

Description

Title of Invention: METHOD AND DEVICE FOR PRODUCING WASTE PLASTIC PYROLYSIS OIL WITH REDUCED CHLORINE

Technical Field

- [1] The present disclosure relates to a method for producing pyrolysis oil with reduced chlorine from waste plastics.

Background Art

- [2] Waste plastics are difficult to recycle and are mostly disposed of as garbage. These wastes take a long time to degrade in nature, which causes contamination of the soil and serious environmental pollution. As a method for recycling waste plastics, a method of converting waste plastics into oil by performing a pyrolysis process has been performed.
- [3] However, pyrolysis oil obtained by pyrolyzing waste plastics cannot be directly used as a high-value-added fuel such as gasoline or diesel oil because it has a high content of impurities such as chlorine, nitrogen, metals, and solid by-products compared to fractions produced from crude oil by a general method, and therefore, pyrolysis oil may be used as a fuel after adsorption of the impurities through a refinery process.
- [4] For example, chlorine has been converted into hydrogen chloride and adsorbed by hydrotreating waste plastic pyrolysis oil in the presence of a hydrotreating catalyst. However, the waste plastic pyrolysis oil has a high content of chlorine, and thus an excessive amount of hydrogen chloride is produced during hydrotreating, which causes problems such as equipment corrosion, an abnormal reaction, and deterioration of product properties.
- [5] In addition, in order to adsorb chlorine, nitrogen, and the like, a technique using an adsorbent such as CaO or a waste fluid catalytic cracking (FCC) catalyst (E-cat) has been performed. However, in order to achieve the adsorption effect, the adsorbent should be used in a significantly high content (a level of 2 to 50 times the content of oil to be refined), and an inactivated adsorbent should be continuously replaced because the adsorption effect is lost after adsorption of chlorine, nitrogen, and the like.
- [6] Therefore, there is a demand for a method for producing waste plastic pyrolysis oil with reduced chlorine at a level that may be introduced into a refinery process.
- [7] Meanwhile, red mud is a waste generated in a process of extracting alumina from bauxite. Worldwide, more than 120 million tons of red mud in the form of sludge and more than 40 million tons of red mud in the form of dried powder have been discharged annually, and the amounts thereof have been increasing. In Korea, more

than 200,000 tons of red mud in the form of sludge has been discharged annually.

- [8] As a method of processing the red mud, a method of utilizing red mud in a building material, a method of utilizing red mud as a heavy metal treatment agent, or the like has been used. However, there are many limitations in utilizing red mud as it is because it exhibits strong alkalinity and high water content. Currently, a pre-treatment process for utilizing red mud is necessarily accompanied, which causes, for example, huge facility costs and processing costs required for drying and grinding red mud, and serious problems such as environmental damage due to dust. Since red mud cannot be landfilled, there is no proper place to load red mud, and leachate leakage causes a lot of problems such as damage to nearby crops and human life. Therefore, processing of red mud is urgently needed.

Disclosure of Invention

Technical Problem

- [9] An object of the present disclosure is to provide a method for producing waste plastic pyrolysis oil capable of utilizing red mud, which is a waste, as a useful resource and effectively reducing a content of chlorine in pyrolysis oil produced by pyrolysis of waste plastics.
- [10] Another object of the present disclosure is to provide a technique for minimizing a content of chlorine in pyrolysis oil produced by using modified red mud having a maximized chlorine adsorption effect.
- [11] Still another object of the present disclosure is to provide pyrolysis oil having a low content of impurities at a level applicable to a refinery process without performing an additional post-treatment process after pyrolysis of a waste plastic feedstock.

Solution to Problem

- [12] In one general aspect, a method for producing waste plastic pyrolysis oil with reduced chlorine includes: a first step of charging a waste plastic feedstock and modified red mud into a reactor; and a second step of pyrolyzing the waste plastic feedstock in the reactor and recovering pyrolysis oil, wherein when the modified red mud is subjected to X-ray diffraction (XRD) analysis, an intensity of a first peak at a 2θ diffraction angle of $14 \pm 0.1^\circ$ is higher than an intensity of a second peak at a 2θ diffraction angle of $14.5 \pm 0.1^\circ$.
- [13] In an embodiment, a ratio $(I_1)/(I_2)$ of the intensity (I_1) of the first peak to the intensity (I_2) of the second peak may be 5 or more.
- [14] In an embodiment, a ratio $(I_1)/(I_3)$ of the intensity (I_1) of the first peak to an intensity (I_3) of a third peak may be 5 or more.
- [15] In an embodiment, in the first step, the modified red mud may be charged into the reactor in an amount of 5 to 30 parts by weight with respect to 100 parts by weight of

the waste plastic feedstock.

[16] In an embodiment, in the first step, the modified red mud may be charged into the reactor in the form of a paste by further containing moisture in an amount of 30 to 80 parts by weight with respect to 100 parts by weight of the modified red mud.

[17] In an embodiment, the second step may be performed at a temperature of 300 to 600°C.

[18] In an embodiment, the second step may be performed in a non-oxidizing atmosphere.

[19]

Advantageous Effects of Invention

[20] As set forth above, in the method for producing waste plastic pyrolysis oil, it is possible to effectively reduce a content of chlorine in pyrolysis oil produced by performing pyrolysis of waste plastics in the presence of modified red mud.

[21] According to the method for producing waste plastic pyrolysis oil according to the present disclosure, it is possible to produce pyrolysis oil having a low content of impurities at a level applicable to a refinery process without performing an additional post-treatment process after pyrolysis of a waste plastic feedstock.

[22]

Brief Description of Drawings

[23] FIG. 1 is a graph showing results of X-ray diffraction (XRD) analysis of red mud of Example 3 and Comparative Example 1 as representative examples of the present disclosure.

[24]

Mode for the Invention

[25] Unless the context clearly indicates otherwise, the singular forms of the terms used in the present specification may be interpreted as including the plural forms.

[26] A numerical range used in the present specification includes upper and lower limits and all values within these limits, all double limited values, and all possible combinations of the upper and lower limits in the numerical range defined in different forms. Unless otherwise specifically defined in the present specification, values out of the numerical range that may occur due to experimental errors or rounded values also fall within the defined numerical range.

[27] The expression "comprise(s)" described in the present specification is intended to be an open-ended transitional phrase having an equivalent meaning to "include(s)", "contain(s)", "have (has)", or "are (is) characterized by", and does not exclude elements, materials, or steps, all of which are not further recited herein.

[28] Unless otherwise defined, a unit of "%" used in the present specification refers to "wt %"

- [29] Unless otherwise defined, a unit of "ppm" used in the present specification refers to "mass ppm"
- [30] Waste plastics include polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), and the like, and the waste plastics contain organic chlorine and inorganic chlorine. Pyrolysis oil produced through a waste plastic pyrolysis process cannot be directly used as a high-value-added fuel such as gasoline or diesel oil because it has a high content of impurities, and therefore, pyrolysis oil may be used as a fuel after adsorption of the impurities through a refinery process. Therefore, there is a demand for a technique capable of producing waste plastic pyrolysis oil in which a content of chlorine is minimized from waste plastics.
- [31] Meanwhile, red mud is a waste generated in a process of extracting alumina from bauxite, and normal red mud is discharged in the form of sludge having a water content of about 30 to 50%. The normal red mud in a high water content state is usually dried through a pre-treatment process and then used as a building material, a heavy metal treatment agent, and the like. Such a pre-treatment process requires enormous facility costs and processing costs, and in particular, physical and chemical properties of red mud are changed due to the drying process, and thus there are many limitations in utilizing red mud.
- [32] Therefore, the present disclosure provides a method for effectively reducing chlorine in pyrolysis oil produced by using modified red mud having maximized selectivity to chlorine and adsorption characteristics in a waste plastic pyrolysis process.
- [33] Specifically, an embodiment of the present disclosure provides a method for producing waste plastic pyrolysis oil with reduced chlorine, the method including: a first step of charging a waste plastic feedstock and modified red mud into a reactor; and a second step of pyrolyzing the waste plastic feedstock in the reactor and recovering pyrolysis oil, wherein when the modified red mud is subjected to X-ray diffraction (XRD) analysis, an intensity of a first peak at a 2θ diffraction angle of $14 \pm 0.1^\circ$ is higher than an intensity of a second peak at a 2θ diffraction angle of $14.5 \pm 0.1^\circ$. The X-ray diffraction (XRD) analysis means an X-ray diffraction pattern using $\text{CuK}\alpha$ rays.
- [34] Specifically, the modified red mud, in which the intensity of the first peak at the 2θ diffraction angle of $14 \pm 0.1^\circ$ is higher than the intensity of the second peak at the 2θ diffraction angle of $14.5 \pm 0.1^\circ$ when subjected to the X-ray diffraction (XRD) analysis, is significantly excellent in selectivity to chlorine and chlorine adsorption characteristics in the pyrolysis process. In a case where red mud according to the related art is used, the red mud is dried at 110°C for 24 hours to be used in the form of dried red mud. On the other hand, the modified red mud of the present disclosure has

peak characteristics unique to the modified red mud that are not exhibited in the dried red mud when subjected to the X-ray diffraction (XRD) analysis, and specifically, modified red mud, in which the intensity of the first peak at the 2θ diffraction angle of $14 \pm 0.1^\circ$ is higher than the intensity of the second peak at the 2θ diffraction angle of $14.5 \pm 0.1^\circ$, may exhibit an excellent chlorine adsorption effect.

[35] In an embodiment, a ratio $(I_1)/(I_2)$ of the intensity (I_1) of the first peak to the intensity (I_2) of the second peak may be 5 or more. When $(I_1)/(I_2)$ satisfies the above range, the pyrolysis efficiency and the chlorine adsorption effect may be significantly excellent, and preferably, when $(I_1)/(I_2)$ is 7 or more, the chlorine adsorption effect may be further excellent. When $(I_1)/(I_2)$ is 10 or more, the modified red mud exhibits uniform dispersibility with waste plastics, and thermal conduction to the waste plastics is thus uniform, such that the yield of pyrolysis oil may be improved, which may be more preferable. Without limitation, $(I_1)/(I_2)$ may be 30 or less.

[36] The modified red mud may be obtained by modifying normal red mud to satisfy the above peak ratio. As a specific example, modified red mud satisfying the above peak ratio may be prepared by performing a process of pressurizing normal red mud in an atmosphere containing water vapor or pressurizing normal red mud in an atmosphere containing polar alcohol, but this is merely an example, and the present disclosure is not limited thereto. Any method for modifying normal red mud to satisfy the above peak ratio may be used without limitation.

[37] In an embodiment, when the modified red mud is subjected to the X-ray diffraction (XRD) analysis, the intensity of the first peak at the 2θ diffraction angle of $14 \pm 0.1^\circ$ may be higher than an intensity of a third peak at a 2θ diffraction angle of $28.2 \pm 0.1^\circ$.

[38] In an embodiment, a ratio $(I_1)/(I_3)$ of the intensity (I_1) of the first peak to the intensity (I_3) of the third peak may be 5 or more. When the intensity of the first peak at the 2θ diffraction angle of $14 \pm 0.1^\circ$ is higher than the intensity of the third peak at the 2θ diffraction angle of $28.2 \pm 0.1^\circ$, in particular, when the ratio $(I_1)/(I_3)$ of the intensity (I_1) of the first peak to the intensity (I_3) of the third peak is 5 or more, the selectivity to chlorine and the chlorine adsorption characteristics in the pyrolysis process may be further excellent. Specifically, $(I_1)/(I_3)$ may be 7 or more. More specifically, $(I_1)/(I_3)$ may be 10 or more and may be 30 or less without limitation.

[39] When the modified red mud is subjected to the X-ray diffraction (XRD) analysis, in a case where the peak intensities simultaneously satisfy $(I_1)/(I_2)$ of 5 or more and $(I_1)/(I_3)$ of 5 or more, the chlorine adsorption effect may be maximized. That is, the modified red mud that satisfies all of the peak characteristics described above has a significantly high chlorine adsorption rate, and therefore, when the pyrolysis process of waste plastics is performed in the presence of the modified red mud, high-quality pyrolysis oil with minimized impurities may be recovered. It is possible to produce high-quality

pyrolysis oil even through a simple process of performing pyrolysis by bringing a waste plastic feedstock to be processed into contact with modified red mud, and due to an excellent chlorine adsorption rate, the amount of modified red mud used may be reduced compared to an adsorbent according to the related art, such that it is possible to achieve a reduction in process costs and improvement of energy efficiency. Furthermore, considering the fact that the environmental contamination is caused by plastic waste and red mud waste and reuse of these wastes is required, as both wastes are used, it is possible to effectively produce high-value-added petroleum while effectively recycling resources.

- [40] In an embodiment, in the first step, the modified red mud may be charged into the reactor in an amount of 5 to 30 parts by weight with respect to 100 parts by weight of the waste plastic feedstock. Within the above range, chlorine may be effectively adsorbed, the pyrolysis efficiency may be improved, and high-quality pyrolysis oil may be obtained. Specifically, the modified red mud may be charged in an amount of 5 to 25 parts by weight, and more specifically, 5 to 20 parts by weight, with respect to 100 parts by weight of the waste plastic feedstock.
- [41] In an embodiment, in the first step, the modified red mud may be charged into the reactor in the form of a paste by further containing moisture in an amount of 30 to 80 parts by weight with respect to 100 parts by weight of the modified red mud. In a case where the modified red mud is charged into the reactor in the form of a paste by further containing moisture within the above range, chlorine dissociated from the waste plastics is trapped by moisture in the pyrolysis process, such that an additional chlorine adsorption effect may be obtained. Specifically, the moisture may be contained in an amount of 30 to 60 wt% with respect to the total weight of the modified red mud.
- [42] The thermal process in the second decomposition step may be performed in a non-oxidizing atmosphere as described below, and when the modified red mud contains moisture within the above range, the non-oxidizing atmosphere may be implemented with water vapor vaporized from the moisture contained in the red mud. It is possible to solve problems that require processing processes such as calcination, drying, and grinding, expensive facilities, expensive processing costs, and the like, which have occurred in the use of red mud in the related art, and it is possible to also improve the process efficiency.
- [43] In an embodiment, the second step may be performed at a temperature of 300 to 600°C. Within the above range, fusion of chlorine-containing waste plastics may be prevented, and the adsorption efficiency of chlorine dissociated from the waste plastics to the modified red mud may be improved. Specifically, the temperature may be 300 to 550°C, and more specifically, may be 350 to 500°C.
- [44] In an embodiment, the second step may be performed in a non-oxidizing atmosphere.

The non-oxidizing atmosphere is an atmosphere in which waste plastics do not combust, for example, an atmosphere in which an oxygen concentration is adjusted to 1 vol% or less, and may be an atmosphere of an inert gas such as nitrogen, water vapor, carbon dioxide, or argon. The pyrolysis process may be stably performed in a low-oxygen atmosphere in which an oxygen concentration is adjusted to 1 vol% or less.

- [45] As described above, when the modified red mud contains moisture within the above range, the non-oxidizing atmosphere may be an atmosphere of water vapor vaporized from the moisture contained in the red mud. Specifically, a melting process may be performed prior to the pyrolysis process to improve reaction efficiency. A process of charging a waste plastic feedstock and modified red mud into a reactor and then uniformly melting them at 100 to 130°C for 1 hour to 2 hours may be performed. In this process, water vapor is generated from moisture contained in the modified red mud, and oxygen may be removed through pressure purging by the water vapor. That is, since a non-oxidizing atmosphere by water vapor generated from the moisture contained in the feedstock may be created, an additional inert gas purge process may not be performed.
- [46] The second step may be performed in the non-oxidizing atmosphere for 150 minutes to 350 minutes, and when the holding time is satisfied, activation of the composition of the non-oxidizing atmosphere and sufficient pyrolysis may be performed. Specifically, the holding time may be 170 minutes to 330 minutes, and more specifically, may be 200 minutes to 300 minutes.
- [47] The reactor may be a batch reactor or a continuous reactor. In the case of the batch reactor, any type of batch reactor capable of performing stirring and controlling temperature rise may be used, and for example, a rotary kiln type batch reactor may be selected. In the case of the continuous reactor, a fixed bed continuous reactor may be exemplified.
- [48] When the modified red mud is dispersed in water, a pH of the modified red mud-dispersed aqueous solution may be 8 to 13. The strongly alkaline modified red mud that satisfies the above range may effectively adsorb chlorine dissociated from waste plastics. Specifically, the pH may be 9 to 12.
- [49] The modified red mud may further contain an inorganic component within a range in which the sum of the components is 100 wt%. Specifically, the modified red mud may further contain at least two or more components selected from 10 to 30 wt% of Fe_2O_3 , 5 to 20 wt% of Al_2O_3 , 1 to 30 wt% of SiO_2 , 0 to 15 wt% of CaO , 1 to 25 wt% of TiO_2 , and 0 to 15 wt% of Na_2O . More specifically, the modified red mud may further contain at least two or more components selected from 10 to 25 wt% of Fe_2O_3 , 5 to 15 wt% of Al_2O_3 , 1 to 25 wt% of SiO_2 , 0 to 10 wt% of CaO , 1 to 20 wt% of TiO_2 , and 0 to 10

wt% of Na₂O.

- [50] The first step may be performed by further containing an admixture. The admixture may be used to improve the pyrolysis reaction efficiency with the waste plastics within a range in which the inherent physical properties of the modified red mud, in particular, XRD peak characteristics are not impaired. As the admixture is further contained, the modified red mud may be more easily mixed with the waste plastic feedstock, and long-term dispersion stability may be improved. The admixture may be, for example, a cellulose ether-based compound such as methyl cellulose, ethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, or carboxymethyl cellulose. The admixture may be contained in an amount of 0.01 to 5 parts by weight, and specifically, 0.01 to 3 parts by weight, with respect to 100 parts by weight of the modified red mud.
- [51] The pyrolysis reaction may be performed by further charging additives into the reactor. For example, the pyrolysis process is performed by further adding one or more dechlorination agents selected from a metal oxide, a metal hydroxide, and a metal carbonate, such that the chlorine adsorption effect may be further improved. The metal may be an alkali metal or an alkaline earth metal. Specifically, the dechlorination agent may be sodium, magnesium, potassium, calcium, or the like, and more specifically, calcium hydroxide, sodium hydroxide, magnesium hydroxide, potassium hydroxide, calcium oxide, magnesium oxide, calcium carbonate, sodium carbonate, potassium carbonate, or the like. The dechlorination agent may be added in an amount of 1 to 10 parts by weight with respect to 100 parts by weight of the waste plastic feedstock. Specifically, the dechlorination agent may be added in an amount of 1 to 5 parts by weight. In addition, additives such as a stabilizer, an antifoaming agent, and a dispersant may be added.
- [52] The waste plastic feedstock may be domestic waste plastic, industrial waste plastic, or mixed waste plastics thereof. The domestic waste plastic is a plastic in which PVC, PS, PET, PBT, and the like in addition to PE and PP are mixed. In the present disclosure, as an example, the domestic waste plastic may be waste plastic including 3 wt% or more of PVC together with PE and PP. Chlorine may be contained in an amount of 5,000 ppm or more with respect to 100 parts by weight of the domestic waste plastic, and specifically, may be contained in an amount of 5,000 to 15,000 ppm with respect to 100 parts by weight of the domestic waste plastic, but this is merely an example, and the present disclosure is not limited thereto.
- [53] The industrial waste plastic is industrial waste generated in a manufacturing process in industries, and may be waste plastic including PE and PP as main components. Since the industrial waste plastic maintains a relatively clean state, a content of chlorine is lower than that in the domestic waste plastic. However, a content of organic

chlorine derived from an adhesive or a dye component is high, and in particular, a ratio of chlorine contained in an aromatic ring is high. Chlorine may be contained in an amount of 100 to 1,000 ppm, specifically, 500 to 1,000 ppm, and more specifically, 700 to 1,000 ppm, with respect to 100 parts by weight of the waste plastic, but the present disclosure is not limited thereto.

- [54] The second step is a step of pyrolyzing the waste plastic feedstock and recovering pyrolysis oil, and the waste plastic feedstock is converted into hydrocarbon products and may contain pyrolysis gas. After the pyrolysis gas is discharged from the reactor, the pyrolysis gas may be cooled and liquefied in a condenser to recover liquid pyrolysis oil in a storage tank.
- [55] The pyrolysis gas may include, with respect to the total weight of the waste plastic feedstock, 5 to 35 wt% of Naphtha (bp of 150°C or lower), 10 to 60 wt% of Kero (bp of 150 to 265°C), 20 to 40 wt% of LGO (bp of 265 to 380°C), and 5 to 40 wt% of UCO-2/AR (bp of 380°C or higher), and specifically, may include, with respect to the total weight of the waste plastic feedstock, 5 to 30 wt% of Naphtha (bp of 150°C or lower), 15 to 50 wt% of Kero (bp of 150 to 265°C), 20 to 35 wt% of LGO (bp of 265 to 380°C), and 10 to 40 wt% of UCO-2/AR (bp of 380°C or higher). In addition, the pyrolysis gas may include a balance of low-boiling point hydrocarbon compounds such as methane (CH₄), ethane (C₂H₆), and propane (C₃H₈).
- [56] Before the pyrolysis gas is introduced into the condenser, a low-boiling point gas containing low-boiling point hydrocarbon compounds such as methane (CH₄), ethane (C₂H₆), and propane (C₃H₈) in the pyrolysis gas may be separately recovered. The pyrolysis gas generally contains combustible materials such as hydrogen, carbon monoxide, and low-molecular-weight hydrocarbon compounds. Examples of the hydrocarbon compounds include methane, ethane, ethylene, propane, propene, butane, and butene. Since the pyrolysis gas contains combustible materials, the pyrolysis gas may be reused as a fuel for heating a batch reactor or a continuous reactor.
- [57] The condenser may include a zone through which a coolant flows, and the pyrolysis gas introduced into the condenser may be liquefied by the coolant and converted into pyrolysis oil. When the pyrolysis oil produced in the condenser rises to a predetermined level, the pyrolysis oil may be transported to and recovered in a storage tank.
- [58] A heat exchanger may be further provided between the condenser and the storage tank. The pyrolysis gas uncondensed in the condenser is introduced into the heat exchanger and condensed again, and the produced pyrolysis oil may be recovered to the storage tank. The uncondensed pyrolysis gas is recovered again, such that a reaction yield may be improved.
- [59] The liquid pyrolysis oil recovered in the storage tank may include an oil layer and a water layer. In addition to the pyrolysis gas, water vapor generated from the modified

red mud is also liquefied and recovered in the storage tank, and oil and water separation proceeds to form an oil layer and a water layer in the liquid pyrolysis oil.

- [60] The water layer contains a chlorine compound, which may cause corrosion of the storage tank, and a neutralizer may be added to the water layer to prevent corrosion of the storage tank. The neutralizer may contain an alkali metal compound or an alkaline earth metal compound having a pH of 7 or higher when dissolved in water. Specifically, the neutralizer may contain a hydroxide, an oxide, a carbonate, a hydrogen carbonate, a basic carbonate, or a fatty acid salt of an alkali metal or an alkaline earth metal. The alkali metal or the alkali earth metal may be a metal commonly used in the art. Examples of the alkali metal include lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr), and examples of the alkaline earth metal include beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). The neutralizer may be added alone or as a mixture with a solvent such as alcohol to improve neutralization efficiency.
- [61] In the case where the neutralizer is added to the water layer, the neutralizer may be added in an appropriate amount by measuring a pH of the water layer using a pH meter located at the bottom of the storage tank.
- [62] When the oil layer and the water layer are separated, the oil layer may be immediately recovered or may be recovered after adsorption of the water layer, such that an oil layer (waste plastic pyrolysis oil) in which a content of chlorine is minimized may be recovered. The water layer may be discharged and adsorbed, and the discharged moisture may be purified and then recirculated to the first step to be used as water to be mixed with the waste plastics.
- [63] An electric field may be applied to effectively separate the oil layer and the water layer, and the oil layer and the water layer may be separated in a short time by electrostatic adhesion due to application of the electric field. In addition, an additive may be added as necessary to increase the oil-water separation efficiency, and the additive may be a common demulsifier known in the art.
- [64] In a case where the water layer is discharged and adsorbed, a density is detected using a density profiler, such that it is possible to prevent the oil layer from being adsorbed together with the water layer when the water layer is adsorbed, and only the water layer may be effectively removed.
- [65] A content of chlorine in the recovered pyrolysis oil may be 300 ppm or less. A content of chlorine in waste plastic pyrolysis oil produced by effectively adsorbing chlorine dissociated from the waste plastic feedstock using the modified red mud may be 300 ppm or less. In particular, when all of the peak characteristics of Relational Expression 1 (I_{1D}/I_{1W})/(I_{2D}/I_{2W}) and Relational Expression 2 (I_{2W}/I_{1W}) are satisfied, the chlorine adsorption effect is maximized, such that the content of chlorine may be 150

ppm or less, and more specifically, 100 ppm or less.

[66] Hereinafter, preferred Examples and Comparative Examples of the present disclosure will be described. However, each of the following Examples is merely a preferred example of the present disclosure, and the present disclosure is not limited to the following Examples.

[67] Example 1

[68] Domestic mixed plastic including 3 wt% or more of PVC together with PE and PP was extruded at 250°C to prepare 400 g of domestic waste plastic pellets. The total content of chlorine in the domestic waste plastic pellets was 4,000 ppm.

[69] Normal red mud recovered from a residue left after preparation of alumina from bauxite was prepared. The composition of the recovered normal red mud is as shown in Table 1.

[70] [Table 1]

	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	Na ₂ O	CaO	H ₂ O
Composition (wt%)	16	7	8	10	2	5	52

[71] The normal red mud was added to a pressurizing device in which a water vapor atmosphere was created, and pressurization was performed at a pressure of 5 bar and a temperature of 25°C for 60 minutes. Thereafter, the pressure was adjusted to normal pressure, and stabilization was performed at a temperature of 60°C for 60 minutes, thereby preparing modified red mud. 400 g of the prepared domestic waste plastic pellets and 20 g of the modified red mud were added to a batch reactor, and a melting process was performed by heating at 110°C for 1 hour. A non-oxidizing atmosphere was created with water vapor generated from the modified red mud in the melting process, and then full-scale pyrolysis was performed at 400°C for 250 minutes. Pyrolysis gas generated in the pyrolysis process was recovered through an outlet at the top of the reactor and trapped in a condenser, and then waste plastic pyrolysis oil was finally recovered in a storage tank.

[72] X-ray diffraction (XRD) analysis was performed to confirm the peak characteristics of the modified red mud. The results thereof are shown in Table 2. I₁, I₂, and I₃ shown in the table below are the same as defined above.

[73] [Table 2]

(I ₁)/(I ₂)	(I ₁)/(I ₃)
10.38	3.52

[74] Example 2

[75] Waste plastic pyrolysis oil was recovered by performing a reaction under the same

conditions as those of Example 1, except that modified red mud having the characteristics shown in Table 3 was used. Specifically, the normal red mud was added to a pressurizing device in which a water vapor atmosphere was created, and pressurization was performed at a pressure of 7 bar and a temperature of 25°C for 60 minutes, thereby preparing modified red mud.

[76] [Table 3]

(I ₁)/(I ₂)	(I ₁)/(I ₃)
10.92	4.86

[77] Example 3

[78] In Example 1, instead of the normal red mud having the composition shown in Table 1, normal red mud having the composition shown in Table 4 was added to a pressurizing device in which an ethanol atmosphere was created, and pressurization was performed at a pressure of 5 bar and a temperature of 25°C for 60 minutes.

[79] [Table 4]

	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	Na ₂ O	CaO	H ₂ O
Composition (wt%)	10	7	8	8	2	5	60

[80] Waste plastic pyrolysis oil was recovered by performing a reaction under the same conditions as those of Example 1, except that modified red mud having the characteristics shown in Table 5 was prepared and used through this.

[81] [Table 5]

(I ₁)/(I ₂)	(I ₁)/(I ₃)
11.74	12.51

[82] **Example 4**

[83] Waste plastic pyrolysis oil was recovered by performing a reaction under the same conditions as those of Example 1, except that modified red mud having the characteristics shown in Table 6 was used in Example 3. Specifically, the normal red mud was added to a pressurizing device in which an ethanol atmosphere was created, and pressurization was performed at a pressure of 15 bar and a temperature of 25°C for 60 minutes, thereby preparing modified red mud.

[84] [Table 6]

(I ₁)/(I ₂)	(I ₁)/(I ₃)
12.98	17.64

[85] Comparative Example 1

[86] Waste plastic pyrolysis oil was recovered by performing a reaction under the same

conditions as those of Example 1, except that dried red mud obtained by drying the normal red mud was used. Specifically, the modified red mud was heated at 110°C for 24 hours to prepare dried red mud.

[87] X-ray diffraction (XRD) analysis was performed to confirm the peak characteristics of the dried red mud. The results thereof are illustrated in FIG. 1 and shown in Table 7.

[88] [Table 7]

$(I_1)/(I_2)$	$(I_1)/(I_3)$
0.66	1.60

[89] Comparative Example 2

[90] Waste plastic pyrolysis oil was recovered by performing a reaction under the same conditions as those of Example 1, except that red mud having the characteristics shown in Table 8 was used.

[91] [Table 8]

$(I_1)/(I_2)$	$(I_1)/(I_3)$
0.8	3.78

[92] Evaluation Example 1

[93] Representatively, the red mud of each of Example 3 and Comparative Example 1 was subjected to X-ray diffraction (XRD) analysis, and peak intensities at 2 θ diffraction angles of $14 \pm 0.1^\circ$, $14.5 \pm 0.1^\circ$, and $28.2 \pm 0.1^\circ$ were measured. The measurement results are shown in Table 9.

[94] [Table 9]

Sample	Peak Intensity		
	I_1 ($2\theta = 14.0 \pm 0.1^\circ$)	I_2 ($2\theta = 14.5 \pm 0.1^\circ$)	I_3 ($2\theta = 28.2 \pm 0.1^\circ$)
Example 3	2690	229	215
Comparative Example 1	2189	3280	1368

[95] Referring to Table 9 and FIG. 1, it could be confirmed that I_1 was higher than I_2 in Example 3, whereas I_1 was lower than I_2 in Comparative Example 1, and it could be confirmed that I_3 in Example 3 was lower than that in Comparative Example 2. From this, it could be confirmed that each of $(I_1)/(I_2)$ and $(I_1)/(I_3)$ satisfied 5 or more in Example 3, but did not satisfy it in Comparative Example 1, and it could be confirmed that the chlorine removal characteristics of the red mud were different due to the difference in peak characteristics as shown in Table 10 described below.

[96] Evaluation Example 2

[97] The recovered waste plastic pyrolysis oil was subjected to ICP and XRF analysis to measure a content of chlorine. The results thereof are summarized in Table 10.

[98] [Table 10]

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Total chlorine in waste plastic feedstock (ppm)	4,000					
(I ₁)/(I ₂)	7.38	9.92	11.74	13.98	0.66	0.8
(I ₁)/(I ₃)	3.32	4.56	12.51	17.64	1.60	3.78
Chlorine in pyrolysis oil(ppm)	270	250	190	170	530	490

[99] In Examples 1 and 2, it could be confirmed that, as the (I₁)/(I₂) values of the modified red mud were 7.38 and 9.92, respectively, which satisfied 5 or more, the content of chlorine in the recovered pyrolysis oil was about 250 to 270 ppm, which showed that chlorine was effectively reduced. In particular, referring to Examples 3 and 4, it could be confirmed that, in a case where the (I₁)/(I₂) values were 11.74 and 13.89, respectively, which satisfied 5 or more, and also the (I₁)/(I₃) values were 12.51 and 17.64, respectively, which satisfied 5 or more, the content of chlorine in the pyrolysis oil was 200 ppm or less, which showed that the chlorine removal characteristics of the modified red mud were further improved.

[100] On the other hand, it was confirmed that, in the case of the commonly used dried red mud of Comparative Example 1, the (I₁)/(I₂) value was 1 or less and the (I₁)/(I₃) value was 3 or less, which were significantly low values, and therefore, it could be confirmed that the chlorine removal characteristics of the modified red mud were deteriorated, and the content of chlorine in the pyrolysis oil was 530 ppm, which showed that chlorine was present in excess.

[101] Also in Comparative Example 2, as the (I₁)/(I₂) value was 1 or less and the (I₁)/(I₃) value was 5 or less, which were low, it could be confirmed that the chlorine removal characteristics of the modified red mud were deteriorated.

[102] Although embodiments of the present invention have been described hereinabove,

the present invention is not limited to the embodiments, but may be implemented in various different forms, and it will be apparent to those skilled in the art to which the present invention pertains that the embodiments may be implemented in other specific forms without departing from the technical idea or essential feature of the present invention. Therefore, it is to be understood that the embodiments described hereinabove are illustrative rather than restrictive in all aspects.

Claims

- [Claim 1] A method for producing waste plastic pyrolysis oil with reduced chlorine, the method comprising:
a first step of charging a waste plastic feedstock and modified red mud into a reactor; and
a second step of pyrolyzing the waste plastic feedstock in the reactor and recovering pyrolysis oil,
wherein when the modified red mud is subjected to X-ray diffraction (XRD) analysis, an intensity of a first peak at a 2θ diffraction angle of $14 \pm 0.1^\circ$ is higher than an intensity of a second peak at a 2θ diffraction angle of $14.5 \pm 0.1^\circ$.
- [Claim 2] The method of claim 1, wherein a ratio (I_1)/(I_2) of the intensity (I_1) of the first peak to the intensity (I_2) of the second peak is 5 or more.
- [Claim 3] The method of claim 1, wherein when the modified red mud is subjected to the X-ray diffraction (XRD) analysis, the intensity of the first peak at the 2θ diffraction angle of $14 \pm 0.1^\circ$ is higher than an intensity of a third peak at a 2θ diffraction angle of $28.2 \pm 0.1^\circ$.
- [Claim 4] The method of claim 1, wherein a ratio (I_1)/(I_3) of the intensity (I_1) of the first peak to an intensity (I_3) of a third peak is 5 or more.
- [Claim 5] The method of claim 1, wherein in the first step, the modified red mud is charged into the reactor in an amount of 5 to 30 parts by weight with respect to 100 parts by weight of the waste plastic feedstock.
- [Claim 6] The method of claim 1, wherein in the first step, the modified red mud is charged into the reactor in the form of a paste by further containing moisture in an amount of 30 to 80 parts by weight with respect to 100 parts by weight of the modified red mud.
- [Claim 7] The method of claim 1, wherein the second step is performed at a temperature of 300 to 600°C.
- [Claim 8] The method of claim 1, wherein the second step is performed in a non-oxidizing atmosphere.
- [Claim 9] The method of claim 1, wherein the first step is performed by further containing an admixture.
- [Claim 10] The method of claim 9, wherein the admixture is a cellulose ether-based compound.