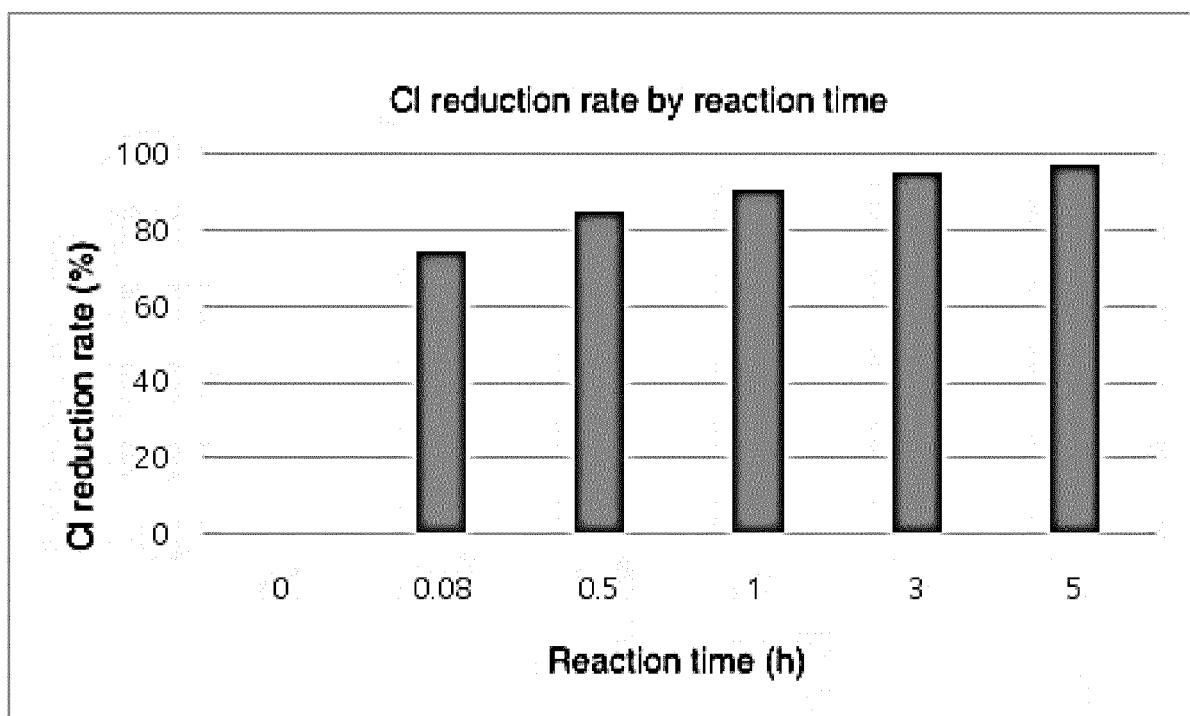
【FIG. 5】



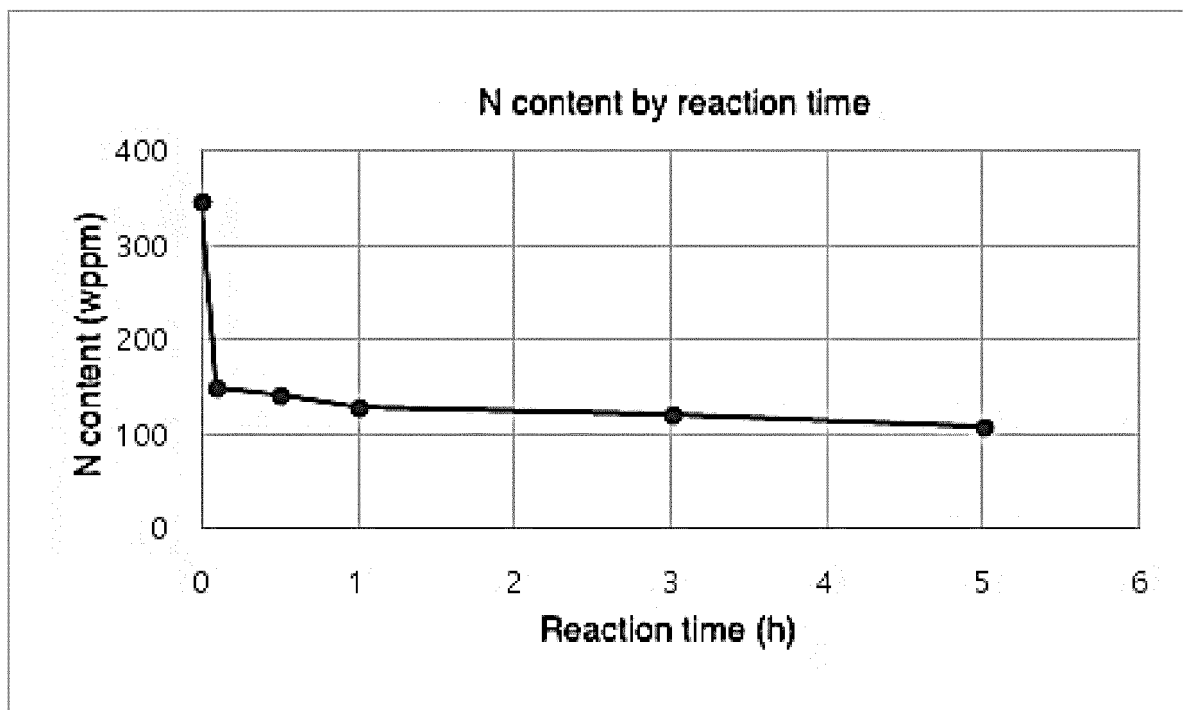
【FIG. 6】



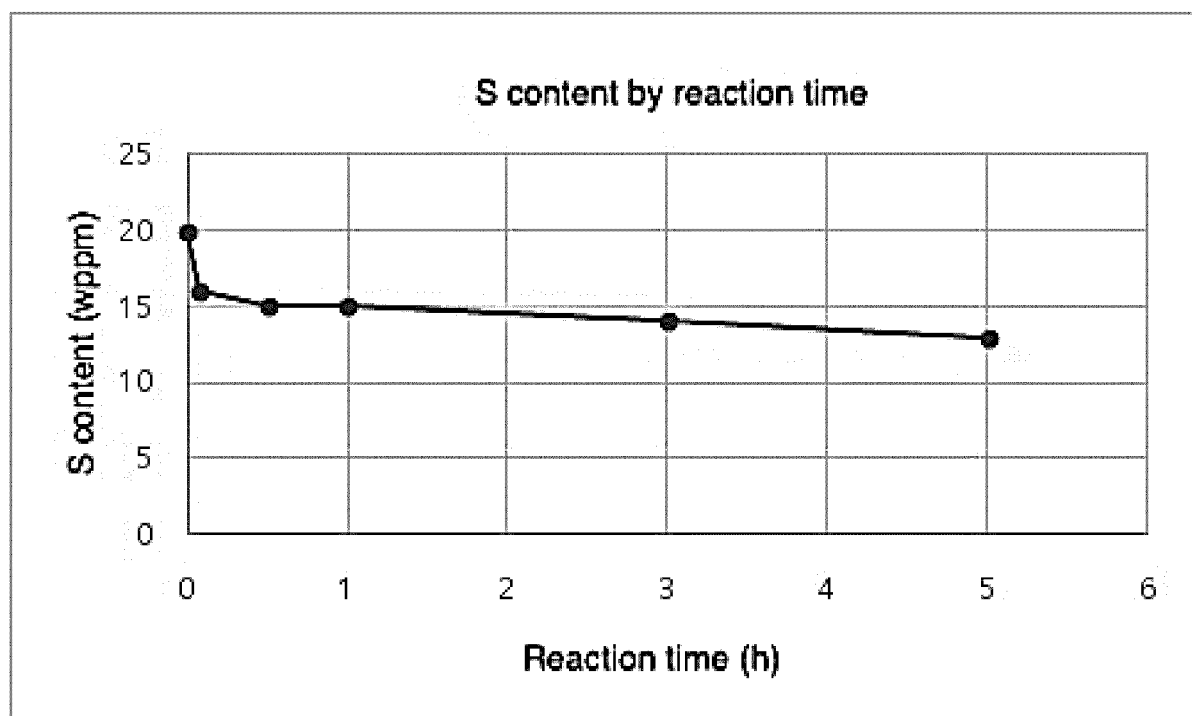
【FIG. 7】



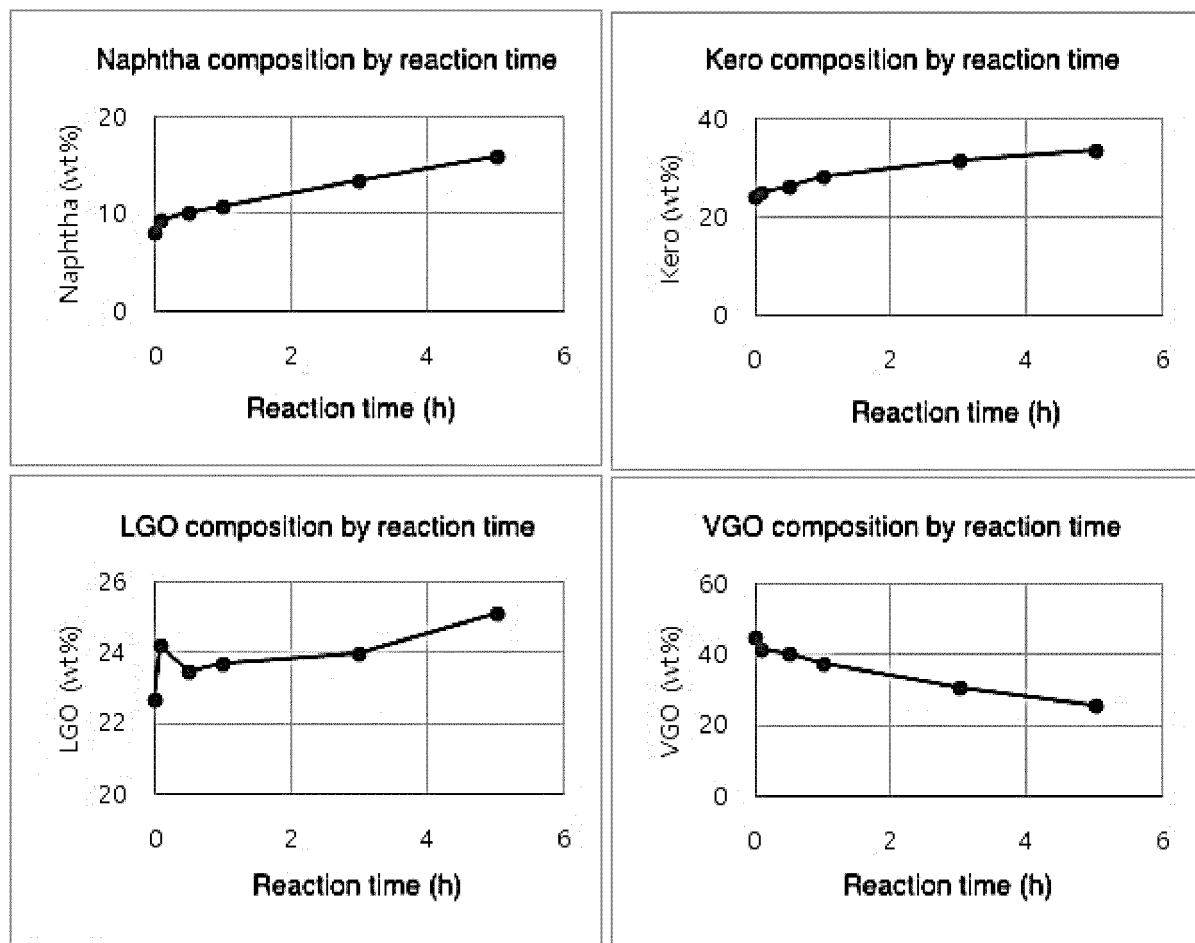
【FIG. 8】



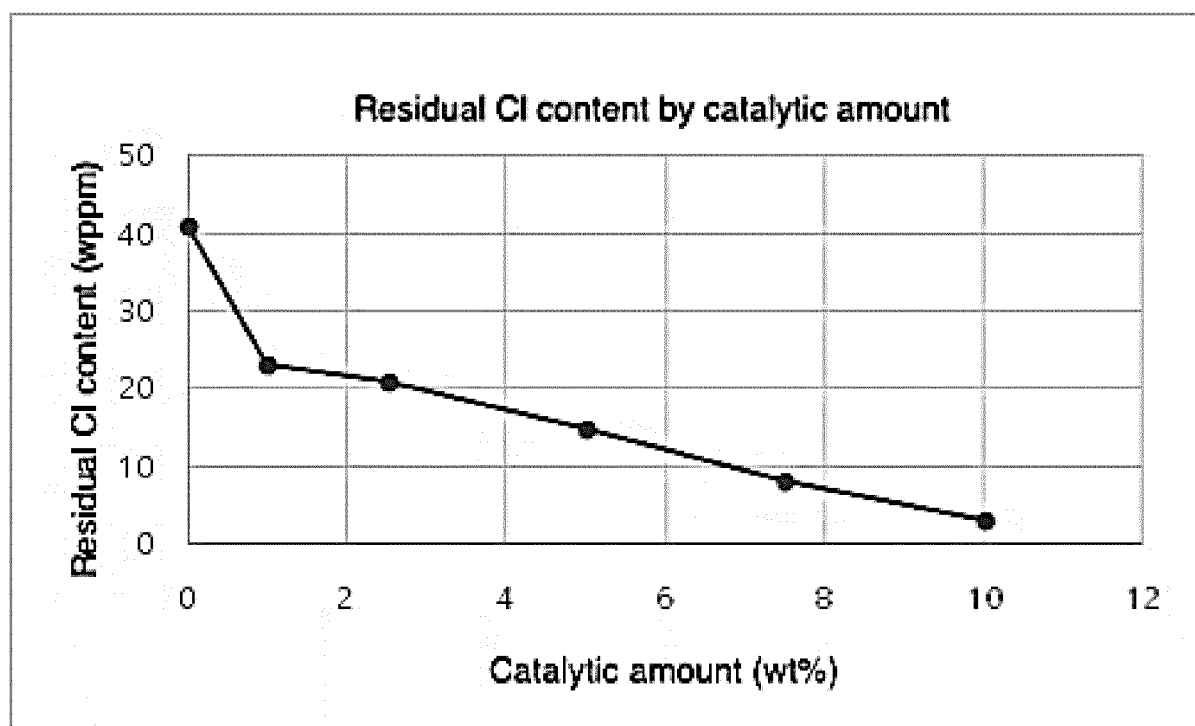
【FIG. 9】



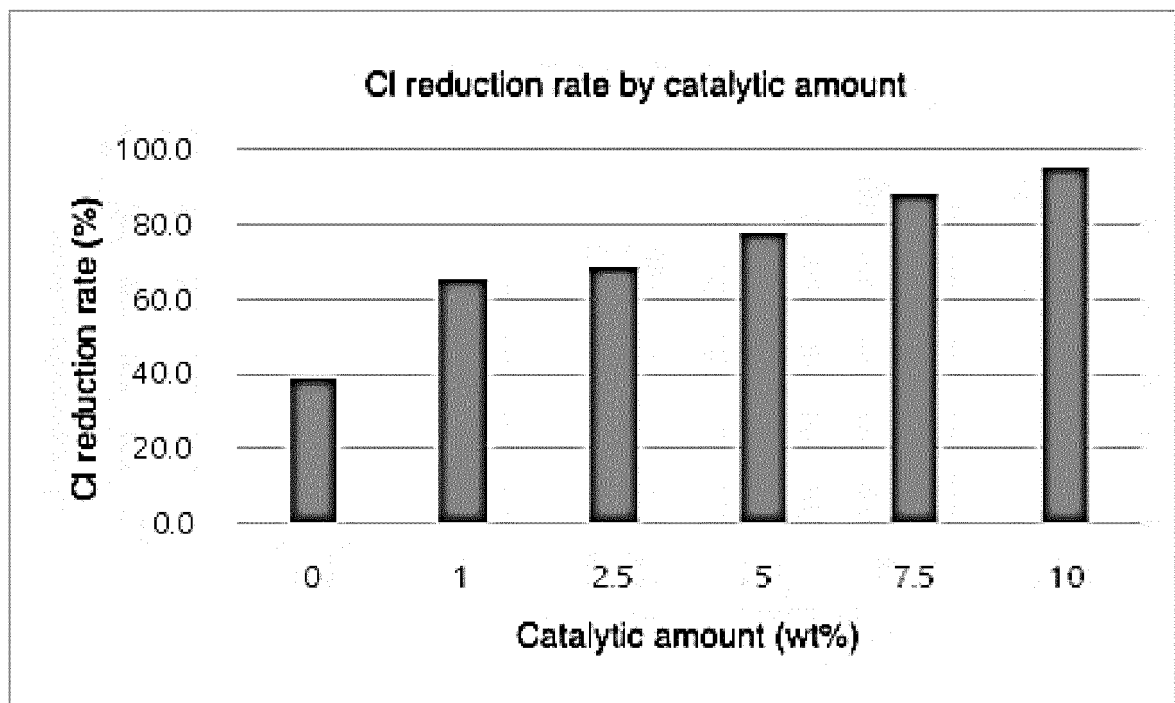
【FIG. 10】



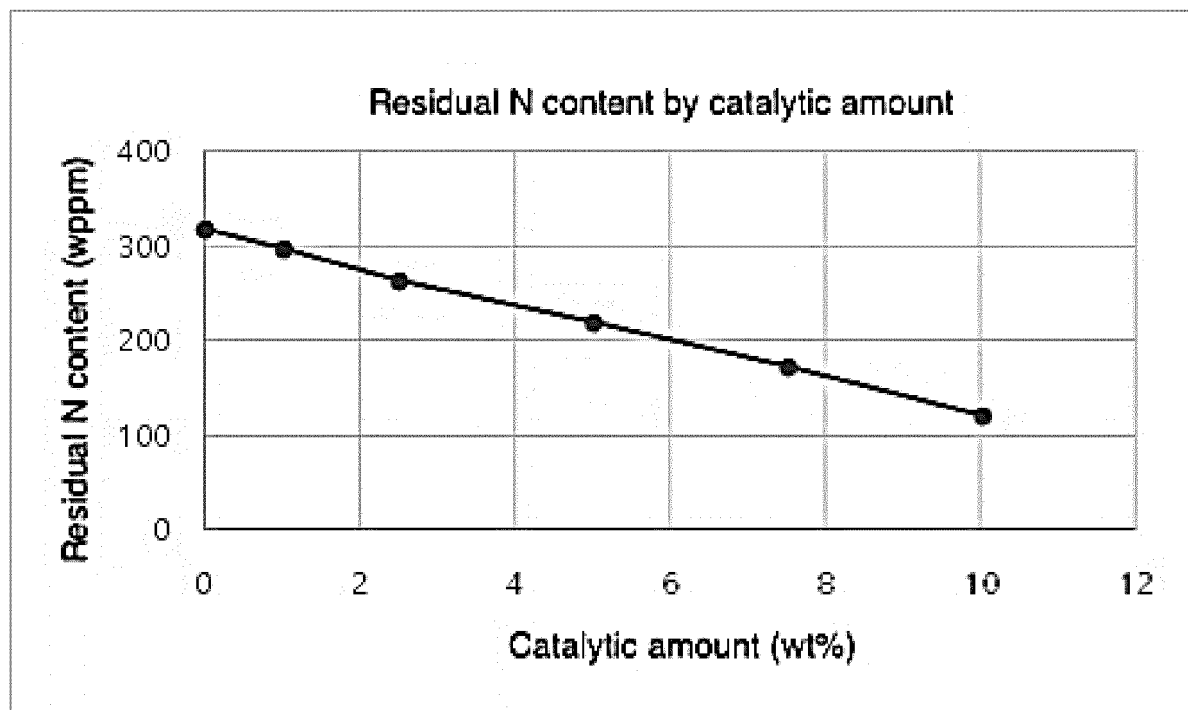
【FIG. 11】



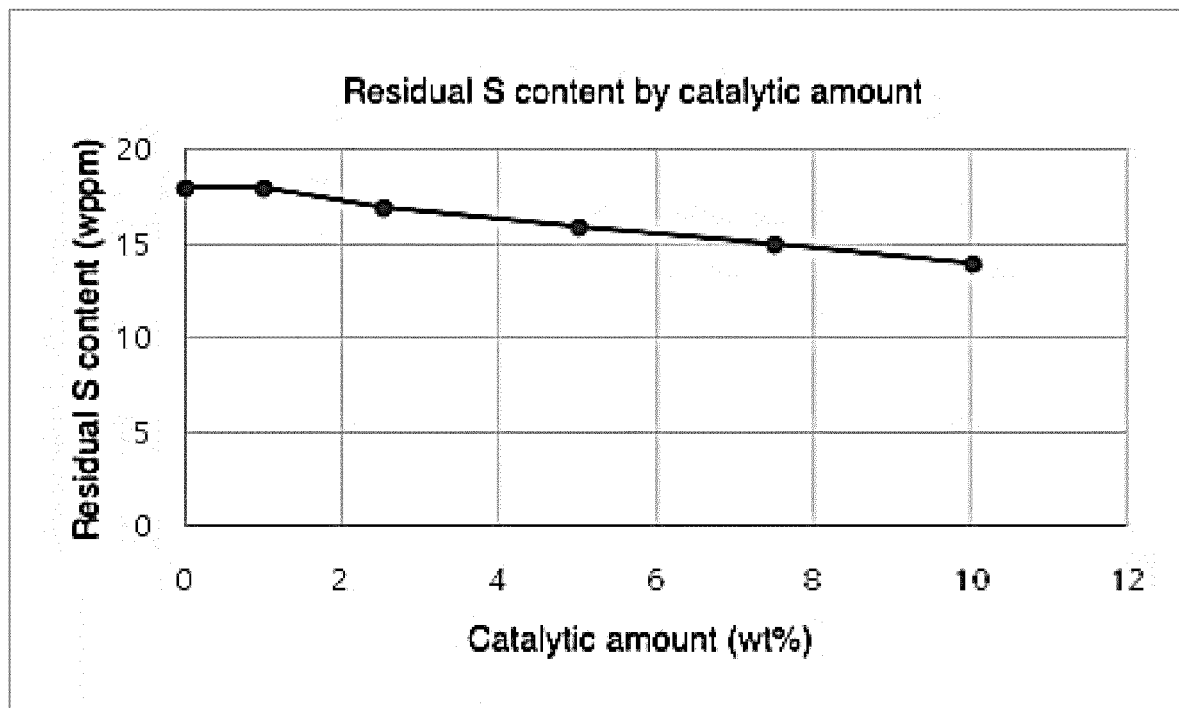
【FIG. 12】



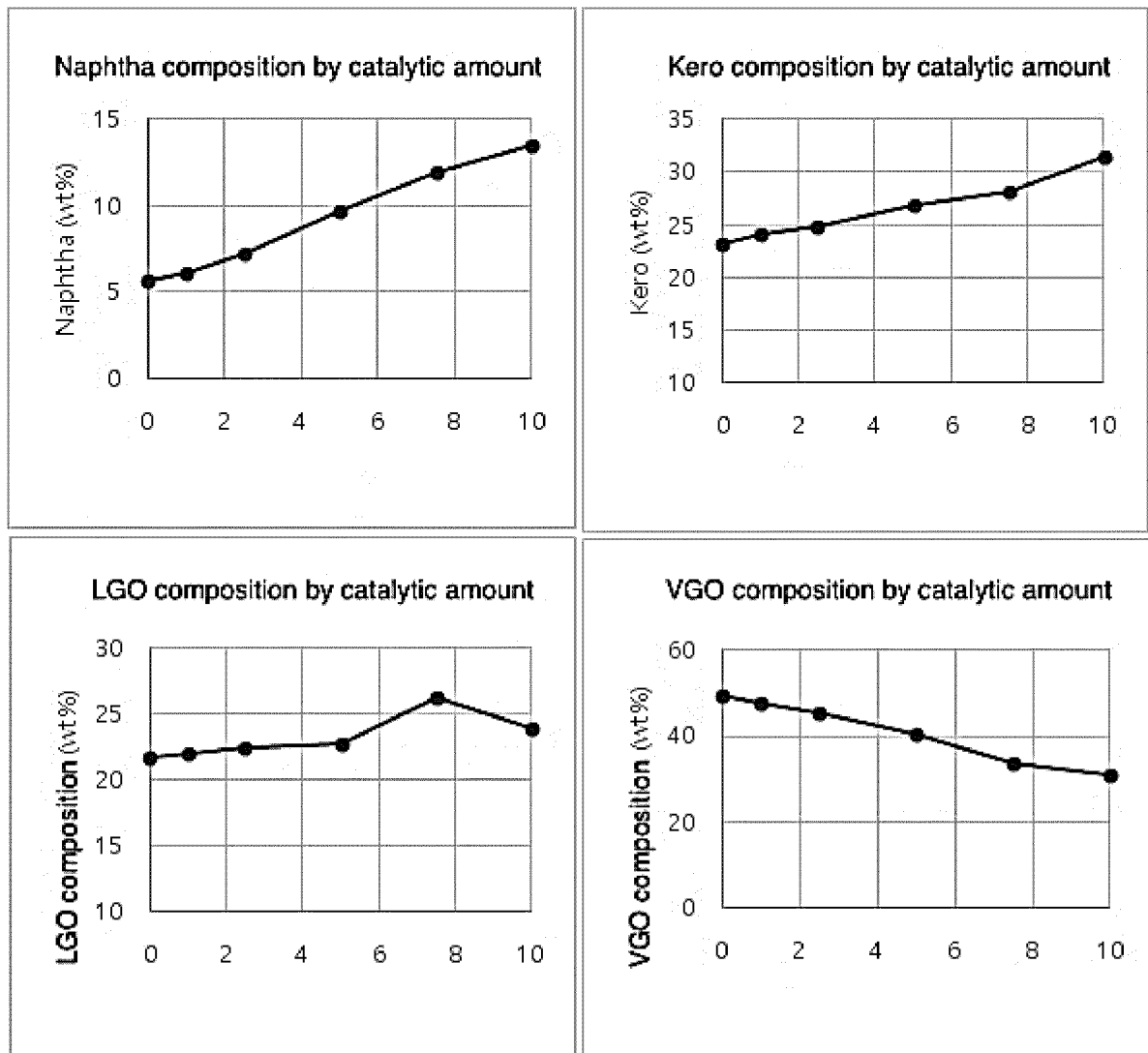
【FIG. 13】



【FIG. 14】



【FIG. 15】



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2020/015786

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); C10G 1/10(2006.01);
C10G 25/03(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: 폐유분(waste oil), 염소(chlorine), 고체산(solid acid), 촉매(catalyst)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 105368486 A (CHINA PETROLEUM & CHEM. CORP. et al.) 02 March 2016 (2016-03-02) See paragraphs [0052]-[0056]; and claims 1-16.	1-12
A	KR 10-2014-0041809 A (CHEVRON U.S.A. INC.) 04 April 2014 (2014-04-04) See entire document.	1-12
A	JP 2019-532118 A (SABIC GLOBAL TECHNOLOGIES BV) 07 November 2019 (2019-11-07) See entire document.	1-12
A	JP 2019-527758 A (SABIC GLOBAL TECHNOLOGIES BV) 03 October 2019 (2019-10-03) See entire document.	1-12
A	KR 10-2008-0068711 A (EXXONMOBIL CHEMICAL PATENTS INC.) 23 July 2008 (2008-07-23) See entire document.	1-12

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"D" document cited by the applicant in the international application	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 03 March 2021	Date of mailing of the international search report 03 March 2021
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208 Facsimile No. +82-42-481-8578	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2020/015786

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
KR 10-2008-0068711 A	23 July 2008	CN 101313052 A	26 November 2008
		CN 101313052 B	20 March 2013
		EP 1957616 A1	20 August 2008
		JP 2009-516051 A	16 April 2009
		JP 5041604 B2	03 October 2012
		TW 200726835 A	16 July 2007
		TW I316541 B	01 November 2009
		US 2007-0112240 A1	17 May 2007
		US 7744750 B2	29 June 2010
		WO 2007-058703 A1	24 May 2007

Form PCT/ISA/210 (patent family annex) (July 2019)

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]