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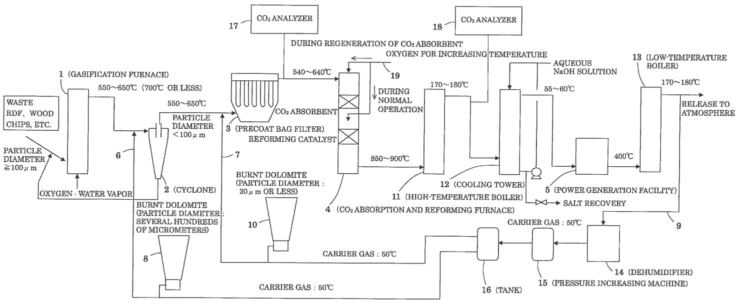
(54) METHOD FOR REMOVING ACID COMPONENTS AT HIGH TEMPERATURE IN GASIFICATION POWER GENERATION SYSTEM, AND DEVICE THEREFOR

(57) After a gasification step but before a cyclone treatment step, a cyclone upstream additive having desalination and desulfurization functions is supplied to a gasified gas using a gas coming out of a power generation step after recovering heat as an additive carrier gas, a CO_2 absorbent used in a CO_2 absorption and reforming step is allowed to absorb CO_2 in a gas temperature range of 450 to 700°C, and when the amount of absorbed CO_2 has reached saturation, the flow of oxygen or air for increasing the temperature of a reforming catalyst layer is switched immediately upstream of a CO_2 absorbent-filled layer, and the temperature of the absorbent-filled layer is increased within a temperature range of 800 to 950°C to separate CO_2 from the absorbent.

FIG. 1



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Description

Technical Field

[0001] The present invention relates to a method for achieving removal of acid components in a gasified gas at high temperature with a high removal rate in a system for performing power generation using a gas turbine or a gas engine by utilizing a combustible gas obtained by gasifying and reforming waste, and a device to be used for carrying out the method.

Background Art

[0002] Recently, measures to cope with global warming have been strongly demanded, and also in power generation utilizing waste, improvement of power generation efficiency by increasing the steam temperature in garbage incineration power generation (BTG power generation) and a system for performing power generation using a gas turbine or a gas engine by utilizing a combustible gas obtained by gasifying and reforming waste are being studied.

[0003] In such a power generation system, gasification of waste containing incombustible materials or various types of metals, particularly, metallic aluminum is performed generally at 700°C or lower, usually at about 500 to 650°C. In a gasified gas, an unburned char or tar component is reformed into a combustible gas by water vapor in a reforming furnace. A reforming reaction is performed at about 1000 to 1200°C when the reaction is performed in the absence of a catalyst, and at about 800 to 1000°C when a catalyst is used.

[0004] For example, in PTL 1, a gasification power generation system composed of a gasification furnace, a high-temperature dust collection facility, a tar cracking facility, a refining facility, and the like is described. In this gasification power generation system, a gas at 800 to 900°C generated in the gasification furnace is subjected to dust removal by the high-temperature dust collection facility provided with a ceramic filter or the like, and thereafter fed to the tar cracking facility provided with a cracking catalyst for a tar component or the like.

[0005] In a gas obtained by gasification of waste, other than unburned char or tar, a combustible gas such as H_2, CH_4, or CO, CO_2 or dust, HCl or SO_2 or SO_3 gas derived from a halogen or S contained in the waste, etc. are contained.

[0006] When a reforming reaction is performed using a catalyst, a nickel-based or a noble metal-based reforming catalyst is used, however, the reforming catalyst is poisoned by HCl or SO_2 or SO_3 gas, or the like contained in the gasified gas. In order to prevent such poisoning of the reforming catalyst, it is necessary to remove a poisoning gas component upstream of the reforming furnace. However, in the high-temperature dust collection facility described in PTL 1, only dust removal is performed and desalination and desulfurization are not performed, and therefore, there was a fear that the performance of the cracking catalyst for a tar component or the like is deteriorated.

[0007] Conventionally, as a desalination and desulfurization technique such as a garbage incineration system that applies a dry method, a technique in which a powder agent such as hydrated lime ($Ca(OH)_2$) or sodium bicarbonate ($NaHCO_3$) is blown into an exhaust gas stream, and a reaction product in a solid form is removed using a bag filter has been known. This technique is applied to an exhaust gas temperature range of 150 to 200°C, and as the temperature is lower, the removal efficiency is higher. In addition, a technique for refining a pyrolysis gas by applying such a technique has been disclosed (PTL 2). In one technique disclosed in PTL 2, refining of a pyrolysis gas is performed using a bag filter for dust removal and a second bag filter for desalination. The pyrolysis gas having been subjected to dust removal is mixed with an alkaline agent such as hydrated lime, calcium oxide (CaO), calcium carbonate, sodium bicarbonate, or sodium carbonate (Na_2CO_3) upstream of the second bag filter, thereby removing HCl as a solid reaction product with the second bag filter, and it is applied at 300 to 600°C which is close to a pyrolysis temperature range. However, in this temperature range, HCl competes with carbonate gas, and the agent in a large amount is required for obtaining a high HCl removal rate. Further, the bag filter for dust removal does not perform desalination and desulfurization, and therefore, there was a fear that refining of the pyrolysis gas is insufficient.

[0008] Further, a sodium aluminate ($NaAlO_2$) -based halide absorbent produced by drying a mixture of sodium carbonate and an alumina sol, followed by pulverization and firing is disclosed (PTL 3). The particle diameter of this halide absorbent is 250 to 500 μm, and in PTL 3, by using a fixed bed flow-type reactor, halide removal performance is evaluated at 400°C. However, when the fixed bed flow-type reactor is placed in a flue of a pyrolysis gas of waste, and dry desalination and desulfurization are performed in a temperature range lower than 500°C, a tar component is adhered to dust or char, which is fixed to the halide absorbent in the fixed bed flow-type reactor to increase the pressure loss due to clogging, and therefore, a stable operation cannot be performed. For example, it has been reported that in a filtration test using polystyrene as an oil component (tar component), polystyrene is adhered to a filter, and that when polystyrene adhered to the filter is subjected to a heating treatment at a temperature of 500°C or higher, the oil component is removed, and the pressure loss is returned to the original value (NPL 1).

Relevant References

Patent Literature

[0009]

PTL 1: JP-A-2006-037012
PTL 2: JP-A-2002-130628
PTL 3: Japanese Patent No. 3571219

Non Patent Literature

[0010] NPL 1: Shoichi Ogawa, et al., "Collection of Hydrocarbon Components of Pyrolysis Gas of Polystyrene by Ceramic Filters and Regeneration Properties" , Journal of the Society of Powder Technology, Japan, Vol. 40, No. 11, pp. 19-25, 2003

Summary of Invention

Technical Problem to be solved

[0011] In order to solve the above-mentioned problem of the related art, an object of the present invention is to provide a method for removing acid components at high temperature in a gasification power generation system, which can achieve high desalination and desulfurization performance in a high temperature range, and does not cause an increase in pressure loss due to adhesion of a tar component to dust or char resulting in clogging of a device, and a device for the method.

Solution to Problem

[0012] The present invention has been made for achieving the above object and includes the following aspects.

(1) A method for removing acid components at high temperature in a gasification power generation method, characterized in that in a gasification power generation system including a gasification step of performing partial combustion gasification of a gasification material, a cyclone treatment step of performing a coarse powder collection treatment of a gasified gas coming out of the gasification step, a bag filter treatment step of performing a dust removal treatment of the gasified gas having been subjected to coarse powder removal coming out of the cyclone treatment step, a CO_2 absorption and reforming step of performing a CO_2 absorption and reforming treatment of the gasified gas having been subjected to dust removal coming out of the bag filter treatment step, and a power generation step of performing power generation by utilizing a reformed gas coming out of the CO_2 absorption and reforming step,
after the gasification step but before the cyclone treatment step, a cyclone upstream additive having desalination and desulfurization functions is supplied to the gasified gas using a gas coming out of the power generation step after recovering heat as an additive carrier gas, and
a CO_2 absorbent used in the CO_2 absorption and reforming step is allowed to absorb CO_2 in a gas temperature range of 450 to 700°C, preferably in a temperature range of 540 to 640°C and when the amount of absorbed CO_2 has reached saturation, the flow of oxygen or air for increasing the temperature of a reforming catalyst layer is switched immediately upstream of a CO_2 absorbent-filled layer, and the temperature of the absorbent-filled layer is increased within a temperature range of 800 to 950°C, preferably 850 to 900°C to separate CO_2 from the absorbent.
(2) The method for removing acid components at high temperature in a gasification power generation method according to the above (1), wherein the cyclone upstream additive also has CO_2 absorption and removal functions.
(3) The method for removing acid components at high temperature in a gasification power generation method according to the above (1) or (2), characterized in that the cyclone upstream additive has an average particle diameter of 100 to 1000 μm.
(4) The method for removing acid components at high temperature in a gasification power generation method according to any one of the above (1) to (3), characterized in that the cyclone upstream additive is selected from the group consisting of burnt dolomite, hydrated lime, sodium aluminate, and sodium bicarbonate.
(5) The method for removing acid components at high temperature in a gasification power generation method according to any one of (1) to (4), characterized in that after the cyclone treatment step but before the bag filter treatment step, an additive which is a cyclone downstream additive that has desalination and desulfurization functions

and may be the same as or different from the cyclone upstream additive and is selected from the group consisting of burnt dolomite, hydrated lime, sodium aluminate, and sodium bicarbonate is supplied to the gasified gas having been subjected to coarse powder removal using a gas coming out of the power generation step after recovering heat as an additive carrier gas.

(6) The method for removing acid components at high temperature in a gasification power generation method according to any one of (1) to (5), characterized in that in the cyclone treatment step, a coarse powder containing the additive is collected, and the collected coarse powder is supplied to the gasification step together with the gasification material.

(7) The method for removing acid components at high temperature in a gasification power generation method according to any one of (1) to (6), characterized in that the CO_2 absorbent used in the CO_2 absorption and reforming step is selected from the group consisting of CaO, $Ca(OH)_2$, and burnt dolomite.

(8) The method for removing acid components at high temperature in a gasification power generation method according to any one of (1) to (7), characterized in that after the heat recovery treatment, the reformed gas is subjected to a CO_2 absorption treatment using an aqueous NaOH solution, and generated Na_2CO_3 is recovered and removed.

(9) A device for removing acid components at high temperature in a gasification power generation system, characterized in that in a gasification power generation system including a gasification furnace that performs partial combustion gasification of a gasification material, a cyclone that is placed downstream of the gasification furnace and performs a coarse powder collection treatment of a gasified gas coming out of the furnace, a bag filter that is placed downstream of the cyclone and performs a dust removal treatment of the gasified gas having been subjected to coarse powder removal coming out of the cyclone, a CO_2 absorption and reforming furnace that is placed downstream of the bag filter and performs a CO_2 absorption and reforming treatment of the gasified gas having been subjected to dust removal coming out of the bag filter, and a power generation facility that is placed downstream of the CO_2 absorption and reforming furnace and performs power generation by utilizing a reformed gas coming out of the furnace,

a cyclone upstream additive supply line for supplying an additive having desalination and desulfurization functions to a flow path to the cyclone from the gasification furnace is provided, a carrier gas line coming from the power generation facility is connected to the supply line, and an oxygen or air supply line for switching oxygen or air for increasing the temperature of the reforming furnace to a CO_2 absorbent-filled layer when the amount of absorbed CO_2 has reached saturation is connected immediately upstream of the CO_2 absorbent-filled layer of the CO_2 absorption and reforming furnace.

(10) The device for removing acid components at high temperature in a gasification power generation system according to the above (9), characterized in that

a cyclone downstream additive supply line for supplying an additive having desalination and desulfurization functions to a flow path to the bag filter from the cyclone is provided, and a carrier gas line coming from the power generation facility is connected to the supply line.

[0013] The average particle diameter of particles is a value measured by a laser diffraction particle size distribution analyzer.

[0014] A gas obtained by partial combustion gasification of a gasification material is referred to as "gasified gas" throughout this description and claims.

Advantageous Effects of Invention

[0015] According to the present invention, by supplying a cyclone upstream additive having desalination and desulfurization functions to the gasified gas before the cyclone treatment step, and further by supplying a cyclone downstream additive having desalination and desulfurization functions to the gasified gas before the bag filter treatment step, high desalination and desulfurization performance for the gasified gas in a high temperature range of 450 to 700°C can be achieved, and poisoning of the reforming catalyst can be prevented.

[0016] Further, by using the additives as described above, a problem of causing an increase in pressure loss due to adhesion of a tar component to dust or char resulting in clogging of a device can be prevented.

[0017] In addition, by allowing a CO_2 absorbent used in the CO_2 absorption and reforming step to absorb CO_2 in a gas temperature range of 450 to 700°C, switching the flow of oxygen or air for increasing the temperature of the reforming catalyst layer immediately upstream of the CO_2 absorbent-filled layer when the amount of absorbed CO_2 has reached saturation, and increasing the temperature of the absorbent-filled layer within a temperature range of 800 to 900°C to separate CO_2 from the absorbent, CO_2 in the gasified gas can be efficiently and persistently removed.

Brief Description of Drawings

[0018]

FIG. 1 is a flow diagram of a gasification power generation system showing an embodiment of the present invention.

FIG. 2 shows graphs and tables showing relationships between desalination and desulfurization agents and desalination and desulfurization performance.

FIG. 3-1 is a graph showing relationships between various types of desalination and desulfurization agents and desalination and desulfurization performance (temperature: 550°C).

FIG. 3-2 is a graph showing relationships between various types of desalination and desulfurization agents and desalination and desulfurization performance (temperature: 600°C) .

FIG. 3-3 is a graph showing relationships between various types of desalination and desulfurization agents and desalination and desulfurization performance (temperature: 650°C) .

Description of Embodiments

[0019] An embodiment of the present invention will be shown with reference to the accompanying drawings. However, this does not limit the present invention.

[0020] First, a gasification power generation system will be described according to FIG. 1.

[0021] The gasification power generation system includes a gasification furnace 1 that performs partial combustion gasification of a gasification material, a bag filter 3 that is placed downstream of the gasification furnace 1 and removes dust from the gasified gas coming out of the furnace, a CO_2 absorption and reforming furnace 4 that is placed downstream of the bag filter 3 and performs a reforming treatment of the gas having been subjected to dust removal, and a power generation facility 5 that is placed downstream of the CO_2 absorption and reforming furnace 4 and performs power generation by utilizing a reformed gas coming out of the furnace.

[0022] In a flow path from the gasification furnace 1 to the bag filter 3, a cyclone 2 is placed, and to a flow path upstream of the cyclone 2, a cyclone upstream additive supply line 6 for supplying an additive having desalination and desulfurization functions and preferably further having a CO_2 removal function from an additive container 8 is connected. Further, a cyclone downstream additive supply line 7 for supplying an additive having desalination and desulfurization functions and preferably further having a CO_2 removal function from an additive tank 10 to a flow path from the cyclone 2 to the bag filter 3 is provided.

[0023] To each of the starting end portions of the cyclone upstream additive supply line 6 and the cyclone downstream additive supply line 7, a carrier gas line 9 is connected from the power generation facility 5 via a low-temperature boiler 13, a dehumidifier 14, a pressure increasing machine 15, and a tank 16.

[0024] To immediately upstream of a CO_2 absorbent-filled layer of the CO_2 absorption and reforming furnace 4, an oxygen or air supply line 19 for switching the flow of oxygen or air for increasing the temperature of a reforming furnace to the CO_2 absorbent-filled layer when the amount of absorbed CO_2 has reached saturation is connected. This line 19 generally supplies oxygen or air for increasing the temperature immediately upstream of a catalyst-filled layer of the CO_2 absorption and reforming furnace 4.

[0025] Next, a method for removing acid components at high temperature in a gasification power generation method according to the present invention will be specifically described for each step with reference to the flow diagram of FIG. 1.

Gasification Step

[0026] A gasification material such as waste, RDF, or a wood chip is subjected to partial combustion gasification in the gasification furnace 1. To the gasification furnace 1, oxygen and water vapor are supplied from the bottom of the furnace.

Cyclone Treatment Step

[0027] The gasified gas coming out of the top of the gasification furnace 1 is sent to the cyclone 2, and particles in the gasified gas are separated into a coarse powder having an average particle diameter of 100 μm or more and a fine powder having an average particle diameter less than 100 μm. The temperature of the gas coming into the cyclone 2 is 700°C or lower, preferably 550 to 650°C, and the temperature of the gas coming out of the cyclone 2 is 550 to 650°C.

[0028] An additive having desalination and desulfurization functions is blown into the flow path upstream of the cyclone 2 from the cyclone upstream additive supply line 6. This additive preferably also has CO_2 absorption and removal functions in addition to the desalination and desulfurization functions. This is a material that can be converted into a chloride or a sulfate at 700°C or lower, and is preferably selected from the group consisting of burnt dolomite, hydrated lime, sodium aluminate, and sodium bicarbonate. The average particle diameter of the additive is preferably from 100 to 1000 μm, more preferably from 300 to 600 μm. Burnt dolomite is preferred from the viewpoint of cost, and sodium aluminate is preferred from the viewpoint of desalination and desulfurization rates. In this embodiment, burnt dolomite having an average particle diameter of several hundreds of micrometers was supplied upstream of the cyclone from the additive container 8 through the line 6.

[0029] By blowing the additive having desalination and desulfurization functions preferably also having CO_2 absorption and removal functions into the flow path upstream of the cyclone 2, the gasified gas is subjected to a desalination and desulfurization treatment and preferably can be subjected to a decarbonation treatment, and also a self-cleaning action of dust or tar adhered to the inside of the cyclone 2 can be performed, and the pressure loss in the bag filter downstream is suppressed, and the operation thereof can be carried out without any troubles. By the cyclone, all or part of the coarse powder additive having an average particle diameter of 100 to 1000 μm, dust, and tar are recovered in a bottom portion, and this recovered material is supplied to the gasification furnace 1 together with the gasification material. By doing this, reforming of tar in the CO_2 absorption and reforming furnace 4 downstream can be complemented.

Bag Filter Treatment Step

[0030] Subsequently, the gasified gas having been subjected to coarse powder removal coming out of the cyclone 2 is sent to the bag filter 3 that performs a dust removal treatment of the gas. The gasified gas having been subjected to coarse powder removal contains particles having an average particle diameter less than 100 μm.

[0031] An additive having desalination and desulfurization functions is blown into the flow path to the bag filter 3 from the cyclone 2 through the cyclone downstream additive supply line 7. This additive preferably also has CO_2 absorption and removal functions in addition to the desalination and desulfurization functions. This additive is a material that can be converted into a chloride or a sulfate at 700°C or lower, and is preferably selected from the group consisting of burnt dolomite, hydrated lime, sodium aluminate, and sodium bicarbonate. The average particle diameter of the additive is preferably 20 μm or less, more preferably 15 μm or less. Burnt dolomite is preferred from the viewpoint of cost, and sodium aluminate is preferred from the viewpoint of desalination and desulfurization rates. The cyclone downstream additive and the cyclone upstream additive may be of the same type or different type. In this embodiment, burnt dolomite having an average particle diameter of 20 μm or less was supplied downstream of the cyclone from the additive tank 10 through the cyclone downstream additive supply line 7.

[0032] By blowing the additive having desalination and desulfurization functions preferably also having CO_2 absorption and removal functions into the flow path downstream of the cyclone 2, the gasified gas having been subjected to coarse powder removal is subjected to a desalination and desulfurization treatment and preferably can be subjected to a decarbonation treatment. In particular, by the desalination and desulfurization treatment, the service life of a Ni-based reforming catalyst that is commonly used in the CO_2 absorption and reforming furnace 4 downstream can be extended.

[0033] The average particle diameter of the additive is preferably 20 μm or less so as to enhance the effect of desalination and desulfurization. A known filter aid can also be used in combination with the cyclone downstream additive.

[0034] The average particle diameter of particles is a value measured by a laser diffraction particle size distribution analyzer.

[0035] In this embodiment, as the bag filter 3, a precoat bag filter is used for preventing adhesion of dust containing a tar component to a filter cloth and enhancing the peelability of a cake layer on the surface of the filter cloth. The temperature of the gas coming into the precoat bag filter is 550 to 650°C, and the temperature of the gas coming out of the bag filter is decreased to about 540 to 640°C due to heat dissipation or the like. When the pressure loss in the precoat bag filter is increased, the cake layer on the surface of the filter cloth is wiped off by a pulse jet system, and thereafter, the cyclone downstream additive or a material using a filter aid in combination with the additive is precoated on the surface of the filter cloth in a short time. The pressure loss during precoating is targeted at 0.5 to 0.6 kPa. The wiping off of the cake layer on the surface of the filter cloth is performed when the pressure loss is preferably within a range of 1.5 to 1.8 kPa (153.0 to 183.5 mmH_2O).

[0036] As for the amount of the precoat, an amount of 3 equivalents to the amount of $HCl+SO_2$ in the gas is blown into for about 20 minutes. As a guide, one cycle is determined to be about 3.5 hours which is the sum of a time required for precoating and a steady operation time. The wiping off by the pulse jet is preferably performed by control of the pressure loss of the bag.

CO_2 Absorption and Reforming Step

[0037] The gasified gas is sent to the CO_2 absorption and reforming furnace 4 after being subjected to dust removal by the bag filter 3. A CO_2 absorbent is filled in an upper portion of the CO_2 absorption and reforming furnace 4, and a reforming catalyst is filled in a lower portion thereof. As the CO_2 absorbent, a compound which is carbonated by CO_2 absorption in a temperature range of 450 to 700°C, preferably 540 to 640°C and causes decarbonation, that is, CO_2

separation in a temperature range of 800 to 950°C, preferably 850 to 900°C is used. Examples of the CO_2 absorbent include CaO, $Ca(OH)_2$, and burnt dolomite (CaO·MgO), and in this embodiment, CaO was used as the CO_2 absorbent.

[0038] The CO_2 separation from the CO_2 absorbent by switching of the flow path of the oxygen or air supply line 19 will be described.

1) The temperature range of the gasified gas during normal CO_2 absorption operation is 450 to 700°C, preferably 540 to 640°C, and the temperature of the CO_2 absorbent is also maintained in this temperature range. When CaO is used as the CO_2 absorbent, CO_2 is absorbed or removed by the absorbent according to the following reaction.

$$CaO + CO_2 \rightarrow CaCO_3$$

In this manner, by removing CO_2 in the gasified gas, the following shift reaction is likely to proceed to the right-hand side.

$$CO + H_2O \rightarrow CO_2 + H_2$$

In this state, oxygen or air for increasing the temperature is supplied immediately upstream of the reforming catalyst layer by the normal flow path of the oxygen or air supply line 19.

2) When the amount of absorbed CO_2 has reached saturation, oxygen or air used for increasing the temperature of the catalyst-filled layer during normal operation is supplied immediately upstream of the CO_2 absorbent-filled layer by switching the flow path of the oxygen or air supply line 19, and the temperature of the absorbent is increased within a temperature range of 800 to 950°C, preferably 850 to 900°C. In this temperature range, a carbonated material of the CO_2 absorbent is thermally decomposed and CO_2 is separated from the absorbent.

[0039] An increase in temperature due to injection of oxygen or air in the CO_2 absorption and reforming furnace 4 is caused by oxidation reaction heat of a tar component, H_2, CO, or CH_4.

[0040] When the amount of absorbed CO_2 of the CO_2 absorbent has reached saturation, the value of a downstream CO_2 analyzer 18 which is provided downstream of a high-temperature boiler 11 and shows a CO_2 concentration in the gasified gas starts to increase, and therefore, as described above, oxygen or air used for increasing the temperature is supplied immediately upstream of the CO_2 absorbent-filled layer. When the temperature of the absorbent is increased within a temperature range of 800 to 950°C, preferably 850 to 900°C, $CaCO_3$ starts to be decomposed, and generated CO_2 flows downstream. At that time, the concentration of CO_2 in the gasified gas is temporarily increased, and therefore, the shift reaction is not accelerated. When the CO_2 concentrations shown by each of an upstream CO_2 analyzer 17 which is provided upstream of the CO_2 absorption and reforming furnace 4 and shows a CO_2 concentration in the gasified gas and the downstream CO_2 analyzer 18 come close to each other, the flow of oxygen or air for increasing the temperature is returned immediately upstream of the reforming catalyst layer, and the temperature of the catalyst-filled layer is decreased to a range of 450 to 700°C, preferably 540 to 640°C.

[0041] Thereafter, the operations of 1) and 2) described above are repeated.

[0042] By removing CO_2 with the CO_2 absorbent-filled layer, the following shift reaction in the reforming catalyst-filled layer can be accelerated.

[0043] When assuming toluene as a representative example of tar, main reactions occurring in the CO_2 absorption and reforming furnace 4 are as follows.

i)

$$C_7H_8 + 9\ O_2 \rightarrow 7\ CO_2 + 4\ H_2O$$

oxidation reaction

ii)

$$C_7H_8 + 7\ H_2O \rightarrow 7\ CO + 11\ H_2$$

reforming reaction

iii)

$$CO + H_2O \rightarrow CO_2 + H_2$$

shift reaction

iv) Other than these, when oxygen is present excessively, an oxidation reaction of H_2, CO, CH_4, or the like also occurs.

Cooling Tower Treatment

[0044] A high temperature gas at 850 to 900°C coming out of a bottom portion of the CO_2 absorption and reforming furnace 4 is sent to the high-temperature boiler 11 and subjected to a heat recovery treatment there, and thereafter sent to a cooling tower 12 at a temperature of 170 to 180°C. In the cooling tower 12, an aqueous NaOH solution is circulated, and by this, CO_2 in the gasified gas is absorbed and a generated Na_2CO_3 salt is recovered and removed. Accordingly, a greenhouse gas is not discharged.

Power Generation Step

[0045] A low temperature gas at a temperature of 55 to 60°C coming out of the cooling tower 12 is sent to the power generation facility 5 provided with a gas turbine or a gas engine and utilized for power generation there.

Carrier Gas

[0046] The gas discharged from the power generation facility 5 at a temperature of 400°C is subjected to a heat recovery treatment by the low-temperature boiler 13, and thereafter partially released to the atmosphere at 170 to 180°C and the remainder is sent to each of the starting end portions of the cyclone upstream additive supply line 6 and the cyclone downstream additive supply line 7 via the dehumidifier 14, the pressure increasing machine 15, and the tank 16 through the carrier gas line 9, and utilized as a carrier gas (gas temperature of 50°C) for the cyclone upstream additive and the cyclone downstream additive. The oxygen concentration in this gas is about 1 to 2 vol%, and the injection ratio of the carrier gas to an outlet gas of the gasification furnace is 1/15 to 1/30, and therefore, a decrease in lower heating value (LHV) due to combustion of a combustible gas is not caused.

Experimental Examples

[0047] Next, experimental examples of the present invention will be shown.

[0048] Experiments were performed by changing respective conditions in the system shown in FIG. 1 that performs power generation utilizing a combustible gas obtained by gasification and reforming of waste. One example of a composition of the outlet gas of the gasification furnace 1 is shown in Table 1, the temperatures of the gasification furnace 1 and the CO_2 absorption and reforming furnace 4 and the air ratio to each outlet gas are shown in Table 2, relationships between desalination and desulfurization agents and desalination and desulfurization performance are shown in FIG. 2, the air ratio to the outlet gas of the power generation facility 5 is shown in Table 3, relationships between various kinds of desalination and desulfurization agents and desalination and desulfurization performance are shown in Table 4 and FIG. 3, and results of thermodynamic equilibrium calculation for generation and decomposition of calcium carbonate ($CaO + CO_2 \leftrightarrow CaCO_3$) are shown in Table 5.

[0049] According to Table 5, in the CO_2 absorption tower, 96.98% CO_2 is absorbed and removed at 600°C with inlet CO_2 at 8.1% according to the equilibrium calculation (at 650°C, 89.37%). Further, when the temperature of the absorption tower is increased to 850°C, decomposition occurs until the outlet CO_2 concentration becomes 38.59% (at 900°C, decomposition occurs until the outlet CO_2 concentration becomes 79.48%).

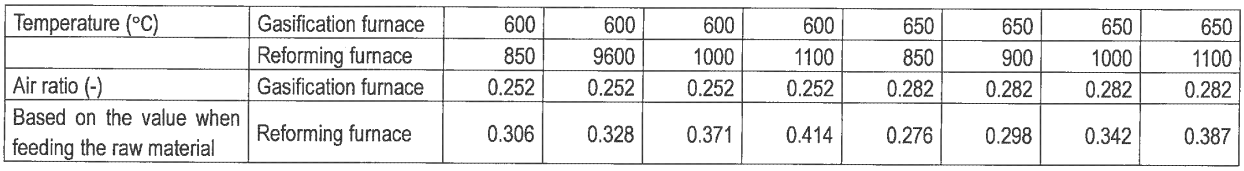
[Table 1]

Composition of exhaust gas from outlet of gasification furnace (one example)		
N_2	vol%-wet	39.8
O_2	vol%-wet	1
H_2	vol%-wet	0.8
H_2O	vol%-wet	44.5
CO_2	vol%-wet	8.1
CO	vol%-wet	2.8
CH4	vol%-wet	0.5
Other H.C	vol%-wet	0.9

(continued)

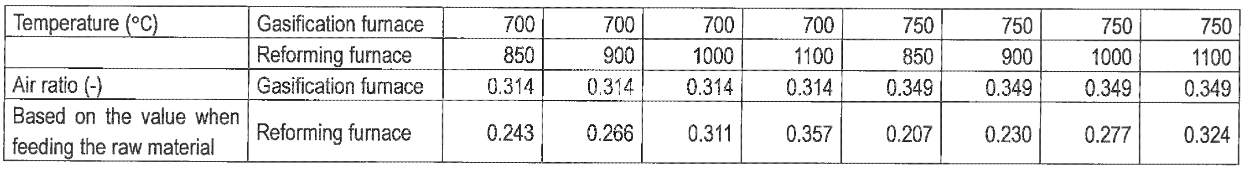
Composition of exhaust gas from outlet of gasification furnace (one example)		
HCl	ppm-wet	3.4
SO_2	ppm-wet	13.5
H_2S	ppm-wet	0.1
Total	vol%-wet	98.40

[Table 2]



Temperature (°C)	Gasification furnace	600	600	600	600	650	650	650	650
	Reforming furnace	850	9600	1000	1100	850	900	1000	1100
Air ratio (-)	Gasification furnace	0.252	0.252	0.252	0.252	0.282	0.282	0.282	0.282
Based on the value when feeding the raw material	Reforming furnace	0.306	0.328	0.371	0.414	0.276	0.298	0.342	0.387

The air ratio in the CO_2 absorption tower is assumed.



Temperature (°C)	Gasification furnace	700	700	700	700	750	750	750	750
	Reforming furnace	850	900	1000	1100	850	900	1000	1100
Air ratio (-)	Gasification furnace	0.314	0.314	0.314	0.314	0.349	0.349	0.349	0.349
Based on the value when feeding the raw material	Reforming furnace	0.243	0.266	0.311	0.357	0.207	0.230	0.277	0.324

[Table 3]

GE outlet gas vs. GE air ratio								
GE air ratio	1.1		1.2		1.3		1.4	
	Nm^3/h	vol%	Nm^3/h	vol%	Nm^3/h	vol%	Nm^3/h	vol%
CO_2	17565	13.96	17565	13.48	17565	13.04	17565	12.64
O_2	1135	0.90	2064	1.58	2994	2.22	3924	2.82
N_2	81106	64.44	84604	64.94	88103	65.40	91601	65.83
H_2O	26054	20.70	26054	20.00	26054	19.34	26054	18.72
Total gas	125860	100	130288	100	134717	100	139145	100

[Table 4]

Desalination and desulfurization agent		Desalination and desulfurization performance (reaction equivalent ratio = 2.0)					
		550°C		600°C		650°C	
Name	Chemical formula	Desalination rate (%)	Desulfurization rate (%)	Desalination rate (%)	Desulfurization rate (%)	Desalination rate (%)	Desulfurization rate (%)
sodium bicarbonate	$NaHCO_3$	80	61	69	63	62	69
hydrated lime	$Ca(OH)_2$	-	-	-	-	37	57
lime	$CaCO_3$	-	-	-	-	27	56
dolomite	$CaCO_3 \cdot MgCO_3$	-	-	-	-	47	77
light burnt dolomite	$CaCO_3 \cdot MgO$	-	-	-	-	47	77
sodium aluminate	$NaAlO_2$	-	-	-	-	64	78
3.2-8.5 $NaAlO_2$-supporting γ-alumina	3.2-8.5 $NaAlO_2/\gamma$-Al_2O_3	-	-	-	-	79	92
40% $NaAlO_2$-supporting γ-alumina	40% $NaAlO_2/\gamma$-Al_2O_3	-	-	-	-	89	93

[Table 5]

CaCO3⇒CaO+CO2

t	T	μ0(kJ/mol)			⊿μ0	Kp	CO2	oval ratio in absorpti	
(℃)	(K)	CaO	CO2	CaCO3	(kJ/mol)	Kp=P_{CO2}	(%)	(inlet CO2=8.1%)	
25	298	-646.482	-457.264	-1236.1	132.353	6.3066E-24			
27	300	-646.553	-457.66	-1236.27	132.059	1.0131E-23			
127	400	-651.063	-479.65	-1246.95	116.239	6.6099E-16			
227	500	-656.747	-502.731	-1260.06	100.583	3.103E-11			
327	600	-663.418	-526.763	-1275.28	85.096	3.9036E-08	3.9E-06	99.99995181	
427	700	-670.934	-551.625	-1292.34	69.78	6.2053E-06	0.000621	99.9923391	
450	723	-672.73	-557.445	-1295.87	65.69	1.7944E-05	0.001794	99.97784699	
527	800	-679.19	-577.219	-1311.04	54.632	0.00027087	0.027087	99.66558744	
600	873	-684.79	-595.59	-1324.02	43.64	0.00244778	0.244778	96.97805185	96.98% CO2 is absorbed and removed at 600·C according to the equilibrium calculation.
627	900	-688.102	-603.469	-1331.22	39.649	0.00499745	0.499745	93.83030318	93.83% CO2 is absorbed and removed at 627·C according to the equilibrium calculation.
650	923	-689.11	-608.605	-1334.21	36.49	0.00860745	0.860745	89.37351921	89.37% CO2 is absorbed and removed at 650·C according to the equilibrium calculation.
675	948	-691.326	-615.169	-1339.45	32.9525	0.01528471	1.528471	81.1299863	
700	973	-693.58	-621.77	-1344.79	29.44	0.02627137	2.627137	67.56621216	
727	1000	-697.606	-630.311	-1352.75	24.83	0.0504623	5.04623	37.70086361	
750	1023	-698.2	-635.085	-1355.78	22.49	0.07105807	7.105807	12.27398734	
800	1073	-702.97	-648.55	-1367.16	15.64	0.17322187	17.32219	-113.8541619	
827	1100	-707.648	-657.695	-1375.51	10.17	0.32888917	32.88892	-306.0360078	
850	1123	-707.89	-662.165	-1378.95	8.89	0.38590483	38.59048	-376.4257143	At 850·C, decomposition occurs until the CO2 concentration becomes 38.59%.
897	1170	-712.652	-675.1	-1392.14	4.38756	0.63695734	63.69573	-686.3670864	
900	1173	-712.96	-675.93	-1391.13	2.24	0.79478083	79.47808	-881.2109007	At 900·C, decomposition occurs until the CO2 concentration becomes 79.48%.
910	1183	-713.992	-678.701	-1393.62	0.922	0.91051726	91.05173	-1024.095388	
917	1190	-714.718	-680.644	-1395.36	0.00178	0.9998201	99.98201	-1134.345806	At 917·C or higher, 100% CaCO3 is decomposed.
927	1200	-718.185	-685.576	-1397.88	-5.88478	1.80371142	180.3711	-2126.804226	
1027	1300	-729.178	-713.919	-1423.88	-19.2188	5.91899445	591.8994	-7207.40055	
1127	1400	-740.599	-742.693	-1451.48	-31.8118	15.37995	1537.995	-18887.59254	
1227	1500	-752.418	-771.871	-1480.68	-43.6068	33.0048539	3300.485	-40646.73322	
1339	1612	-763.915	-803.227	-1515.29	-51.8536	47.8965833	4789.658	-59031.58435	

Decomposition temperature of CaCO3: 825·C, At 1339·C, decomposition equilibrium is reached when the CO2 pressure becomes 102.5 atm (10.25 MPa).

Claims

1. A method for removing acid components at high temperature in a gasification power generation method **characterized in that** in a gasification power generation system including a gasification step of performing partial combustion gasification of a gasification material, a cyclone treatment step of performing a coarse powder collection treatment of a gasified gas coming out of the gasification step, a bag filter treatment step of performing a dust removal treatment of the gasified gas having been subjected to coarse powder removal coming out of the cyclone treatment step, a CO_2 absorption and reforming step of performing a CO_2 absorption and reforming treatment of the gasified gas having been subjected to dust removal coming out of the bag filter treatment step, and a power generation step of performing power generation by utilizing a reformed gas coming out of the CO_2 absorption and reforming step,
after the gasification step but before the cyclone treatment step, a cyclone upstream additive having desalination and desulfurization functions is supplied to the gasified gas using a gas coming out of the power generation step after recovering heat as an additive carrier gas, and
a CO_2 absorbent used in the CO_2 absorption and reforming step is allowed to absorb CO_2 in a gas temperature range of 450 to 700°C, and when the amount of absorbed CO_2 has reached saturation, the flow of oxygen or air for increasing the temperature of a reforming catalyst layer is switched immediately upstream of a CO_2 absorbent-filled layer, and the temperature of the absorbent-filled layer is increased within a temperature range of 800 to 950°C to separate CO_2 from the absorbent.

2. The method for removing acid components at high temperature in a gasification power generation method according to claim 1, wherein the cyclone upstream additive also has CO_2 absorption and removal functions.

3. The method for removing acid components at high temperature in a gasification power generation method according to claim 1 or 2, **characterized in that** the cyclone upstream additive has an average particle diameter of 100 to 1000 μm.

4. The method for removing acid components at high temperature in a gasification power generation method according to any one of claims 1 to 3, **characterized in that** the cyclone upstream additive is selected from the group consisting of burnt dolomite, hydrated lime, sodium aluminate, and sodium bicarbonate.

5. The method for removing acid components at high temperature in a gasification power generation method according to any one of claims 1 to 4, **characterized in that** after the cyclone treatment step but before the bag filter treatment step, an additive which is a cyclone downstream additive that has desalination and desulfurization functions and may be the same as or different from the cyclone upstream additive and is selected from the group consisting of burnt dolomite, hydrated lime, sodium aluminate, and sodium bicarbonate is supplied to the gasified gas having been subjected to coarse powder removal using a gas coming out of the power generation step after recovering heat as an additive carrier gas.

6. The method for removing acid components at high temperature in a gasification power generation method according to any one of claims 1 to 5, **characterized in that** in the cyclone treatment step, a coarse powder containing the additive is collected, and the collected coarse powder is supplied to the gasification step together with the gasification material.

7. The method for removing acid components at high temperature in a gasification power generation method according to any one of claims 1 to 6, **characterized in that** the CO_2 absorbent used in the CO_2 absorption and reforming step is selected from the group consisting of CaO, $Ca(OH)_2$, and burnt dolomite.

8. The method for removing acid components at high temperature in a gasification power generation method according to any one of claims 1 to 7, **characterized in that** after the heat recovery treatment, the reformed gas is subjected to a CO_2 absorption treatment using an aqueous NaOH solution, and generated Na_2CO_3 is recovered and removed.

9. A device for removing acid components at high temperature in a gasification power generation system, **characterized in that** in a gasification power generation system including a gasification furnace that performs partial combustion gasification of a gasification material, a cyclone that is placed downstream of the gasification furnace and performs a coarse powder collection treatment of a gasified gas coming out of the furnace, a bag filter that is placed downstream of the cyclone and performs a dust removal treatment of the gasified gas having been subjected to coarse powder removal coming out of the cyclone, a CO_2 absorption and reforming furnace that is placed downstream of the bag filter and performs a CO_2 absorption and reforming treatment of the gasified gas having been subjected to dust

removal coming out of the bag filter, and a power generation facility that is placed downstream of the CO_2 absorption and reforming furnace and performs power generation by utilizing a reformed gas coming out of the furnace,
a cyclone upstream additive supply line for supplying an additive having desalination and desulfurization functions to a flow path to the cyclone from the gasification furnace is provided, a carrier gas line coming from the power generation facility is connected to the supply line, and an oxygen or air supply line for switching oxygen or air for increasing the temperature of the reforming furnace to a CO_2 absorbent-filled layer when the amount of absorbed CO_2 has reached saturation is connected immediately upstream of the CO_2 absorbent-filled layer of the CO_2 absorption and reforming furnace.

10. The device for removing acid components at high temperature in a gasification power generation system according to claim 9, **characterized in that**
a cyclone downstream additive supply line for supplying an additive having desalination and desulfurization functions to a flow path to the bag filter from the cyclone is provided, and a carrier gas line coming from the power generation facility is connected to the supply line.

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FIG. 1

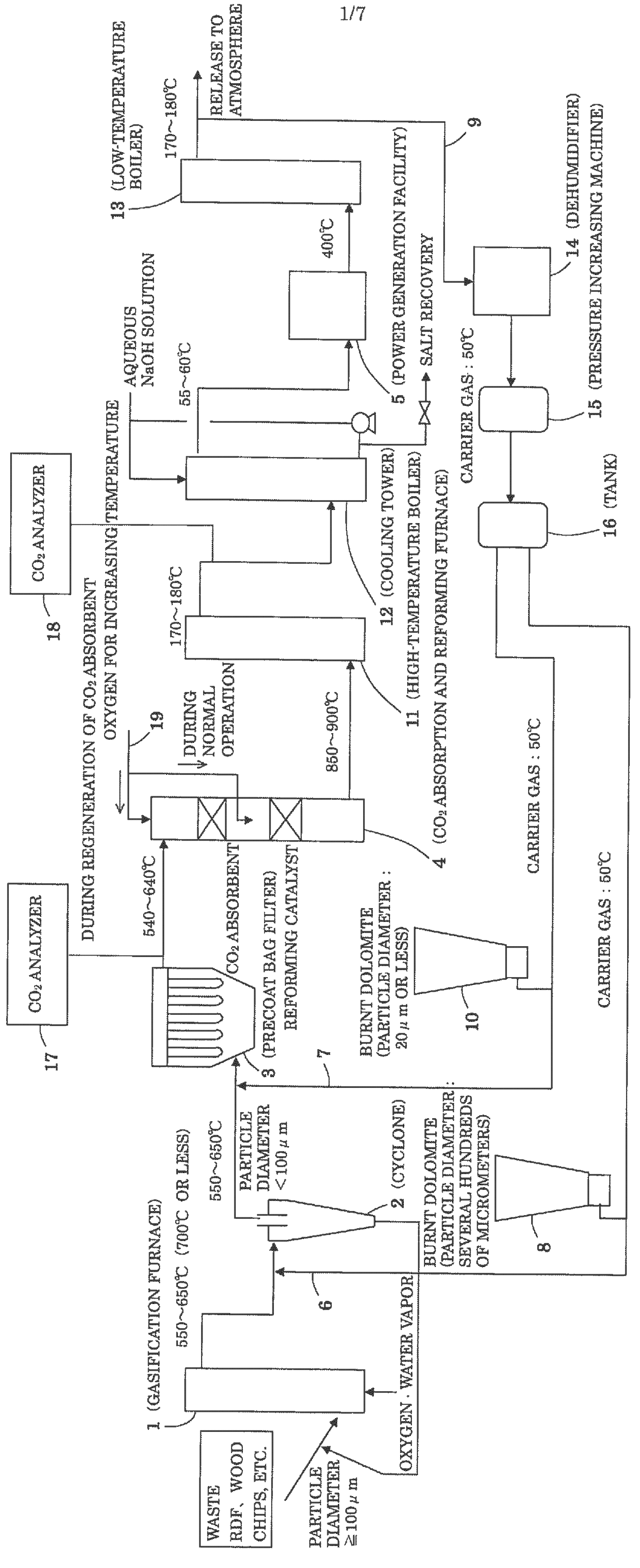
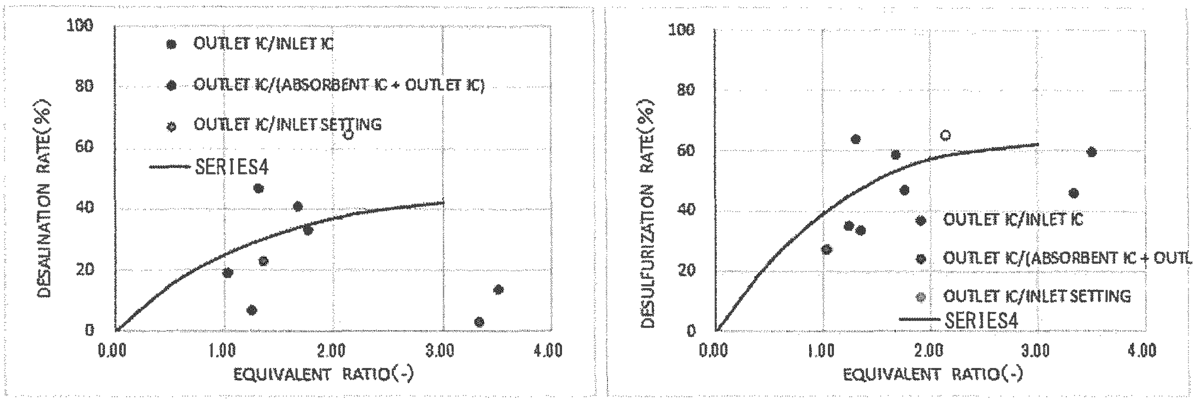

WASTE
RDF, WOOD
CHIPS, ETC.
PARTICLE
DIAMETER
≧100 μ m
OXYGEN · WATER VAPOR
1 (GASIFICATION FURNACE)
550~650℃ (700℃ OR LESS)
6
550~650℃
PARTICLE
DIAMETER
<100 μ m
2 (CYCLONE)
BURNT DOLOMITE
(PARTICLE DIAMETER :
SEVERAL HUNDREDS
OF MICROMETERS)
8
3 (PRECOAT BAG FILTER)
CO₂ ABSORBENT
REFORMING CATALYST
7
17
CO₂ ANALYZER
BURNT DOLOMITE
(PARTICLE DIAMETER :
20 μ m OR LESS)
10
540~640℃
DURING REGENERATION OF CO₂ ABSORBENT
OXYGEN FOR INCREASING TEMPERATURE
19
DURING
NORMAL
OPERATION
4 (CO₂ ABSORPTION AND REFORMING FURNACE)
850~900℃
11 (HIGH-TEMPERATURE BOILER)
170~180℃
18
CO₂ ANALYZER
12 (COOLING TOWER)
AQUEOUS
NaOH SOLUTION
55~60℃
SALT RECOVERY
5 (POWER GENERATION FACILITY)
400℃
13 (LOW-TEMPERATURE
BOILER)
170~180℃
RELEASE TO
ATMOSPHERE
9
14 (DEHUMIDIFIER)
15 (PRESSURE INCREASING MACHINE)
16 (TANK)
CARRIER GAS : 50℃
CARRIER GAS : 50℃
CARRIER GAS : 50℃

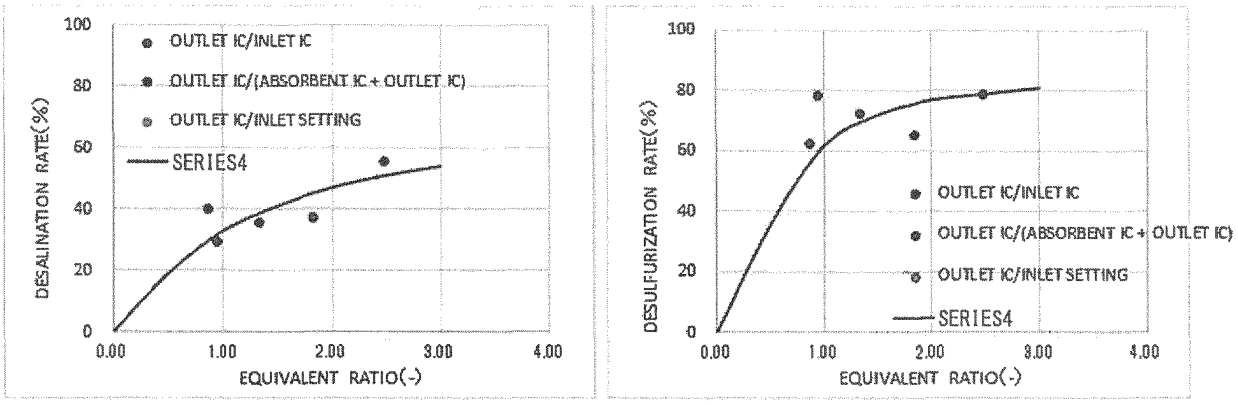
FIG. 2-1



HYDRATED LIME	DESALINATION RATE	DESULFURIZATION RATE
0.0	0	0
0.5	15	23
1.0	25	39
1.5	32	50
2.0	37	57
2.5	40	60
3.0	42	62

HYDRATED LIME(CALCIUM HYDROXIDE) : KISHIDA CHEMICAL
COMPOSITION: $Ca(OH)2$:
PURITY: 96%
PARTICLE DIAMETER: 22μm(75μ OR LESS)

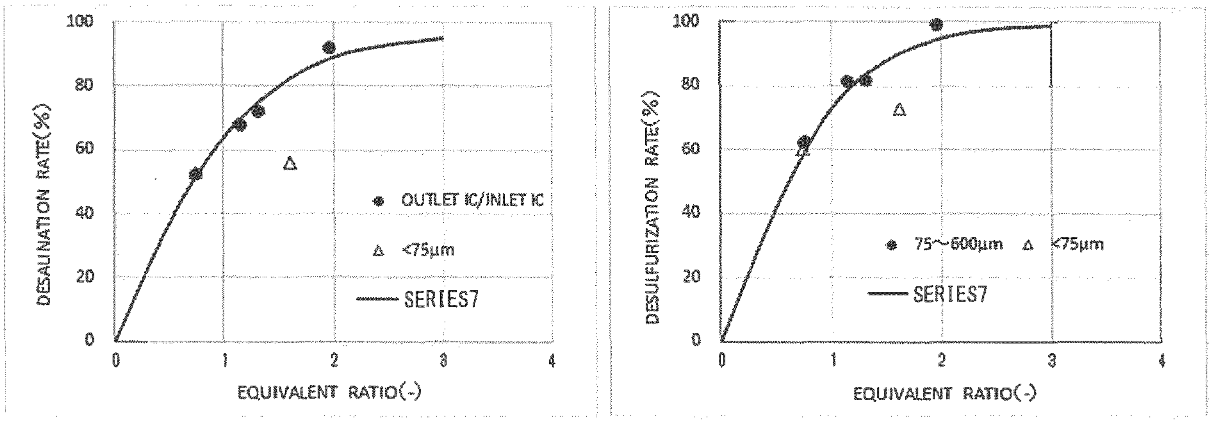
FIG. 2-2



BURNT DOLOMITE	DESALINATION RATE	DESULFURIZATION RATE
0.0	0	0
0.5	19	36
1.0	33	62
1.5	41	72
2.0	47	77
2.5	51	79
3.0	54	81

LIGHTLY BURNT DOLOMITE: YOSHIZAWA LIME INDUSTRY
COMPOSITION: $CaCO_3 \cdot MgO$
PARTICLE DIAMETER: 75 μm OR LESS

FIG. 2-3



SODIUM ALUMINATE	DESALINATION RATE	DESULFURIZATION RATE
0.0	0	0
0.5	37	42
1.0	64	73
1.5	80	88
2.0	89	95
2.5	93	98
3.0	95	99
40% $NaAl_2$-SUPPORTING/g-ALUMINA		
PARTICLE DIAMETER OF γ_b-ALUMINA: 75μm OR LESS		

FIG. 3-1

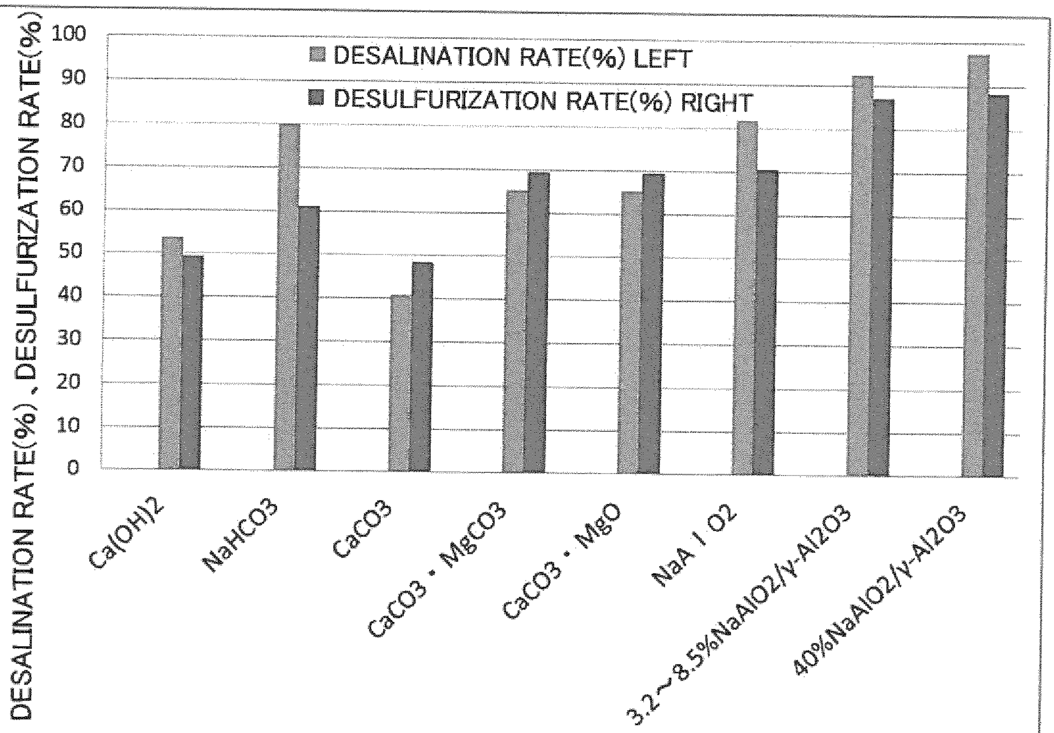


FIG. 3-1 COMPARISON OF PERFORMANCE OF VARIOUS DESALINATION AND DESULFURIZATION AGENTS(EQUIVALENT RATIO 2. 0、550°C)

FIG. 3-2

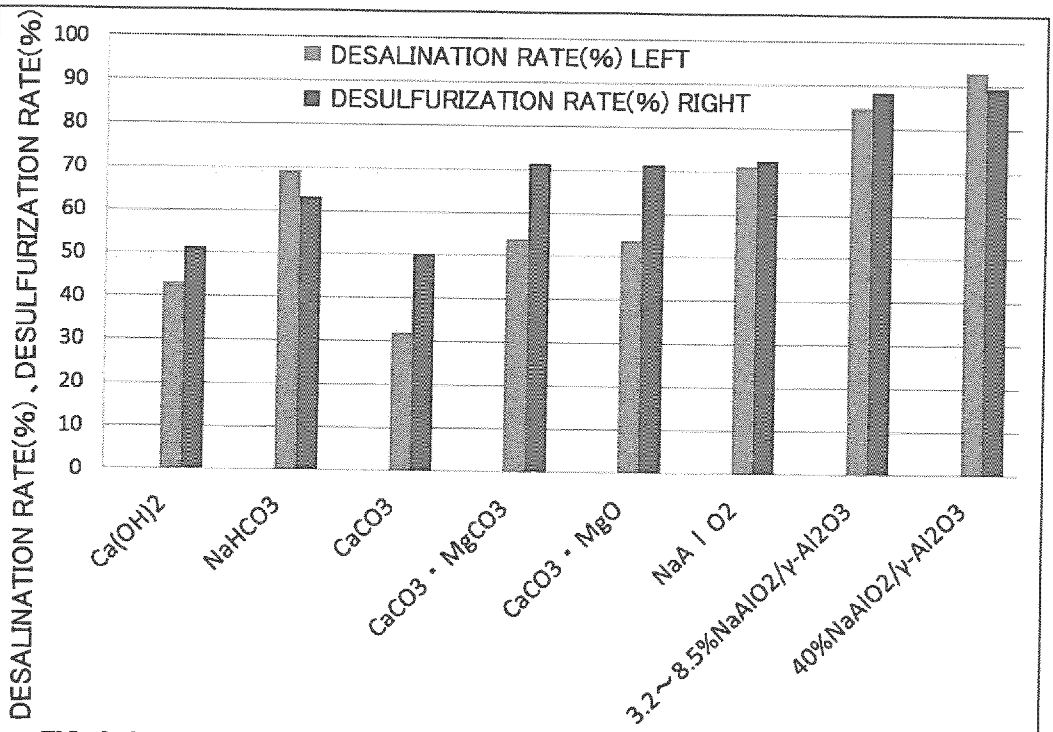


FIG. 3-2 COMPARISON OF PERFORMANCE OF VARIOUS DESALINATION AND DESULFURIZATION AGENTS(EQUIVALENT RATIO 2. 0、600°C)

FIG. 3-3

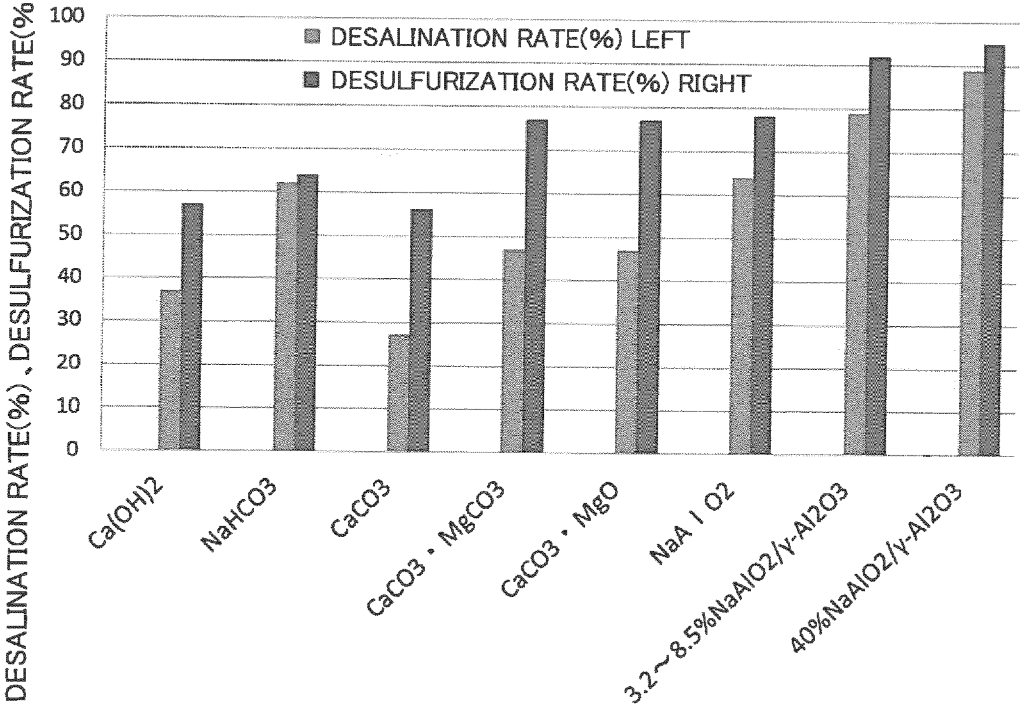


FIG. 3-3 COMPARISON OF PERFORMANCE OF VARIOUS DESALINATION AND DESULFURIZATION AGENTS(EQUIVALENT RATIO 2. 0、650°C)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/032202

A. CLASSIFICATION OF SUBJECT MATTER
C10K1/20(2006.01)i, *C10J3/46*(2006.01)i, *C10K1/12*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10K1/20, C10J3/46, C10K1/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 63-135491 A (Babcock-Hitachi Kabushiki Kaisha), 07 June 1988 (07.06.1988), (Family: none)	1-10
A	JP 2009-242714 A (Mitsui Engineering & Shipbuilding Co., Ltd.), 22 October 2009 (22.10.2009), (Family: none)	1-10
A	JP 2011-202119 A (Mitsui Engineering & Shipbuilding Co., Ltd.), 13 October 2011 (13.10.2011), (Family: none)	1-10

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

* Special categories of cited documents:

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“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“&” document member of the same patent family

Date of the actual completion of the international search 21 September 2017 (21.09.17)	Date of mailing of the international search report 03 October 2017 (03.10.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2006037012 A **[0009]**
- JP 2002130628 A **[0009]**
- JP 3571219 B **[0009]**

Non-patent literature cited in the description

- **SHOICHI OGAWA et al.** Collection of Hydrocarbon Components of Pyrolysis Gas of Polystyrene by Ceramic Filters and Regeneration Properties. *Journal of the Society of Powder Technology,* 2003, vol. 40 (11), 19-25 **[0010]**