

MARINE ENGINE PRETREATMENT DESULFURIZATION CONTROL AND MONITORING SYSTEM

Technical Field

5 **[1]** The present invention relates to a pretreatment desulfurization control and monitoring system for a marine engine. More particularly, the present invention relates to a marine engine pretreatment desulfurization control and monitoring system for performing a pretreatment desulfurization function to reduce emissions of sulfur oxides (SO_x) when marine fuel oil such as bunker-C oil is burned in a marine engine.

Background Art

10 **[2]** Sulfur oxides (SO_x) and nitrogen oxides (NO_x) are pointed out as pollutants that cause air pollution. Sulfur oxides are contained in industrial flue gas emitted from the combustion of fossil
15 fuels containing sulfur, and the sulfur oxides cause various environmental pollution problems such as acid rain.

20 **[3]** Desulfurization technology for removing sulfur oxides from industrial flue gas has been continuously studied, and a flue gas desulfurization method of treating flue gas generated through combustion of fissile fuels has been generally used in factories or power plants.

25 **[4]** The flue gas desulfurization method refers to a method of desulfurizing the flue gas after burning a fossil fuel containing sulfur, and the flue gas desulfurization methods are categorized into wet treatment and dry treatment. In the wet treatment, sulfur oxides are removed by washing flue gas with ammonia water, sodium hydroxide solution, lime milk, etc. while in the dry treatment, sulfur oxides are removed by contacting particles or powders of activated carbon or carbonates with flue gas to adsorb or react with sulfur dioxide.

30 **[5]** In particular, the sulfur oxide content of heavy fuel oil (MGO, MDO, DDO) such as bunker-C oil used in marine engines is 1,000 to 3,000 times higher than that of automobile fuel. The amount of sulfur oxides emitted by ships around the world is 130 times higher than that of automobiles, and thus is known as the main cause of environmental pollution.

[6] For this reason, conventionally, flue gas desulfurization is performed as a post-treatment process using a marine wet desulfurization system to remove sulfur oxides emitted from marine engines. In the wet desulfurization system, a pump is used to supply washing water (NaOH) supplied to a scrubber through a cooler, and exhaust gas and the washing water come into contact with each other in the scrubber to remove sulfur oxides through post-treatment.

[7] In this case, to maintain a predetermined level of the sulfur oxide removal capability of the wet desulfurization system, the pH of the washing water is monitored to automatically control the supply amount of the washing water. The used washing water is purified to recycle the washing water. This purification process generates a large amount of sludge, and the sludge is collected and stored in a sludge tank, and the sludge is treated after the ship is anchored.

[8] As described above, the conventional post-treatment wet desulfurization technology requires a lot of manpower and cost due to the complicated washing water purification process, and it is necessary to separately construct a separate complex desulfurization facility. Therefore, it is difficult to apply such a conventional desulfurization system to currently operating ships. That is, there is a problem that it is not easy and practical to use the conventional desulfurization system in an existing ship in terms of space and cost.

[9] Therefore, in order to dramatically reduce the environmental pollution caused by the combustion of marine fuel oil and the emission of sulfur oxides, research on an effective pretreatment desulfurization control and monitoring system that can significantly reduce the emission of sulfur oxides, can easily remove sulfur oxides, and can be easily applied to an existing ship is urgently needed.

Disclosure

Technical Problem

[10] The present invention has been made to solve the problems occurring in the related art, and an objective of the present invention is to provide a pretreatment desulfurization control and

monitoring system for a marine engine, the system being capable of preventing sulfur oxides generated through the combustion of high-sulfur-content marine fuel oil from being discharged into the air, having a simple structure to be easily applied to an existing ship, and being capable of effectively controlling desulfurization in real time.

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Technical Solution

[11] In order to accomplish the objective of the present invention provides, one embodiment of the present invention provides a desulfurization control and monitoring system including: a fuel injection amount sensor installed on a fuel supply line connected between a fuel tank and a marine engine and configured to detect an injection amount of fuel; a pretreatment desulfurization agent injection amount sensor disposed between a pretreatment desulfurization agent tank and a downstream fuel supply line installed downstream of the fuel injection amount sensor and configured to detect an injection amount of a pretreatment desulfurization agent; and a control panel for controlling and monitoring the injection amount of the pretreatment desulfurization agent, the control panel being connected to the sensors in a bi-directionally communicable manner so that the pretreatment desulfurization agent can be mixed with the fuel in a predetermined mixing ratio.

[12] In addition, according to one embodiment, the system may further include an RPM sensor that is added to the marine engine and detects the number of revolutions per minute (RPM) of the marine engine.

[13] In addition, according to one embodiment, the system may further include a gas sensor that is added to an exhaust port of the marine engine, and which detects the concentration of sulfur oxides contained in an exhaust gas.

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[14] In addition, according to one embodiment, the system may further include a water level sensor added to the pretreatment desulfurization agent tank.

[15] In addition, according to one embodiment, reservoir tank having a large-capacity for storing the pretreatment desulfurization agent for replenishment may be further connected to the pretreatment desulfurization agent tank, and the pretreatment desulfurization agent may be automatically replenished from the reservoir tank to the pretreatment desulfurization agent tank

when a lower water level than a predetermined water level is detected by the water level sensor.

[16] In addition, according to one embodiment, the control panel may be connected to an administrator's mobile terminal through a wireless communication scheme and may be remotely controlled and monitored through a mobile application.

[17] In addition, according to one embodiment, the pretreatment desulfurization agent may include: (a) at least one oxide selected from the group consisting of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , MnO , CaO , Na_2O , K_2O , and P_2O_3 ; (b) at least one metal selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb; and (c) at least one liquid composition selected from the group consisting of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), and hydrogen peroxide (H_2O_2).

[18] In addition, according to one embodiment, the oxide may include 15 to 90 parts by weight of SiO_2 , 15 to 100 parts by weight of Al_2O_3 , 10 to 50 parts by weight of Fe_2O_3 , 5 to 15 parts by weight of TiO_2 , 20 to 150 parts by weight of MgO , 10 to 20 parts by weight of MnO , 20 to 200 parts by weight of CaO , 15 to 45 parts by weight of Na_2O , 20 to 50 parts by weight of K_2O , and 5 to 20 parts by weight of P_2O_3 . The metal may include 0.0035 to 0.009 parts by weight of Li, 0.005 to 0.01 parts by weight of Cr, 0.001 to 0.005 parts by weight of Co, 0.006 to 0.015 parts by weight of Ni, 0.018 to 0.03 parts by weight of Cu, 0.035 to 0.05 parts by weight of Zn, 0.04 to 0.08 parts by weight of Ga, 0.02 to 0.05 parts by weight of Sr, 0.002 to 0.01 parts by weight of Cd, and 0.003 to 0.005 parts by weight of Pb.

[19] In addition, according to one embodiment, the oxide and metal particles may have a size of 1 to 2 μm , and a specific gravity of 2.5 to 3.0.

[20] In addition, according to one embodiment, the sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) may be contained in an amount of 20 to 130 parts by weight, the sodium hydroxide (NaOH) may be contained in an amount of 15 to 120 parts by weight, the sodium silicate (Na_2SiO_3) may be contained in an amount of 50 to 250 parts by weight, and hydrogen peroxide (H_2O_2) may be contained in an amount of 10 to 50 parts by weight.

[21] In addition, according to one embodiment, in the pretreatment desulfurization agent, the oxide, the metal, and the liquid composition may form a metal chelate compound.

[22] In addition, according to one embodiment, the sulfur oxide (SO_x) adsorption effect of the pretreatment desulfurization agent may be activated at a temperature within a range from 400°C to 1200°C.

[23] In addition, according to one embodiment, the pretreatment desulfurization agent may be mixed in a ratio from 0.1 to 10 parts by weight relative to 100 parts by weight of the marine fuel oil.

[24] In addition, according to one embodiment, the pretreatment desulfurization agent may be mixed in a ratio of 6 parts by weight relative to 100 parts by weight of the marine fuel oil.

[25] In addition, according to one embodiment, the fuel supply line may be equipped with a line mixer, and the pretreatment desulfurization agent may be injected into the marine fuel oil in a state in which the pretreatment desulfurization agent tank is connected to the line mixer.

[26] In addition, according to one embodiment, the marine fuel oil may be any one of heavy oil such as bunker-A oil, bunker-B oil, or bunker-C oil, or light oil such as MGO, MDO, or DDO.

Advantageous Effects

[27] The pretreatment desulfurization control and monitoring system for a marine engine, of the present invention, can prevent a large amount of sulfur oxides generated in a process of burning high-sulfur-content marine fuel oil from being discharged into the air in real time, thereby greatly contributing to solving the problem of air pollution caused by sulfur oxides.

[28] In addition, the pretreatment desulfurization control and monitoring system of the present invention is different from a conventional method of desulfurizing flue gas after the combustion of fuel. That is, the system mixes a pretreatment desulfurization agent with the fuel before the combustion of the fuel so that the pretreatment desulfurization agent and the fuel are combusted together in the marine engine. Therefore, the system can control and monitor the pretreatment

desulfurization process if it is simply connected to a fuel supply system of an existing marine engine without requiring an additional investment for installation of new desulfurization facilities. Therefore, the system can be simply and easily applied to an existing ship and can improve the desulfurization effect in real time.

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Description of Drawings

10 [29] FIG. 1 is an exemplary view illustrating the construction of a pretreatment desulfurization system according to the present invention;

[30] FIG. 2 is a partially enlarged view illustrating a “A” portion of FIG. 1;

15 [31] FIG. 3 is a view illustrating the result of analysis of a sulfur oxide (SO₂) concentration in the entire session of Test Example 1;

[32] FIG. 4 is a view illustrating the result of analysis of a sulfur oxide (SO₂) concentration in the entire session of Test Example 2;

20 [33] FIG. 5 is an exemplary view showing a configuration in which a pretreatment desulfurization control and monitoring system for a marine engine, of the present invention, is added to the configuration of FIG. 1

Best Mode

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[34] In the following description, the specific structural or functional descriptions for exemplary embodiments according to the concept of the present disclosure are merely for illustrative purposes. Therefore, those skilled in the art will appreciate that various modifications and changes to the exemplary embodiments are possible, without departing from the scope and spirit of the present disclosure. Therefore, the present disclosure is intended to cover not only the exemplary
30 embodiments but also various alternatives, modifications, equivalents, and other embodiments that

may be included within the spirit and scope of the embodiments as defined by the appended claims. Hereinafter, embodiments of the present invention will be described in detail in conjunction with the accompanying drawings.

5 **[35]** The present invention uses a desulfurization catalyst (hereinafter, referred to as “pretreatment desulfurization agent”) including: (a) at least one oxide selected from the group consisting of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , MnO , CaO , Na_2O , K_2O , and P_2O_3 ; (b) at least one metal selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb; and (c) at least one liquid composition selected from the group consisting of sodium tetraborate
10 ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), and hydrogen peroxide (H_2O_2).

[36] The pretreatment desulfurization agent according to the present invention preferably includes at least one oxide selected from the group consisting of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , MnO , CaO ,
15 Na_2O , K_2O , and P_2O_3 . Preferably, the pretreatment desulfurization agent includes all the oxides selected from the group consisting of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , MnO , CaO , Na_2O , K_2O , and P_2O_3 as in Examples described below.

[37] When including all of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , MnO , CaO , Na_2O , K_2O , and P_2O_3 ,
20 the basic formula is $\text{K}_{0.8-0.9}(\text{Al}, \text{Fe}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$ which is a mineral commonly called illite. The illite has a 2:1 structure in which one octahedral layer is bonded between two tetrahedral layers. The octahedral layer has a dioctahedral structure in which only 2 cation sites out of 3 cation sites in the bonding structure are filled with cations. Due to the lack of positive ions, the illite has an overall negative charge (-). For this reason, sulfur oxides (SO_x) can be adsorbed when the mixture
25 of a combustible material and the desulfurization catalyst is burned.

[38] As the oxides, the pretreatment desulfurization agent may include 15 to 90 parts by weight of SiO_2 , 15 to 100 parts by weight of Al_2O_3 , 10 to 50 parts by weight of Fe_2O_3 , 5 to 15 parts by weight of TiO_2 , 20 to 150 parts by weight of MgO , 10 to 20 parts by weight of MnO , and 20 to 50 parts by
30 weight of CaO , 15 to 45 parts by weight of Na_2O , 20 to 50 parts by weight of K_2O , and 5 to 20 parts by weight of P_2O_3 .

[39] In addition, the oxides may be mixed and pulverized into fine particles having a particle size of 1 to 2 μm by a pulverizer before being prepared as the desulfurization catalyst. The oxides may have a specific gravity of 2.5 to 3.0 and may be in the form of powder that is streak-colored or silvery white.

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[40] The pretreatment desulfurization agent according to the present invention may include one or more metals selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb. As in one embodiment, all the metals including Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb are preferably included.

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[41] As the metals, the pretreatment desulfurization agent may include 0.0035 to 0.009 parts by weight of Li, 0.005 to 0.01 parts by weight of Cr, 0.001 to 0.005 parts by weight of Co, 0.006 to 0.015 parts by weight of Ni, 0.018 to 0.03 parts by weight of Cu, 0.035 to 0.05 parts by weight of Zn, 0.04 to 0.08 parts by weight of Ga, 0.02 to 0.05 parts by weight of Sr, 0.002 to 0.01 parts by weight of Cd, and 0.003 to 0.005 parts by weight of Pb.

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[42] In addition, the metals, like the oxides, may be mixed and pulverized into fine particles having a particle size of 1 to 2 μm by a pulverizer, the metals may have a specific gravity of 2.5 to 3.0, and the metals may be in the form of powder that is streak-colored and silvery white.

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[43] The pretreatment desulfurization agent according to the present invention may include at least one liquid composition selected from the group consisting of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), and hydrogen peroxide (H_2O_2). Preferably, as in one embodiment, all the liquid compositions including sodium tetraborate, sodium hydroxide, sodium silicate, and hydrogen peroxide may be included.

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[44] The pretreatment desulfurization agent according to the present invention forms a metal chelate compound through coordination with the metals because the oxides and the liquid compositions are mixed and reacted to serve as a chelating agent.

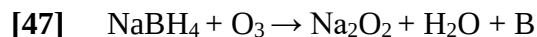
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[45] In addition, the liquid composition may be adsorbed on ash generated when a combustible material so that the liquid composition may react with sulfur oxides in the ash to remove the sulfur

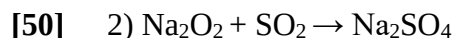
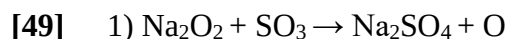
oxides. Sodium metaborate(NaBO_2) is derived from the sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$), NaBH_4 is produced through hydrogenation, and the produced NaBH_4 reacts with oxygen and sulfur oxides to form sodium sulfate (Na_2SO_4). Thus, the sulfur oxides are removed. The reactions are represented by Reaction Formulas 1 and 2 below.

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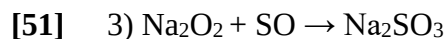
[46] [Reaction Formula 1]



10 **[48]** [Reaction Formula 2]



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[52] In addition, as the liquid compositions, the sodium tetraborate, the sodium hydroxide, the sodium silicate, and the hydrogen peroxide may be included in amounts of 20 to 130 parts by weight, 15 to 120 parts by weight, 50 to 250 parts by weight, and 10 to 50 parts by weight, respectively in the pretreatment desulfurization agent.

20 **[53]** When the pretreatment desulfurization agent in accordance with the present invention is mixed with a combustible material and combusted together in a temperature range from 400°C to 1200°C , the adsorption effect of sulfur oxides can be activated. However, when the mixture is combusted in a temperature range from 600°C to 900°C , high efficiency can be obtained.

[54] Hereinafter, a method of preparing the pretreatment desulfurization agent according to the present invention will be described.

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[55] The pretreatment desulfurization agent according to the present invention is prepared to include: (a) at least one oxide selected from the group consisting of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO ,

MnO, CaO, Na₂O, K₂O, and P₂O₃; (b) at least one metal selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb; and (c) at least one liquid composition selected from the group consisting of sodium tetraborate (Na₂B₄O₇·10H₂O), sodium hydroxide (NaOH), sodium silicate (Na₂SiO₃), and hydrogen peroxide (H₂O₂).

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[56] In step (a), a powder including at least one oxide selected from the group consisting of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, MgO, MnO, CaO, Na₂O, K₂O, and P₂O₃ is mixed and finely ground by a fine pulverizer.

10 **[57]** In this step, the oxide power includes 15 to 90 parts by weight of SiO₂, 15 to 100 parts by weight of Al₂O₃, 10 to 50 parts by weight of Fe₂O₃, 5 to 15 parts by weight of TiO₂, 20 to 150 parts by weight of MgO, 10 to 20 parts by weight of MnO, and 20 to 50 parts by weight of CaO, 15 to 45 parts by weight of Na₂O, 20 to 50 parts by weight of K₂O, and 5 to 20 parts by weight of P₂O₃.

15 **[58]** In addition, the finely ground oxide powder may be further pulverized repeatedly so that the particle size of the powder is in a range from 1 to 2 μm.

[59] In step (b), one or more metal powders selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd and Pb are mixed and pulverized by a fine pulverizer.

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[60] The metal powder may include 0.0035 to 0.009 parts by weight of Li, 0.005 to 0.01 parts by weight of Cr, 0.001 to 0.005 parts by weight of Co, 0.006 to 0.015 parts by weight of Ni, 0.018 to 0.03 parts by weight of Cu, 0.035 to 0.05 parts by weight of Zn, 0.04 to 0.08 parts by weight of Ga, 0.02 to 0.05 parts by weight of Sr, 0.002 to 0.01 parts by weight of Cd, and 0.003 to 0.005 parts by weight of Pb.

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[61] In addition, the finely ground metal powder may be ground repeatedly so that the particle size of the powder is in a range from 1 to 2 μm.

30 **[62]** In step (c), at least one liquid composition selected from the group consisting of sodium tetraborate (Na₂B₄O₇·10H₂O), sodium hydroxide (NaOH), sodium silicate (Na₂SiO₃), and hydrogen peroxide (H₂O₂) is mixed with the finely ground oxide powder and the finely ground metal powder

prepared in step (a) and step (b) to prepare a desulfurization catalyst.

[63] In this step, the sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) may be contained in an amount of 20 to 130 parts by weight, the sodium hydroxide (NaOH) may be contained in an amount of 15 to 120 parts by weight, the sodium silicate (Na_2SiO_3) may be contained in an amount of 50 to 250 parts by weight, and hydrogen peroxide (H_2O_2) may be contained in an amount of 10 to 50 parts by weight.

[64] In addition, in this step, when mixing and reacting with the mixed and finely ground oxide and metal powders prepared in steps (a) and (b), the oxide powder and the liquid composition act as a chelating agent so that a metal chelate compound can be formed.

[65] In addition, the pretreatment desulfurization agent formed in this step is stabilized by sedimentation for 24 to 72 hours, and the sedimented pretreatment desulfurization agent is separated and dried naturally to be used as a powder catalyst for desulfurization. The liquid composition remaining after the sedimented desulfurization agent is separated may be used as a liquid catalyst for desulfurization.

[66] In addition, in the desulfurization method using the pretreatment desulfurization agent according to the present invention, the desulfurization function may be activated when it is mixed and combusted with a combustible material.

[67] A conventional desulfurization method removes sulfur oxides (SO_x) from flue gas generated during combustion of a combustible material. The conventional method requires a desulfurization facility for performing the desulfurization process which increases manpower requirements and cost for operating the desulfurization facility. However, since the desulfurization method of the present invention burns the pretreatment desulfurization agent along with the combustible material, the pretreatment desulfurization agent removes sulfur oxides through adsorption during the combustion, thereby reducing the content of sulfur oxides in flue gas. In this way, the method of the present invention exhibits a desulfurization effect.

[68] In addition, the combustible material to which the pretreatment desulfurization agent in accordance with the present invention can be applied may be a combustible material that generates

heat through combustion. Examples of the combustible material include coal, petroleum, waste, and biogas.

[69] In addition, as described above, the pretreatment desulfurization agent is separated into a powder catalyst for desulfurization and a liquid catalyst for desulfurization. Each of the powder catalyst and the liquid catalyst is used alone or in combination with the other, depending on the contents of C, H, N, and S of the combustible material. Therefore, the pretreatment desulfurization agent of the present invention can exhibit an excellent desulfurization effect in a simple and easy way of use.

[70] Hereinafter, the configuration of a pretreatment desulfurization system according to one embodiment of the present invention, which is to be applied to a marine engine, will be described in detail with reference to FIG. 1.

[71] The pretreatment desulfurization system in accordance with the present invention is connected to a fuel supply line 30 of a marine engine 70 to supply the pretreatment desulfurization agent (liquid catalyst for desulfurization) in a certain mixing ratio with respect to fuel.

[72] Usually, as the fuel of the marine engine 70, marine fuel oil, for example, heavy oil such as bunker-A oil, bunker-B oil, and bunker-C oil or light oil such as MGO, MDO, or DDO is used. Among them, bunker-C oil has a high sulfur content and generates a large amount of sulfur oxide during combustion. Therefore, the use of bunker-C oil with high sulfur content is regulated due to air pollution.

[73] In FIG. 1, reference numerals 10, 20, 30, 40, 50, and 60 denote a fuel tank, a fuel supply pump, a fuel supply line, a fuel filter, an injection pump, and an injection nozzle, respectively. A detailed description of the components will be omitted.

[74] To this end, the pretreatment desulfurization system in accordance with the present invention is equipped with a pretreatment desulfurization agent tank 110 having a predetermined volume for storing the pretreatment desulfurization agent, and one end of the pretreatment desulfurization agent tank 110 is connected to a metering pump 130 for quantitatively supplying the pretreatment

desulfurization agent.

[75] In addition, a flow meter 130 for checking the input flow rate of the pretreatment desulfurization agent, a check valve 140 for adjusting the input flow rate, and a pressure gauge 150 are installed on the fuel supply line 30 between the metering pump 130 and the marine engine 70. Therefore, it is possible to continuously check the fuel supply amount to the marine engine 70 and regulate the supply of the pretreatment desulfurization agent so that the pretreatment desulfurization agent is supplied in a predetermined ratio with respect to the fuel supply amount.

[76] The pretreatment desulfurization agent is preferably supplied and mixed in an amount of 0.1% to 10% by weight relative to 100% by weight of the marine fuel oil.

[77] Referring to FIG. 2, the pretreatment desulfurization agent tank is connected to a line mixer 160 provided on the fuel supply line 30 for supplying the marine fuel oil, and the pretreatment desulfurization agent injected from one side and the marine fuel oil are sufficiently mixed in the line mixer 160 (this process is called line mixing). The sufficiently mixed fluid mixture of the marine fuel oil and the pretreatment desulfurization agent is supplied to the marine engine.

[78] Thereafter, the fluid mixture is combusted in the marine engine. Therefore, sulfur oxides generated during a combustion process are adsorbed and removed by the pretreatment desulfurization agent before being discharged to the outside.

[79] Through this process, even when high-sulfur marine fuel oil such as bunker-C oil is used as fuel, since sulfur oxides are almost perfectly removed during the combustion, it is possible to solve the air pollution problem caused by sulfur oxides.

[80] Hereinafter, the present invention will be described in more detail with reference to Examples and Test Examples.

[81] Examples and Test Examples presented herein are only for illustrative purposes and are not intended to limit the scope of the present invention.

[82] <Example> Preparation of Pretreatment Desulfurization Agent

[83] As oxides, SiO₂ 150kg, Al₂O₃ 150kg, Fe₂O₃ 100kg, TiO₂ 50kg, MgO 200kg, MnO 100kg, CaO 200kg, Na₂O 150kg, K₂O 200kg, and P₂O₃ 50kg were mixed and finely ground to form fine oxide powder.

[84] As metals, Li 35g, Cr 50g, Co 10g, Ni 60g, Cu 180g, Zn 350g, Ga 400g, Sr 200g, Cd 20g, and Pb 30g were mixed and finely ground to form fine metal powder.

[85] The fine oxide powder and the fine metal powder are repeatedly ground to have a particle size of 1 to 2 μm.

[86] 3000 kg of water was put into a reactor, the water was maintained at a temperature of 50°C to 60°C, and 50 kg of sodium tetraborate (Na₂B₄O₇·10H₂O) was added thereto. After stirring for 30 minutes, 100 kg of sodium hydroxide (NaOH) was added and stirred. Next, after 10 minutes, the fine oxide powder was added in units of 100 kg at intervals of 5 minutes and stirred for 2 hours or more. While stirring, the temperature was raised to 60°C to 80°C, and 100 kg of sodium silicate (Na₂SiO₃) was added. After stirring for 30 minutes, the fine metal powder was added in units of 20 g at intervals of 3 minutes and stirred. After stirring for 1 hour, 30 kg of hydrogen peroxide (H₂O₂) was added, stirred for another 30 minutes, and then naturally cooled for 1 hour.

[87] After cooling and stabilizing for 48 hours, the liquid composition and the sedimented powder composition are separated from each other.

[88] The sedimented powder composition was dried naturally and named as a powder catalyst for desulfurization (GTS-P).

[89] In addition, the liquid composition remaining after the sedimented powder composition was removed and moved to a separate container, which is named as a liquid catalyst for desulfurization (GTS-W).

[90] <Test Example 1> Test for Checking Reduction in Sulfur oxide in Marine Engine Exhaust Gas

[91] (1) Test Condition

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[92] In order to evaluate the desulfurization efficiency of the pretreatment desulfurization agent (liquid catalyst for desulfurization) prepared as described above, 3.5% and 6.0% by weight of the pretreatment desulfurization agent was supplied to a fuel supply line connected to a marine engine to be mixed with 100% by weight of fuel and burned. Next, a sulfur oxide reduction performance test was conducted to analyze and compare the concentration of sulfur oxides in exhaust gas.

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[93] The specifications of the marine engine used for the test are shown in Table 1 below.

[94] [Table 1] Specifications of engine for test

Maker	Yanmar
Model	4LOD
Horsepower (Hp)	200
Number of Cylinders	4 in-line
Combustion system	Direct injection
Aspiration	Natural aspirated
Dimensions (L x W x H, mm)	500 X 1550 X 1400
Cooling system	Direct water cooling
Marine gear	Mechanical
Fuel consumption rate	100mL/min

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[95] ○ Fuel used: Bunker-C oil

[96] ○ Operating conditions: no-load operation

[97] ○ Supply amount and method of pretreatment desulfurization agent: an amount of 3.5% by weight of the pretreatment desulfurization agent was supplied to the fuel supply line with a metering

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pump with respect to the fuel flow rate, and then and an amount of 6.0% by weight of the pretreatment desulfurization agent was supplied.

[98] ○ Exhaust gas analysis equipment: Germany VarioPlus Ind. MRU Emission Monitoring System

[99] ○ Exhaust gas analysis method: exhaust gas was sampled from an exhaust pipe connected to the engine and with an analysis equipment (standard oxygen concentration of 17%)

[100] * Since the oxygen concentration in the exhaust gas was maintained at 17% to 18% in the engine no-load operation condition, the reference oxygen concentration was set to 17% to prevent an excessive difference between the measured concentration and the corrected concentration that is based on the reference oxygen concentration.

[101] (2) Test Method and Procedures

[102] 1) Operate engine and maintain a normal state

[103] 2) Preheat exhaust gas analysis equipment and perform zero setting

[104] 3) Perform measurement in a condition in which no pretreatment desulfurization agent was injected (30 minutes)

[105] 4) Perform measurement in a condition in which 6.0% by weight of pretreatment desulfurization agent was injected (1 hour)

[106] 5) Repeat step 3) and step 4) once

[107] 6) Perform measurement in a condition in which no pretreatment desulfurization agent was injected (30 minutes)

[108] 7) Perform measurement in a condition in which 3.5% by weight of pretreatment

desulfurization agent was injected (1 hour)

[109] 8) Perform measurement in a condition in which no pretreatment desulfurization agent was injected (30 minutes)

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[110] 9) Perform measurement in a condition in which 6.0% by weight of pretreatment desulfurization agent was injected (1 hour)

[111] 10) Saving data and stop testing

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[112] [Table 2] Test Condition

Time	Test condition
11:21-11:54	Fuel oil
11:54-13:20	Pretreatment desulfurization agent 6.0% by weight
13:20-14:03	Fuel oil
14:03-15:06	Pretreatment desulfurization agent 6.0% by weight
15:06-15:46	Fuel oil
15:46-16:46	Pretreatment desulfurization agent 3.5% by weight
16:46-17:23	Fuel oil
17:23-18:25	Pretreatment desulfurization agent 6.0% by weight

[113] (3) Result of Analysis of Sulfur Oxide (SO₂) Concentration (in Terms of 17% Reference Oxygen Concentration)

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[114] FIG. 3 shows the analysis results of sulfur oxide (SO₂) concentration for the entire session of Test Example 1 performed according to the test conditions, methods, and procedures described above, and Table 3 shows concentration variation of SO₂ in each measurement session of FIG. 3 are summarized. (in terms of 17% of reference oxygen concentration)

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[115] [Table 3] SO₂ concentration for measurement session (in terms of 17% of reference oxygen concentration)

Measurement time	Test condition	SO ₂ concentration (ppm)	Note
11:35-12:00	Fuel oil	102.00	Average value
12:23-13:00	Pretreatment desulfurization agent 6.0% by weight	0.01	Average value
14:08	Fuel oil	100.0	Peak value
14:26-15:15	Pretreatment desulfurization agent 6.0% by weight	0.00	Average value
15:51	Fuel oil	95.2	Peak value
16:22-16:52	Pretreatment desulfurization agent 3.5% by weight	29.19	Average value
17:28	Fuel oil	94.5	Peak value
17:50-18:25	Pretreatment desulfurization agent 6.0% by weight	0.00	Average value

[116] Referring to FIG. 3 and Table 3, after 6.0% by weight and 3.5% by weight of the pretreatment desulfurization agent relative to 100% by weight of the fuel oil were sequentially injected into the fuel supply line, the concentration of SO₂ was measured for each case. That is, the test was performed with four measurement sessions.

[117] In a first measurement session, when only fuel oil was burned (measurement time: 11:35-12:00), the concentration of SO₂ in the exhaust gas was 102.00 ppm, but when 6.0% by weight of the pretreatment desulfurization agent was input (measurement time: 12:23-13:00), the concentration of SO₂ reduced to 0.01 ppm.

[118] In a second measurement session, when only fuel oil was burned (measurement time: 18:08), the concentration of SO₂ in the exhaust gas was 100.00 ppm, but when 6.0% by weight of the pretreatment desulfurization agent was added relative to 100% by weight of fuel oil (measurement time: 4:26-15:15), the concentration of SO₂ reduced to 0.00 ppm.

[119] In a third measurement session, when only fuel oil was burned (measurement time 15:51), the concentration of SO₂ in the exhaust gas was 95.2 ppm, but when 3.5% by weight of the pretreatment desulfurization agent was added relative to 100% by weight of fuel oil (measurement time 16:22-16:52), the concentration of SO₂ reduced to 29.19 ppm.

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[120] In a fourth measurement session, when only fuel oil was burned (measurement time 17:28), the concentration of SO₂ in the exhaust gas was 94.5 ppm, but when 6.0% by weight of the pretreatment desulfurization agent was added relative to 100% by weight of fuel oil (measurement time 17:50-18:25), the concentration of SO₂ reduced to 0.00 ppm.

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[121] The measurement results show that the SO₂ emissions are reduced when the mixing ratio of the pretreatment desulfurization agent is increased from 3.5% by weight to 6.0% by weight.

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[122] <Test Example 2> Test for Checking Reduction in Sulfur oxide in Marine Engine Exhaust Gas

[123] (1)Test Condition

[124] The same as in Text Example 1

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[125] (2) Test Method and Procedures

[126] The same as in Text Example 1

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[127] [Table 4] Test Condition

Time	Test condition
09:06-09:44	Fuel oil
09:44-10:54	Pretreatment desulfurization agent 3.5% by weight
10:54-11:10	Fuel oil
11:10-11:37	Engine stop
11:37-13:02	Fuel oil

12:02-13:08	Pretreatment desulfurization agent 6.0% by weight
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[128] (3) Result of Analysis of Sulfur Oxide (SO₂) Concentration (in Terms of 17% Reference Oxygen Concentration)

5 **[129]** FIG. 4 shows the analysis results of the sulfur oxide (SO₂) concentration for the entire session of Test Example 2 performed according to the test conditions, methods, and procedures described above, and Table 5 shows concentration variation of SO₂ in each measurement session of FIG. 3 are summarized. (In terms of a reference oxygen concentration of 17%)

10 **[130]** [Table 5] SO₂ concentration for each measurement session (in terms of the reference oxygen concentration of 17%)

Measurement time	Test condition	SO ₂ concentration (ppm)	Note
09:12-09:40	Fuel oil	96.43	Average value
10:18-10:51	Pretreatment desulfurization agent 3.5% by weight	29.54	Average value
11:55-12:44	Fuel oil	98.93	Average value
12:57-13:06	Pretreatment desulfurization agent 6.0% by weight	0.00	Average value

[131] Referring to FIG. 4 and Table 5, after 6.0% by weight and 3.5% by weight of the pretreatment desulfurization agent relative to 100% by weight of the fuel oil were injected into the fuel supply line, the concentration of SO₂ was measured for each case. That is, the test was performed with four measurement sessions.

[132] In a first measurement session, when only fuel oil was burned (measurement time: 09:12-09:40), the concentration of SO₂ in the exhaust gas was 96.43 ppm, but when 6.0% by weight of the pretreatment desulfurization agent was input (measurement time: 10:18-10:51), the concentration of

SO₂ reduced to 29.54 ppm.

[133] In a second measurement session, when only fuel oil was burned (measurement time: 11:55-12:44), the concentration of SO₂ in the exhaust gas was 98.93 ppm, but when 6.0% by weight of the pretreatment desulfurization agent was input (measurement time: 12:57-13:06), the concentration of

5 SO₂ reduced to 0.00 ppm.

[134] The measurement results show that the SO₂ emissions are reduced when the mixing ratio of the pretreatment desulfurization agent is increased from 3.5% by weight to 6.0% by weight.

10 **[135]** As can be seen from the results of Test Examples 1 and 2, when fuel and the pretreatment desulfurization agent were burned together, the SO₂ concentration in the exhaust gas was reduced by at least 69% and by 100% at a maximum compared to the case where only fuel is burned. In addition, when the pretreatment desulfurization agent increased from 3.5% by weight to 6.0% by weight, the reduction in the SO₂ emission increased.

15 **[136]** FIG. 5 is an exemplary view showing a configuration in which the pretreatment desulfurization control and monitoring system for a marine engine, of the present invention, is added to the configuration of FIG. 1.

20 **[137]** Looking at the configuration of the present invention with reference to FIG. 5, the present invention has a configuration in which multiple sensors 210, 220, 230, 240, 250 and a control panel 270 are added to the pretreatment desulfurization system of FIG. 1.

[138] The multiple sensors include: an RPM sensor 210 added to the marine engine 70 to detect the number of revolutions per minute (RPM) of the marine engine 70; a gas sensor 220 added to an exhaust port 80 of the marine engine 70 to detect the concentration of sulfur oxides contained in an exhaust gas; a fuel injection amount sensor 230 installed on a fuel supply line 30 between a fuel tank 10 and the marine engine 70 to detect an injection amount of fuel; a pretreatment desulfurization agent amount sensor 240 installed between a downstream supply pipe 30 installed downstream of the fuel injection amount sensor 230 and a pretreatment desulfurization agent tank 110 to detect an

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30 injection amount of a pretreatment desulfurization agent mixed with the fuel; and a water level sensor 250 added to the pretreatment desulfurization agent tank 110.

[139] In addition, the pretreatment desulfurization agent tank 110 is connected to a separately provided large-capacity reservoir tank 260. When the water level sensor 250 detects a lower water level than a predetermined level, the pretreatment desulfurization agent is automatically replenished from the reservoir tank 260.

[140] Pumps, flow meters, check valves, pressure gauges (not denoted by reference numerals), etc. may be appropriately installed between each of the reservoir tank 260, the pretreatment desulfurization agent tank 110, the fuel tank 10, and the fuel supply line 30 of the marine engine 70. A detailed description of the components will be omitted.

[141] In addition, the control panel 270 is connected to an administrator's mobile terminal 300 by a wireless communication scheme so that the administrator can remotely control and monitor the operation of the system of the present invention in real time using a mobile application (hereinafter referred to as "management app").

[142] On the other hand, looking at the operating relationship between the components of the system having the configuration described above, when fuel is injected into the marine engine 70 from the fuel tank 10, the marine engine 70 is driven to operate. Since the fuel injection amount sensor 230 is installed on the fuel supply line 30 between the fuel tank 10 and the marine engine 70, the control panel 270 receives information on the fuel injection amount from the fuel injection amount sensor 230.

[143] When the fuel injection amount is detected, the pretreatment desulfurization agent is mixed with the fuel in a predetermined mixing ratio relative to the fuel injection amount. The predetermined ratio may be within a range from 0.1% to 10% by weight compared to 100% by weight of the fuel as described above.

[144] Then, when the mixture of the fuel and the pretreatment desulfurization agent is supplied to the marine engine 70, the marine engine 70 is driven while the mixture is burned. Since the marine engine 70 is equipped with the RPM sensor 210, the control panel 270 continuously receives information on the RPM of the marine engine 70 from the RPM sensor 210. Since the gas sensor

220 is installed in the exhaust port of the marine engine 70, the concentration of sulfur oxides in the exhaust gas can be detected in real time.

[145] When a change (increase or decrease) in the RPM is detected by the RPM sensor 210, or a change (increase or decrease) in the concentration of sulfur oxides is detected by the gas sensor 220, the control panel 270 increases or decreases the mixing ratio of the pretreatment desulfurization agent to prevent an increase in the concentration of sulfur oxides in the exhaust gas.

[146] For example, the RPM of the marine engine 70 is increased or decreased, or the concentration of sulfur oxides in the exhaust gas is increased or decreased in a state in which the pretreatment desulfurization agent is supplied in a ratio of 6% by weight with respect to 100% by weight of the initial fuel, the injection amount of the pretreatment desulfurization agent is increased or decreased so that the mixing ratio of the pretreatment desulfurization agent with respect to the injection amount of the fuel is maintained at 6% by weight.

[147] It is preferable that the control of increasing or decreasing the mixing ratio of the pretreatment desulfurization agent is automatically performed according to a control value preset in the control panel 270. The history of detection of the changes, the control and monitoring history of the changes, etc. are transmitted to the administrator's mobile terminal 300 in real time so that the administrator can remotely control and monitor the system in real time.

[148] For example, the items that the administrator can remotely control and monitor through the management app of the mobile terminal 300 are exemplified below.

[149] 1. Monitoring of exhaust gas concentration (sulfur oxide, nitric oxide, carbon monoxide, oxygen, etc.)

[150] 2. Monitoring of fuel injection to the marine engine

[151] 3. Monitoring of residual amount of the pretreatment desulfurization agent

[152] 4. Controlling of the injection amount of the pretreatment desulfurization agent

[153] 5. Alarm function (for example, when the exhaust gas concentration exceeds a tolerable concentration)

5 **[154]** In addition, the present invention is not limited by the above-described embodiments. Since the same effect can be obtained even when the detailed configuration, the number of components, and arrangement of the components, those who are ordinarily skilled in the art will appreciate that various additions, deletions, and modifications to or from the embodiments are possible without departing from scope of the technical idea of the present invention.

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Industrial Applicability

[155] The present invention can be widely used in pretreatment desulfurization control and monitoring systems.

CLAIMS

1. A pretreatment desulfurization control and monitoring system for a pretreatment desulfurization system of a marine engine, characterized in that the pretreatment desulfurization control and monitoring system comprises:

a fuel injection amount sensor installed on a fuel supply line between a fuel tank and the marine engine, the fuel injection amount sensor configured to detect an injection amount of a marine fuel oil;

a pretreatment desulfurization agent amount sensor disposed between a pretreatment desulfurization agent tank and a downstream fuel supply line installed downstream of the fuel injection amount sensor, the pretreatment desulfurization agent amount sensor configured to detect an amount of pretreatment desulfurization agent mixed with the marine fuel oil;

an RPM sensor added to the marine engine and configured to detect the number of revolutions per minute (RPM) of the marine engine;

a gas sensor added to an exhaust port of the marine engine and configured to detect the concentration of sulfur oxides in an exhaust gas discharged from the marine engine;

a control panel connected to the sensors, an actuator for actuating a valve connected to the fuel tank and an actuator for actuating a valve connected to the pretreatment desulfurization agent tank, in a bi-directionally communicable manner;

wherein, the control panel, in response to detecting an increase or decrease in angular velocity of the marine engine detected by the RPM sensor or in response to detecting

an increase or decrease in the concentration of sulfur oxides in the exhaust gas of the marine engine by the gas sensor, is configured to increase or decrease the amount of the pretreatment desulfurization agent such that the pretreatment desulfurization agent is mixed with the marine fuel oil in an amount ranging from 0.1 to 10 parts by weight with respect to 100 parts by weight of the marine fuel oil.

2. The system according to claim 1, further comprising a water level sensor added to the pretreatment desulfurization agent tank and configured to detect a water level.

3. The system according to claim 2, wherein a large capacity reservoir tank for storing the pretreatment desulfurization agent for replenishment is connected to the pretreatment desulfurization agent tank, and the pretreatment desulfurization agent is automatically replenished from the reservoir tank to the pretreatment desulfurization agent tank when a water level lower than a predetermined water level is detected by the water level sensor.

4. The system according to claim 1, wherein the control panel is connected to an administrator's mobile terminal in a wirelessly communicable manner so that control and monitoring can be remotely preformed through a mobile application.

5. The system according to claim 1, wherein the pretreatment desulfurization agent comprises: (a) at least one oxide selected from the group consisting of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO , MnO , CaO , Na_2O , K_2O , and P_2O_3 ; (b) at least one metal selected from the group consisting of Li, Cr, Co, Ni, Cu, Zn, Ga, Sr, Cd, and Pb; and (c) at least one liquid composition selected from the group consisting of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$),

sodium hydroxide (NaOH), sodium silicate (Na₂SiO₃), and hydrogen peroxide (H₂O₂).

6. The system according to claim 5, as the oxide comprises 15 to 90 parts by weight of SiO₂, 15 to 100 parts by weight of Al₂O₃, 10 to 50 parts by weight of Fe₂O₃, 5 to 15 parts by weight of TiO₂, 20 to 150 parts by weight of MgO, 10 to 20 parts by weight of MnO, 20 to 200 parts by weight of CaO, 15 to 45 parts by weight of Na₂O, 20 to 50 parts by weight of K₂O, and 5 to 20 parts by weight of P₂O₃, and the metal comprises 0.0035 to 0.009 parts by weight of Li, 0.005 to 0.01 parts by weight of Cr, 0.001 to 0.005 parts by weight of Co, 0.006 to 0.015 parts by weight of Ni, 0.018 to 0.03 parts by weight of Cu, 0.035 to 0.05 parts by weight of Zn, 0.04 to 0.08 parts by weight of Ga, 0.02 to 0.05 parts by weight of Sr, 0.002 to 0.01 parts by weight of Cd and 0.003 to 0.005 parts by weight of Pb.
7. The system according to claim 5, wherein the oxide and metal have a particle size of 1 to 2 μm and a specific gravity of 2.5 to 3.0.
8. The system according to claim 5, wherein the sodium tetraborate (Na₂B₄O₇·10H₂O) is contained in an amount of 20 to 130 parts by weight, the sodium hydroxide (NaOH) is contained in an amount of 15 to 120 parts by weight, the sodium silicate (Na₂SiO₃) is contained in an amount of 50 to 250 parts by weight, and the hydrogen peroxide (H₂O₂) is contained in an amount of 10 to 50 parts by weight.
9. The system according to claim 5, wherein in the pretreatment desulfurization agent, the oxide, the metal and the liquid composition form a metal chelate compound.

10. The system according to claim 5, wherein an effect of adsorbing sulfur oxides (SO_x) by the pretreatment desulfurization agent is activated in a temperature range from 400°C to 1200°C.
- 5 11. The system according to claim 1, wherein the pretreatment desulfurization agent is mixed in an amount of 6 parts by weight with respect to 100 parts by weight of marine fuel oil.
12. The system according to claim 1, further comprising a line mixer disposed on the fuel supply line, wherein the pretreatment desulfurization agent is injected into marine fuel oil
10 in a state in which the pretreatment desulfurization agent tank is connected to the line mixer.
13. The system according to claim 1, wherein the marine fuel oil is heavy oil selected from among bunker-A oil, bunker-B oil, and bunker-C oil or light oil selected from among
15 MGO, MDO, and DDO.