



(51) International Patent Classification:

C02F 11/08 (2006.01) **B09B 5/00** (2006.01)
C02F 1/66 (2006.01)

(21) International Application Number:

PCT/KR2009/007678

(22) International Filing Date:

22 December 2009 (22.12.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10-2009-0059724 1 July 2009 (01.07.2009) KR

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

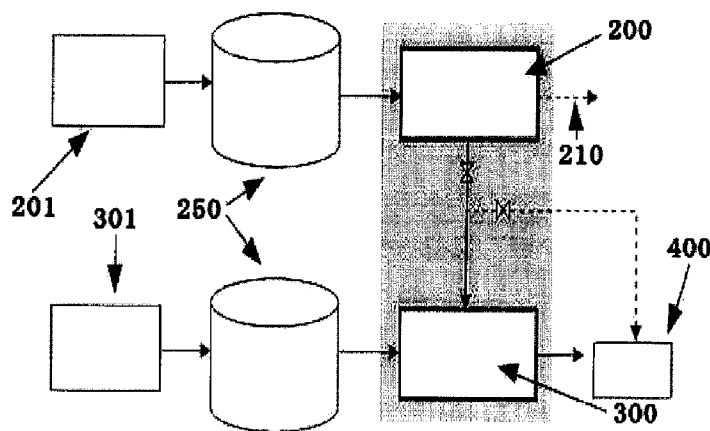
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD OF TREATING WASTE CAUSTIC SODA

[Fig. 3]



(57) Abstract: Disclosed herein is a method of treating waste caustic soda, including: neutralizing waste caustic soda produced by an oil refining process using sulfuric acid; and wet-air-oxidizing the neutralized waste caustic soda. Since the waste caustic soda produced by an oil refining process can be treated at medium temperature and pressure using a wet air oxidation method, costs can be reduced. Further, the wet air oxidation method does not require high-cost equipment compared to other treatment methods, such as incineration, evaporation and concentration, and the like, and fuel consumption can be reduced. Moreover, since the equipment has a simple structure, maintenance costs can be reduced.

Description

Title of Invention: METHOD OF TREATING WASTE CAUSTIC SODA

Technical Field

- [1] The present invention relates to a method of oxidatively treating waste caustic soda using air at a predetermined temperature and pressure.

Background Art

- [2] The products of oil refining or petrochemical processes are brought into contact with caustic soda (NaOH) in order to remove therefrom impurities, such as hydrogen sulfide, mercaptans (R-HS), organic acids and the like. The caustic soda which comes into contact with these impurities is converted into waste caustic soda(spent caustic), and this waste caustic soda is discharged to the atmosphere or the drainage system after removing harmful components therefrom using a treatment facility such as an incinerator or the like.
- [3] Currently, the waste caustic soda of oil refining processes is treated by vaporization and concentration, neutralization, liquid-phase incineration, or the like.
- [4] However, the vaporization and concentration thereof is problematic in that a large investment is required and a facility for treating a bad smell is required although various kinds of waste liquids are easily treated. In addition, high rate of steam consumption and additional facilities, such as a incinerator of a concentrated liquid, raise investment cost.
- [5] The neutralization thereof has the good point of the investment which is required being low, but has the negative points of, similarly to vaporization and concentration, a facility for treating a bad smell being required, and waste water treatment being additionally required.
- [6] The liquid-phase incineration thereof has the positive point of waste water treatment not being required, but has the negative points of fuel consumption being increased and the air pollution control equipment being excessively expensive to operate, so that the liquid-phase incineration is difficult to be applied to the treatment of waste caustic soda.
- [7] For these reasons a wet air oxidation method has been introduced to treat waste caustic soda produced by an oil refining process. The wet air oxidation method is referred to as a Zimpro process, which was developed by Zimpro Co., Ltd. in the U.S. About 60 years have passed since the Zimpro process was commercialized in the 1940 s. The wet air oxidation method is chiefly used to treat industrial waste, such as waste caustic soda containing sulfides or the like. In this wet air oxidation method, a

treatment system is designed such that waste water and air are injected into a bubble column reactor through the bottom thereof to cause an oxidation reaction at high temperature and pressure, and the oxidized waste water is discharged to the outside through the top thereof to generate reaction heat, which is used to maintain the operation temperature of the treatment system. This wet air oxidation method has been widely used as a standard process for treating waste caustic soda in ethylene plants since the 1980 s.

- [8] According to the basic principle of the wet air oxidation method, pollutants are treated by transferring gaseous oxygen to pollutant-containing water to oxidize the pollutants and then dispersing the condensed reaction product using a bulk liquid. That is, owing to the increase in mass transfer rate between the gaseous oxygen and the pollutant-containing water, organic matter is oxidized and converted into carbon dioxide and water, and sulfide (S^{2-}), which is inorganic matter, is converted into thiosulfate ($S_2O_3^{2-}$) or sulfate (SO_4^{2-}). In this wet air oxidation method, under the condition of high pressure, water is maintained in the liquid phase, and the solubility of oxygen is increased, thus meeting the minimum oxygen demand. Further, under the condition of high temperature, the diffusion coefficient of oxygen and the reaction rate constant of oxidation are increased.
- [9] A wet air oxidation system includes a heat exchanger, a wet air oxidation reactor, a cooler and a separator. In this wet air oxidation system, air is injected into the wet air oxidation reactor using an air compressor. Once the wet air oxidation reactor is heated up to the temperature necessary for an oxidation reaction using steam during a start-up, the temperature of the wet air oxidation reactor is maintained by oxidation reaction heat without continuous injection of steam. The waste caustic soda oxidized in the wet air oxidation reactor under the condition of high temperature and high pressure increases the temperature of the reactor through the heat exchanger and is then cooled by the cooler. Then, off gas is separated from the treated waste caustic soda by the separator. The off gas separated from the cooled waste caustic soda is transferred to an off gas treatment facility (RTO or the like), and the remaining waste caustic soda is transferred to a waste water disposal plant and then discharged after biological treatment.
- [10] Such a wet air oxidation method is frequently used to treat waste caustic soda in petrochemical processes, but is not often used to treat the waste caustic soda in oil refining processes. The reason for this is that acidic oil components, such as naphthenic, cresylic, mercaptide and the like, contained in the waste caustic soda produced by the oil refining process, are difficult to treat using the conventional wet air oxidation method. Therefore, the conventional wet air oxidation method requires a high temperature and pressure even though the acid oil components can be treated.

- [11] Such a wet air oxidation method includes a wet air oxidation method in which the waste caustic soda produced by both the oil refining process and the petrochemical process is introduced together into a wet air oxidation reactor at high temperature and pressure, and a wet air oxidation method in which the waste caustic soda produced by the oil refining process is wet-oxidized at high temperature and pressure and the caustic soda produced by the petrochemical process is wet-oxidized at a medium temperature and pressure.
- [12] However, when the waste caustic soda produced by the oil refining process is treated using the wet air oxidation method under the reaction conditions of high temperature and high pressure, there are problems of large operation costs and relatively long reaction time. Moreover, organic acids produced during the oxidation reaction causes the corrosion of facilities. Furthermore, when the waste caustic soda produced by both the oil refining process and the petrochemical process is treated at the same time, the former wet air oxidation method is problematic in that an additional cost for treating the waste caustic soda produced by a petrochemical process which does not need the high temperature and pressure conditions is required, and the later wet air oxidation method is problematic in that different treatment conditions should be used, so that two wet air oxidation reactors are required. The above disadvantages which occur when the waste caustic soda produced by the oil refining process is to be treated are not solved yet.

Disclosure of Invention

Technical Problem

- [13] Accordingly, the present invention has been devised to solve the above-mentioned problems, and the present invention intends to efficiently treat the waste caustic soda produced by an oil refining process and the waste caustic soda produced by a petrochemical process using a wet air oxidation method. More particularly, the present invention intends to provide a wet air oxidation method for treating waste caustic soda, which can remove sulfur compounds from the waste caustic soda solutions produced by an oil refining process and a petrochemical process, can minimize the generation of hydrogen sulfide gas, and can be used even under the operating conditions of lower temperature and pressure.

Solution to Problem

- [14] An aspect of the present invention provides a method of treating waste caustic soda, including: neutralizing waste caustic soda produced by an oil refining process containing sulfuric acid; and wet-air-oxidizing the neutralized waste caustic soda.
- [15] The method may further include: introducing waste caustic soda produced by a petrochemical process before wet-air-oxidizing the neutralized waste caustic soda.

- [16] In the method, the wet-air-oxidized waste caustic soda may be further treated in an integrated neutralization tank in which a gas-liquid separator is integrated with a neutralization tank.

Advantageous Effects of Invention

- [17] According to the present invention, since the waste caustic soda produced by an oil refining process can be treated at medium temperature and pressure using a wet air oxidation method, costs can be reduced. Further, according to the present invention, the wet air oxidation method does not require high-cost equipment compared to other treatment methods, such as incineration, evaporation and concentration, and the like, and fuel consumption can be reduced. Moreover, since the equipment has a simple structure, maintenance costs can be reduced.
- [18] In addition, according to the present invention, since a small amount of air pollutants are discharged compared to other treatment methods, such as incineration, evaporation and concentration, and the like, the causes of environmental problems can be reduced.
- [19] Furthermore, the present invention is advantageous in that naphthenic acid oil obtained from waste caustic treatment can be recycled to make other products.

Brief Description of Drawings

- [20] The above and other objects, features and advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:
- [21] FIG. 1 is a process view showing a neutralization process which is conducted before a wet air oxidation process;
- [22] FIG. 2 is a process view showing a wet air oxidation process after the neutralization process;
- [23] FIG. 3 is a schematic view showing a process of treating waste caustic soda produced by an oil refining process and a petrochemical process using a wet air oxidation process;
- [24] FIG. 4 is a sectional view showing a wet air oxidation reactor;
- [25] FIG. 5 is an enlarged view of a static mixer for increasing gas-liquid contact, wherein liquid phase stream (waste caustic soda) is designated by a red color and gas phase stream (air) is designated by a blue color;
- [26] FIG. 6 is a view showing the state of contact and mixing of air and waste caustic soda according to the operation of the static mixer;
- [27] FIG. 7 is a view showing the design of a tray of the present invention;
- [28] FIG. 8 is a view showing the procedure in which air and waste caustic soda are brought into contact with each other and then diffused in each stage of an oxidation reactor equipped with a tray;

- [29] FIG. 9 is a view comparing a conventional gas-liquid separator and neutralizing apparatus with an integrated neutralizing apparatus;
- [30] FIG. 10 is a view showing a process of neutralizing waste caustic soda produced by an oil refining process and then recycling the neutralized waste caustic soda;
- [31] FIG. 11 shows the generation of minute air bubbles; and
- [32] FIG. 12 is a graph showing the solubility of oxygen according to temperature.
- [33] ※ Description of the Elements in the Drawings
- [34] 10: waste caustic soda supply line
- [35] 20: sulfuric acid supply line
- [36] 30: organic oil drain pump
- [37] 35: organic acid discharge line
- [38] 40: caustic soda introduction line
- [39] 50: heat exchanger
- [40] 60: neutralization reactor
- [41] 70: mixer for mixing waste caustic soda with sulfuric acid
- [42] 80: control valve
- [43] 90: oxidation reaction introduction line
- [44] 100: waste caustic soda storage tank
- [45] 101: waste caustic soda transfer pump
- [46] 103: high-pressure pump
- [47] 105: heat exchanger for heat recovery
- [48] 107: waste caustic soda transfer pump
- [49] 109: heat exchanger for cooling
- [50] 110: wet air oxidation reactor
- [51] 111: steam supply pipe
- [52] 113: waste caustic soda discharge tank
- [53] 115: exhaust gas discharge line
- [54] 117: sulfuric acid introduction line
- [55] 119: waste caustic soda discharge line
- [56] 120: integrated neutralization tank
- [57] 121: static mixer
- [58] 123: tray
- [59] 200: neutralizing process
- [60] 201: oil refining process
- [61] 210: organic oil separation and recovery unit
- [62] 250: waste caustic soda storage tank
- [63] 300: wet air oxidation process
- [64] 301: petrochemical process

- [65] 400: waste water disposal plant
 [66] 500: neutralized waste caustic soda recycling line
 [67] 550: conventional gas-liquid separator and neutralization tank

Best Mode for Carrying out the Invention

- [68] Hereinafter, a preferred embodiment of the present invention will be described in detail with reference to the attached drawings.
- [69] The present invention provide a method of treating the waste caustic soda produced by an oil refining process using a wet air oxidation method under the condition of middle temperature and pressure. A system for conducting the method of the present invention includes a neutralizing apparatus for neutralizing the waste caustic soda produced by an oil refining process and a wet air oxidation apparatus for oxidizing the neutralized waste caustic soda.
- [70] Waste caustic soda is difficult to treat because it has high chemical oxygen demand (COD). Further, it is provided in the U.S. Resources Conservation and Recovery Act (RCRA) that waste caustic soda is D003 (reactive sulfide). Therefore, liquid effluent from a wet air oxidation process must be easy to be dealt with in a waste water treatment plant.
- [71] Sources of waste caustic soda are given in Table 1 below.
- [72] Table 1
- [Table 1]

Class.	Processes	Function of caustic soda
Oil refining process	Solid Bed Merox process	Removing H ₂ S and Naphthenic acid from Diesel
	LPG Merox process	Removing H ₂ S and Mercaptan from LPG
	LSR Merox process	Removing H ₂ S and Mercaptan from Gasoline
	FCC and GSU processes	Removing H ₂ S and Mercaptan from Gasoline
Petrochemical process	Naphtha Cracking process	Removing H ₂ S and CO ₂ from Naphtha Gas

- [73] Waste caustic soda is classified into three types of sulfurized waste caustic soda, naphthenic waste caustic soda and cresylic waste caustic soda according to the kinds of major impurities (sulfides, naphthenic acids, cresylic acids and the like) removed from hydrocarbons.
- [74] Sulfurized waste caustic soda is the typical waste caustic soda produced by a naphtha cracking process in a petrochemical process and an LPG Merox process in an oil refining process. The sulfurized waste caustic soda is characterized in that Na₂S, NASR and NaSH having high COD and BOD are produced, and H₂S, which is a mal-odorous and toxic gas, is produced when it is neutralized with sulfuric acid. Naphthenic waste caustic soda includes a large amount of naphthenic acid and NaSR and has high COD and BOD. Cresylic waste caustic soda includes the organic acids,

such as phenol, cresol and aqueous cresylate. It was found that naphthenic hydrocarbons are organic components which are difficult to treat using a wet air oxidation method. When a wet air oxidation method is used to treat the hydrocarbons included in waste caustic soda, a high-temperature and high-pressure treating process is required to prevent foaming. The waste caustic soda produced by a petrochemical process rarely includes hydrocarbons, but the waste caustic soda produced by an oil refining process includes a large amount of hydrocarbons, particularly, naphthenic acids.

[75] In order to confirm the above fact, air oxidation reactions were performed on the waste caustic soda produced by a petrochemical process and the waste caustic soda produced by an oil refining process, and the results thereof are given in Table 2 below.

[76] Table 2

[Table 2]

Class.	Component	Chemical Reaction Formula	Note
Waste caustic soda produced by a petrochemical process	sulfide	$\text{Na}_2\text{S} + 2\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4$	normal
	bis-sulfide	$2\text{NaHS} + 2\text{O}_2 \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$ $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{O}_2 + 2\text{NaOH} \rightarrow 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	
Waste caustic soda produced by an oil refining process	naphthenic	$\text{RCOONa} + 3/2 \text{O}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{RCOOH}$	generation of carboxylic acid-based organic acids
	cresylic	$\text{RONa} + \text{O}_2 \rightarrow \text{CO}_2 + \text{RCOOH}$	
	mercaptide	$\text{NaSR} + 2\text{O}_2 \rightarrow \text{NaHSO}_4 + \text{CO}_2 + \text{RCOOH}$	

[77] As shown in Table 2, it was found that the waste caustic soda produced by a petrochemical process reacts with oxygen to form stable salts, but the waste caustic soda produced by an oil refining process reacts with oxygen to form organic acids having a carboxylic group of RCOOH, which causes the corrosion of facilities.

[78] Meanwhile, when both types of waste caustic soda are simultaneously neutralized with sulfuric acid, the results thereof are given in Table 3 below.

[79] Table 3

[Table 3]

Class.	Component	Chemical Reaction Formula	Note
Waste caustic soda produced by petrochemical process	sulfide	$\text{Na}_2\text{S} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S} \uparrow$	generation of H_2S gas
	bi-sulfide	$2\text{NaHS} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{H}_2\text{S} \uparrow$	
Waste caustic soda produced by oil refining process	naphthenic	$2\text{RCOONa} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{RCOOH}$	no problem
	cresylic	$2\text{RONa} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{ROH}$	
	mercaptide	$2\text{NaSR} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{RHS}$	

[80] As shown in Table 3, the waste caustic soda produced by a petrochemical process reacts with sulfuric acid to produce H_2S gas and give off a bad smell, and the waste caustic soda produced by an oil refining process reacts with sulfuric acid to produce a small amount of organic acids and malodorous material, but there is no serious problem. In conclusion, it was found that, the waste caustic soda produced by an oil refining process entails a higher reaction temperature and a longer reaction time than does the waste caustic soda produced by a petrochemical process and produces organic acids which corrode facilities when it can be treated using a general wet air oxidation method. But the wet air oxidation method can be practically used under conditions similar to those of the waste caustic soda produced by a petrochemical process when oil components and organic acids are removed from the waste caustic soda produced by an oil refining process through a neutralizing reaction using sulfuric acid.

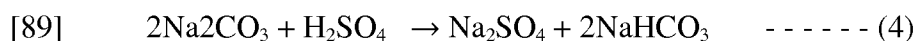
[81] Accordingly, the present invention was completed based on these findings.

[82] According to an embodiment of the present invention, the waste caustic soda produced by an oil refining process is neutralized using sulfuric acid in a neutralization reactor. The waste caustic soda neutralized by sulfuric acid can be treated with a wet air oxidation method at lower temperature and pressure than those when the waste caustic soda is not neutralized.

[83] FIG. 1 shows a neutralizing process according to an embodiment of the present invention. Here, waste caustic soda produced by an oil refining process is introduced along a waste caustic soda supply line 10, and sulfuric acid is introduced along a sulfuric acid supply line 20. The waste caustic soda and sulfuric acid are mixed in a mixer 70, and is introduced into a neutralization reactor 60. The neutralized waste caustic soda moves along an oxidation reaction introduction line 90 provided for the wet oxidation reaction. A drain pump 30 is used to discharge the neutralized organic oil through an organic acid discharge line 35.

[84] Since a large amount of H_2S gas is produced when the waste caustic soda of a petrochemical process is neutralized with sulfuric acid, only the waste caustic soda of an oil refining process should be neutralized with sulfuric acid other than the treatment of the waste caustic soda of an oil refining process together with the waste caustic soda of a petrochemical process.

[85] The main reactions of the waste caustic soda of an oil refining process with sulfuric acid in the neutralization reactor 60 are as follows.



- [91] Although a very small amount of sulfuric compounds, such as Na_2S , NaHS and the like, are present in the waste caustic soda produced by an oil refining process, H_2S gas is slightly generated when this waste caustic soda is reacted. In this case, an organic acid (RCOOH), which is an acidic oil, is formed, and the formed organic acid is removed along the organic acid discharge line 35 by the organic oil drain pump 30 shown in FIG. 1.
- [92] As represented by Formula (1) and (2), RSH and ROH are formed. RSH and ROH form the ions HS^- and OH^- in aqueous solutions and are introduced into a wet air oxidation process along an oxidation reaction introduction line 90 and then oxidatively treated.
- [93] As shown in FIG. 2, Na_2S , which is a major component of the waste caustic soda produced by a petrochemical process, and NaHS and ROH , which are formed by neutralizing the waste caustic soda produced by an oil refining process, react as follows.
- [94] $\text{Na}_2\text{S} + 2\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4$ ----- (6)
- [95] $2\text{NaHS} + 4\text{O}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ ---- (7)
- [96] $\text{ROH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ ----- (8)
- [97] Referring to the above Reaction Formula, since efficiency of the oxidation reaction depends on the degree of gaseous transfer rate into a liquid waste caustic soda, the solubility of oxygen in the waste caustic soda solution should be increased.
- [98] The above oxidation reactions may be conducted at a medium temperature of $180 \sim 230^\circ\text{C}$, preferably, $190 \sim 210^\circ\text{C}$ (200°C) and at a medium pressure of $25 \sim 35 \text{ kg}_f/\text{cm}^2\text{g}$, preferably, $28 \sim 32 \text{ kg}_f/\text{cm}^2\text{g}$ ($30 \text{ kg}_f/\text{cm}^2\text{g}$). The oxidation reactions do not proceed easily at a temperature less than 180°C . In contrast, although the oxidation reactions are more easily conducted at a temperature greater than 230°C , most sulfides are 90% or more decomposed within an hour near 200°C by an air oxidation reaction, and residual sulfides are decomposed by a biological reaction during waste water treatment, so that the reaction temperature over 200°C is not required.
- [99] Further, when the oxidation reactions are conducted at a pressure below $25 \text{ kg}_f/\text{cm}^2\text{g}$, there is a disadvantage in that the partial pressure of oxygen in a reactor is lowered, and thus the solubility of oxygen is decreased, so that residence time must be increased. In contrast, when the oxidation reactions are conducted at a pressure over $35 \text{ kg}_f/\text{cm}^2\text{g}$, the residence time is decreased at the expense of the increased capacity of the air compressors.
- [100] As shown in FIG. 12, the solubility of oxygen is the lowest near 100°C , and increases to about 370°C (critical point) as temperature rises.
- [101] From FIG. 12, it can be seen that the solubility of oxygen at 200°C increases as much as of that at 150°C . Therefore, at 200°C , the oxidation reactions can be conducted using an air supply unit smaller than that at 150°C .

- [102] If the waste caustic soda of an oil refining process without neutralization process is treated through a wet air oxidation process together with the waste caustic soda of a petrochemical process, the organic components, such as NaSR, RONA, RCOONa and the like, requires a high reaction temperature over 250°C and a high pressure over 90 kg/cm².
- [103] Therefore, the waste caustic soda of an oil refining process is neutralized to remove the organic components which cause the increase of the reaction temperature and pressure, and then the neutralized waste caustic soda is introduced into a wet air oxidation process, so that the waste caustic soda of an oil refining process can be treated under conditions similar to those of treatment for the waste caustic soda of a petrochemical process.
- [104] As the temperature and pressure of the wet air oxidation process can be greatly lowered, equipment cost can be reduced, operating costs can be decreased, and corrosion can be minimized. Accordingly, as given Table 4 below, the reaction time in the reactor can be decreased to half.

[105] Table 4

[Table 4]

Wet air oxidation process	Reaction temperature (°C)	Reaction pressure (kg/cm ²)	Reaction time
Waste caustic soda of oil refining process + waste caustic soda of petrochemical process	250 or more	90	120 minutes
Neutralized waste caustic soda of oil refining process + waste caustic soda of petrochemical process	200	30	60 minutes

- [106] In order to easily treat waste water and prevent the corrosion of facilities, organic acids (RCOOH) (which are acidic compounds) are removed through the neutralizing process represented by Reaction Formula (3) above, and residual NaSH and ROH are oxidized as represented by Reaction Formula (7) and (8), respectively. In Reaction Formula (7), since caustic soda (NaOH) is consumed, the caustic soda (NaOH) is added before waste water is introduced into a wet air oxidation process to keep the pH high, thus preventing the facilities from corrosion. In Reaction Formula (6), Na₂S is oxidized to form stable salts through a wet air oxidation process, so that waste water treatment may be stably conducted. In the wet air oxidation process, comparing the concentration of the neutralized water discharged after the oxidation reactor with that of the water which was not neutralized, as given in Table 5 below, it can be seen that the neutralized water has a COD half that of the water which was not neutralized. Therefore, the efficiency of waste water treatment is improved two fold.

[107] Table 5

[Table 5]

Class.	COD (ppm)
Waste caustic soda of oil refining process + waste caustic soda of petrochemical process	8,000 ~ 9,000
Neutralized waste caustic soda of oil refining process + waste caustic soda of petrochemical process	4,000 ~ 4,500

[108] According to another embodiment of the present invention, first, the waste caustic soda produced by an oil refining process is neutralized using sulfuric acid to remove organic substances therefrom, and then the neutralized waste caustic soda from which the organic substances have been removed is treated together with the waste caustic soda produced by a petrochemical process in a single wet air oxidation apparatus. As described above, when organic substances are removed from the waste caustic soda produced by an oil refining process by the neutralizing treatment using sulfuric acid, the wet air oxidation treatment can be conducted under conditions similar to those used to treat the waste caustic soda produced by a petrochemical process.

[109] FIG. 2 shows a wet air oxidation process according to an embodiment of the present invention. The waste caustic soda is introduced into a waste caustic soda storage tank 100 through the oxidation reaction introduction line 90, is pressurized by a transfer 101 pump and a high-pressure pump 103, is heated by a heat exchanger 105 for heat recovery, and is then transferred to an oxidation reactor 110. In this case, steam may be introduced into the oxidation reactor 110 through a steam supply pipe 111 in order to increase the temperature of the oxidation reactor 110. The waste caustic soda which was oxidatively-treated in the oxidation reactor 110 increases the inlet temperature of the oxidation reactor 110 through the heat exchanger 105 for heat recovery, is cooled by a heat exchanger 109 for cooling, and is then transferred to a neutralization tank 120. The waste caustic soda which was not oxidatively-treated in the oxidation reactor 110 is returned to a waste caustic soda storage tank 100 by a transfer pump 107. Sulfuric acid is introduced into the neutralization tank 120 along a sulfuric acid introduction line 117, and the waste caustic soda neutralized with sulfuric acid in the neutralization tank is sent to a waste water treatment plant along a waste caustic soda discharge line 119. The exhaust gas generated from the neutralization tank 120 is discharged through an exhaust gas discharge line 115.

[110] FIG. 3 schematically shows a method of treating waste caustic soda produced by an oil refining process and a petrochemical process using a wet air oxidation apparatus. As shown in FIG. 3, waste caustic soda produced by each of the oil refining and petrochemical processes is stored in each storage tank 250, and the waste caustic soda produced by an oil refining process undergoes a neutralizing process 200 prior to wet

air oxidation treatment. The waste caustic soda of an oil refining process which underwent the neutralizing process and the waste caustic soda of a petrochemical process which did not undergo the neutralizing process 200 are introduced into a single wet air oxidation process 300. The waste caustic soda oxidatively treated through the single wet air oxidation process 300 is sent to a waste water treatment plant 400.

- [111] According to another embodiment of the present invention, in order to increase the wet air oxidation efficiency of waste caustic soda, a high-efficiency static mixer 121 for increasing gas-liquid contact, serving to increase the oxidation rate of waste caustic soda by increasing the contact efficiency between waste caustic soda and minute air particles, can be additionally used, and air diffusion using a tray 123 can also be applied. As shown in FIG. 4, the static mixer 121 for increasing gas-liquid contact is provided at the end of a waste caustic soda inlet located in the lower portion of the oxidation reactor 110 in order to increase the oxidation rate of waste caustic soda by increasing the contact efficiency between waste caustic soda and air. FIG. 6 shows the contact and mixing of air and waste caustic soda by the static mixer 121. Air bubbles may have a diameter of 75 ~ 300 μm . Owing to the static mixer, it is expected that air bubbles are minute and thus receive torque to be uniformly diffused in the oxidation reactor 110, so that gas-liquid contact area increases, thereby increasing the contact efficiency of waste caustic soda and air.
- [112] FIG. 5 shows the experimental results of the fluidity of gas and liquid in a static mixer. The static mixer includes four small-size mixers. Each of the small-size mixers torques gas and liquid, decreases the particle size of air and improves the fluidity of gas and liquid. The distribution of gas and liquid is shown in FIG. 5.
- [113] From FIG. 6, it can be seen that, due to the torque, the velocity of fluid at the final stage was increased to 9.8 m/sec.
- [114] FIG. 7 shows a tray installed in the oxidation reactor. The tray has five holes through which fluid passes. The tray is installed in the oxidation reactor by three stages.
- [115] FIG. 8 shows the vortex flow and velocity distribution of the fluid formed in the oxidation reactor owing to the torque of the static mixer.
- [116] The velocity distribution of air bubbles in the oxidation reactor is entirely uniform because the size of the air bubbles is decreased by the static mixer and the vortex current is formed by the torque of the static mixer. When the size of air bubbles in the oxidation reactor is arranged in the groups shown in Table 6 below, it can be seen from FIG. 11 that minute air bubbles having a diameter of 75 ~ 300 μm , which is the size of group 2 and group 3, are formed. Therefore, since the air bubbles formed using the static mixer have smaller sizes than air bubbles having a diameter of 100 ~ 30000 μm formed when the static mixer is not used, the static mixer serves to greatly improve the contact efficiency of waste caustic soda and air.

[117] Table 6

[Table 6]

Group	Air bubble size (diameter)
Group 1	$2.9500 \times 10^{-2} \text{ mm} = 30 \mu \text{ m}$
Group 2	$7.4500 \times 10^{-2} \text{ mm} = 75 \mu \text{ m}$
Group 3	$2.9550 \times 10^{-1} \text{ mm} = 300 \mu \text{ m}$
Group 4	$7.4950 \times 10^{-1} \text{ mm} = 750 \mu \text{ m}$
Group 5	$1.2495 \text{ mm} = 1250 \mu \text{ m}$
Group 6	$1.7495 \text{ mm} = 1750 \mu \text{ m}$
Group 7	$2.2495 \text{ mm} = 2250 \mu \text{ m}$
Group 8	$2.7495 \text{ mm} = 2750 \mu \text{ m}$
Group 9	$3.2495 \text{ mm} = 3250 \mu \text{ m}$
Group 10	$3.7495 \text{ mm} = 3750 \mu \text{ m}$

[118] The method of treating waste caustic soda according to another embodiment of the present invention may further include a tray, shown in FIG. 7, which is designed such that air bubbles are uniformly diffused and efficiently brought into contact with waste caustic soda in an oxidation reactor. The tray may be installed in the oxidation reactor in one, two or three stages. Minute air bubbles flow upwards losing their velocity, but trays can help the air bubbles become uniformly distributed in the oxidation reactor, and prevent from being locally concentrated. FIG. 8 shows the procedure in which air and waste caustic soda are brought into contact with each other and then diffused in each stage of the oxidation reactor equipped with the trays. From FIG. 8, it can be seen that air bubbles are widely and uniformly distributed throughout the oxidation reactor.

[119] In the wet air oxidation process of the present invention, since a gas-liquid separator and a neutralization tank are separately provided, there is a problem in that equipment is complicated and a large installation space is required. Therefore, according to another embodiment of the present invention, in the wet air oxidation process, since the gas-liquid separator and the neutralization tank are integrally fabricated, equipment is simplified and installation space is minimized. FIG. 9 shows the integrated neutralization tank.

[120] In a general wet air oxidation process, the waste caustic soda solution having undergone an oxidation reaction in an oxidation reactor includes gaseous components, such as CO_2 , N_2 , O_2 and the like. Liquid and gas are separated in a gas-liquid separator at atmospheric, and discharged to separator overhead. The residual waste caustic soda solution is neutralized with sulfuric acid in a neutralization tank and then introduced into a waste water treatment plant.

- [121] However, in the present invention, since the gas-liquid separator and the neutralization tank are integrally designed, the gas-liquid separation and neutralization of the waste caustic soda solution are accomplished in a vessel, and the installation space thereof is decreased from 121 to 64 m² by decreasing the width thereof from about 11 to about 8 m.
- [122] The method of treating waste caustic soda according to another embodiment of the present invention may further include a process of recycling a part of the neutralized waste caustic soda solution produced by an oil refining process to a neutralization reactor. When the waste caustic soda solution produced by an oil refining process is neutralized with sulfuric acid, reaction heat is generated. the temperature of the neutralization reactor reaches around 80 ~ 120°C. In a process of using low-concentrated sulfuric acid, corrosivity increases as temperature increases.
- [123] Therefore, as shown in FIG. 10, a part of the neutralized waste caustic soda solution is recycled to decrease the reaction temperature. Further, the flow rate of the recycled waste caustic soda solution is 4 times that of the waste caustic soda solution introduced into neutralization reactor in order to maintain the reaction temperature at 40°C or lower.
- [124] Thus, construction and maintenance costs can be reduced because the corrosion rate of facilities is decreased, and stable operation can be ensured because there are fewer changes in the pH of the reactor according to the change in operation conditions.
- [125] The results of the wet air oxidation reaction of the neutralized waste caustic soda produced by an oil refining process are given in Table 7 below. From Table 7, it can be seen that the wet air oxidation reaction of the waste caustic soda, which was not neutralized, was conducted at a high reaction temperature of 260°C or more and a high reaction pressure of 90 kg/cm² and took a long reaction time of about 120 minutes, whereas the wet air oxidation reaction of the waste caustic soda, which was neutralized, was conducted at a reaction temperature of 200°C or more and a reaction pressure of 30 kg/cm² and take a relatively short reaction time of about 60 minutes. That is, it can be seen that the wet air oxidation reaction of the waste caustic soda, which was neutralized, was conducted more efficiently than that of the waste caustic soda, which was not neutralized.
- [126] Table 7

[Table 7]

Wet air oxidation process	Component	Reaction temperature (°C)	Reaction pressure (kg/cm ²)	Reaction time (min)	Removal ratio (%)
Waste caustic soda of oil refining process, which was not neutralized	<u>sulfide-S</u>	268	90	113	99.99
	<u>phenol</u>	268	90	113	97.4
	<u>bis sulfide-S</u>	260	90	120	82
	<u>thio sulfide-S</u>	260	90	120	80
	<u>Mercaptans</u>	260	90	120	80
	<u>O-Cresol</u>	260	90	120	80
	<u>P-Credol</u>	260	90	120	80
Neutralized waste caustic soda of oil refining process	sulfide-S	200	30	60	100
	mercaptans	200	30	60	99.99
	Na ₂ S	200	30	60	100
	NaHS	200	30	60	100
	phenol	200	30	60	98.2
	oil	200	30	60	95.8

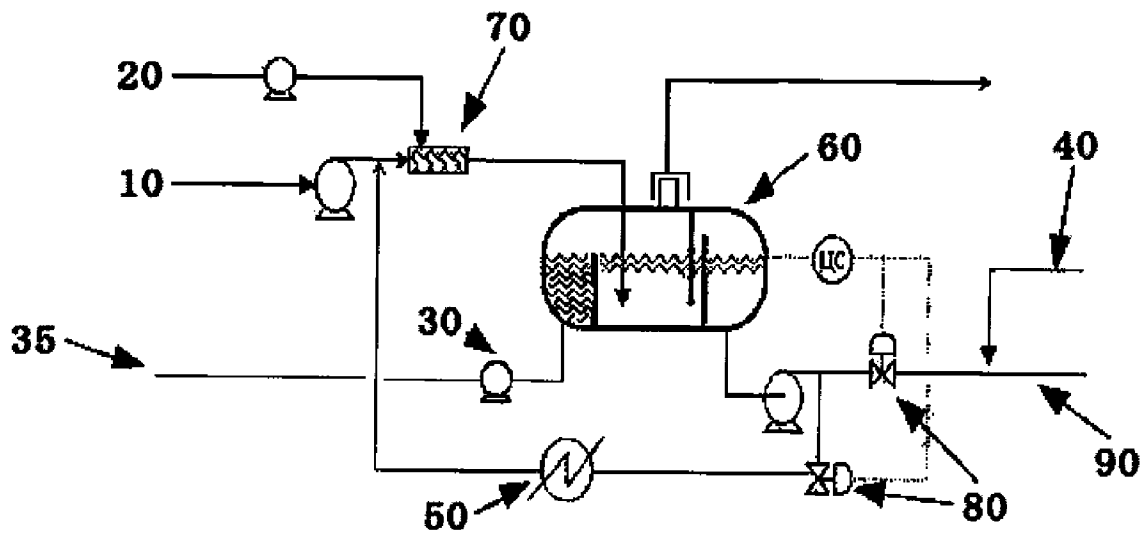
[127] As shown in Table 7, when waste caustic soda does not undergo a neutralization process, desired removal ratios of the organic components included in the waste caustic soda cannot be obtained at low reaction temperature and pressure. Therefore, in this case, there is a disadvantage in that much higher temperature and pressure are required.

[128] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

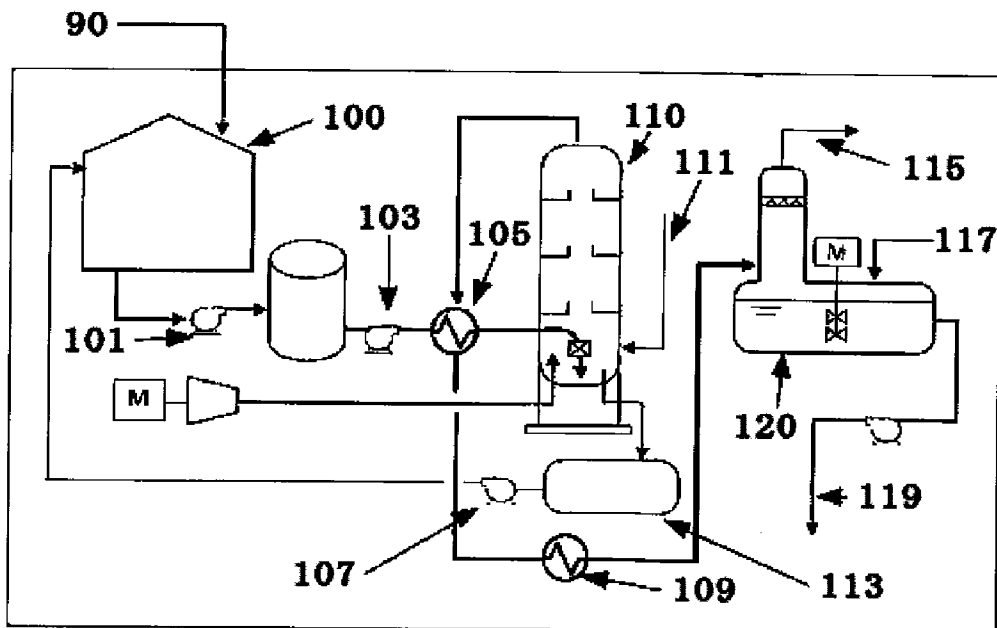
Claims

- [Claim 1] A method of treating waste caustic soda, comprising:
neutralizing waste caustic soda produced by an oil refining process
using sulfuric acid; and
wet-air-oxidizing the neutralized waste caustic soda.
- [Claim 2] The method of treating waste caustic soda according to claim 1, further
comprising: introducing waste caustic soda produced by a petro-
chemical process before wet-air-oxidizing the neutralized waste caustic
soda.
- [Claim 3] The method of treating waste caustic soda according to claim 1 or 2,
wherein the wet-air-oxidizing of the neutralized waste caustic soda is
conducted at a temperature of 180 ~ 230°C.
- [Claim 4] The method of treating waste caustic soda according to claim 1 or 2,
wherein the wet-air-oxidizing of the neutralized waste caustic soda is
conducted at a pressure of 25 ~ 35 kg/cm².
- [Claim 5] The method of treating waste caustic soda according to claim 1 or 2,
wherein, in the wet-air-oxidizing of the neutralized waste caustic soda,
a static mixer for increasing gas-liquid contact is provided at an end of
a waste caustic soda inlet located in a lower portion of an oxidation
reactor.
- [Claim 6] The method of treating waste caustic soda according to claim 5,
wherein, in the wet-air-oxidizing of the neutralized waste caustic soda,
the oxidation reactor is further provided therein with a tray of two
stages or more.
- [Claim 7] The method of treating waste caustic soda according to claim 1 or 2,
wherein the wet-air-oxidized waste caustic soda is further treated in an
integrated neutralization tank in which a gas-liquid separator is in-
tegrated with a neutralization tank.
- [Claim 8] The method of treating waste caustic soda according to claim 1 or 2,
further comprising: recycling a part of the neutralized waste caustic
soda solution to a neutralization reactor.

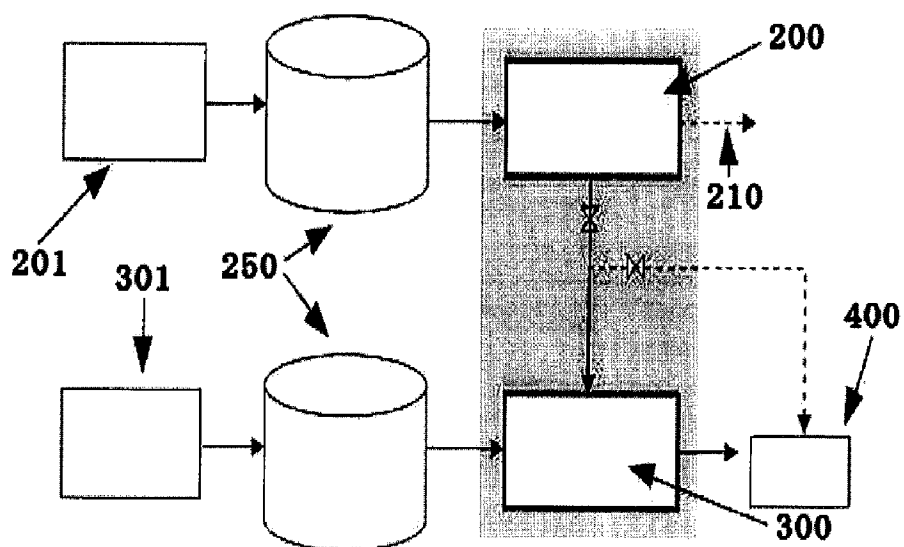
[Fig. 1]



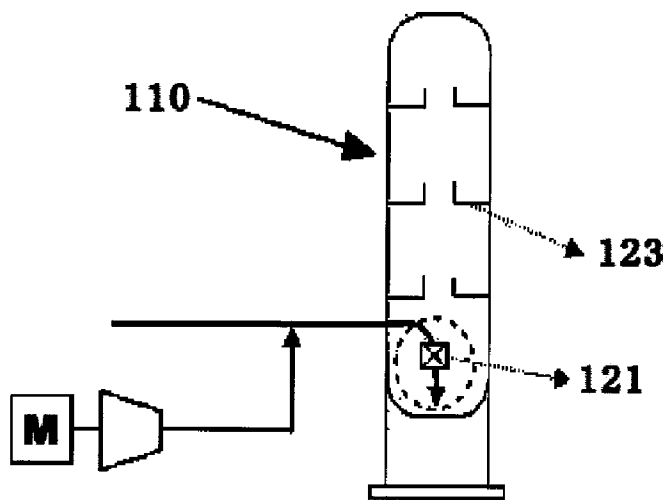
[Fig. 2]



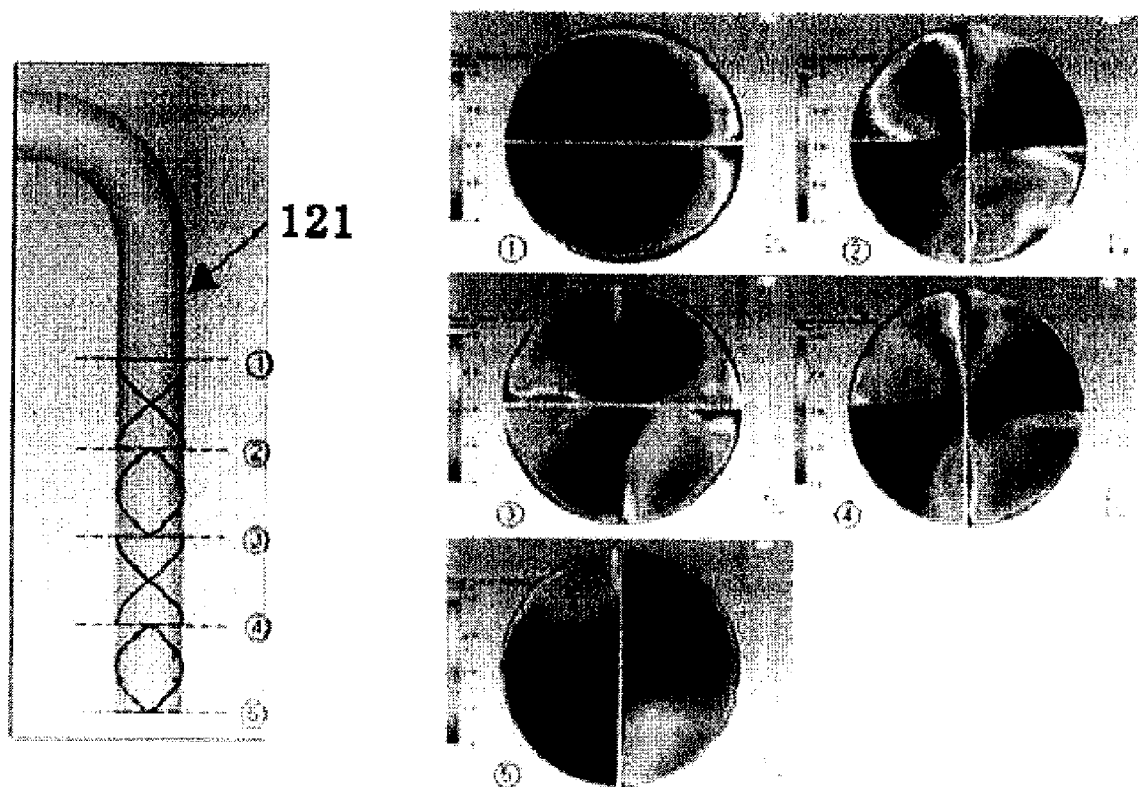
[Fig. 3]



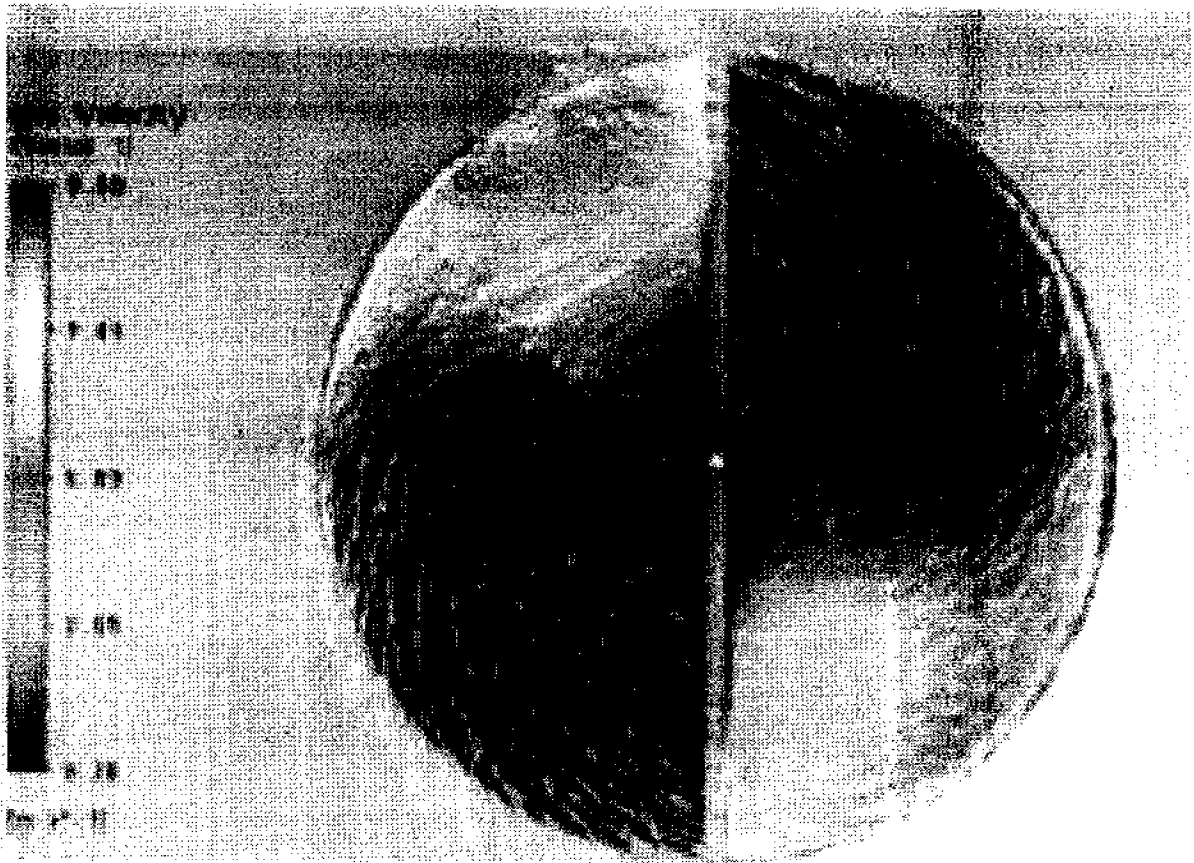
[Fig. 4]



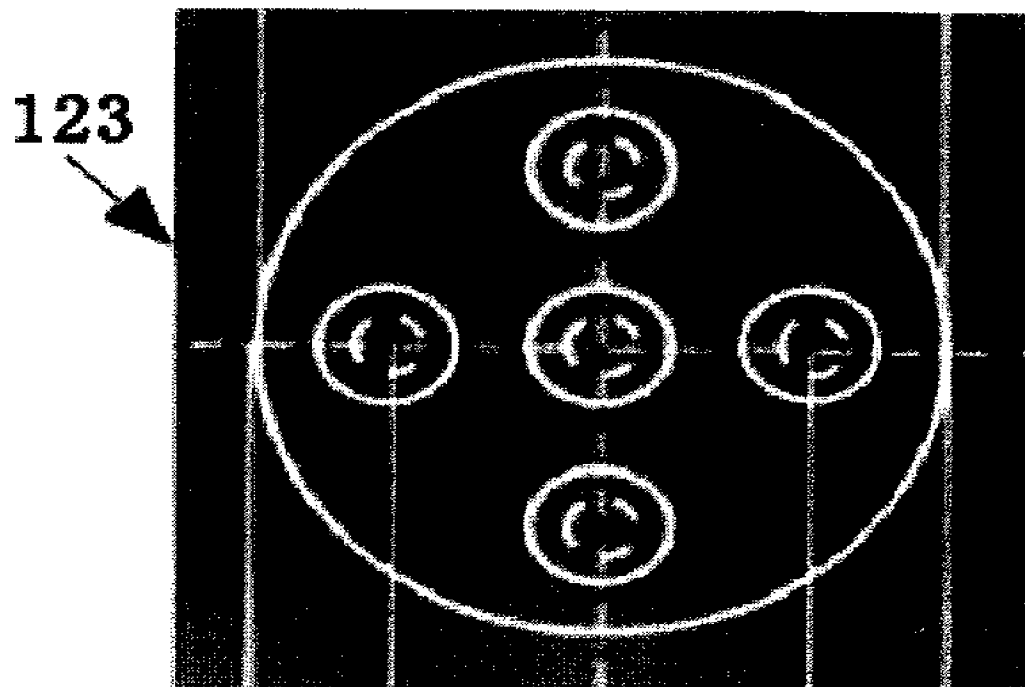
[Fig. 5]



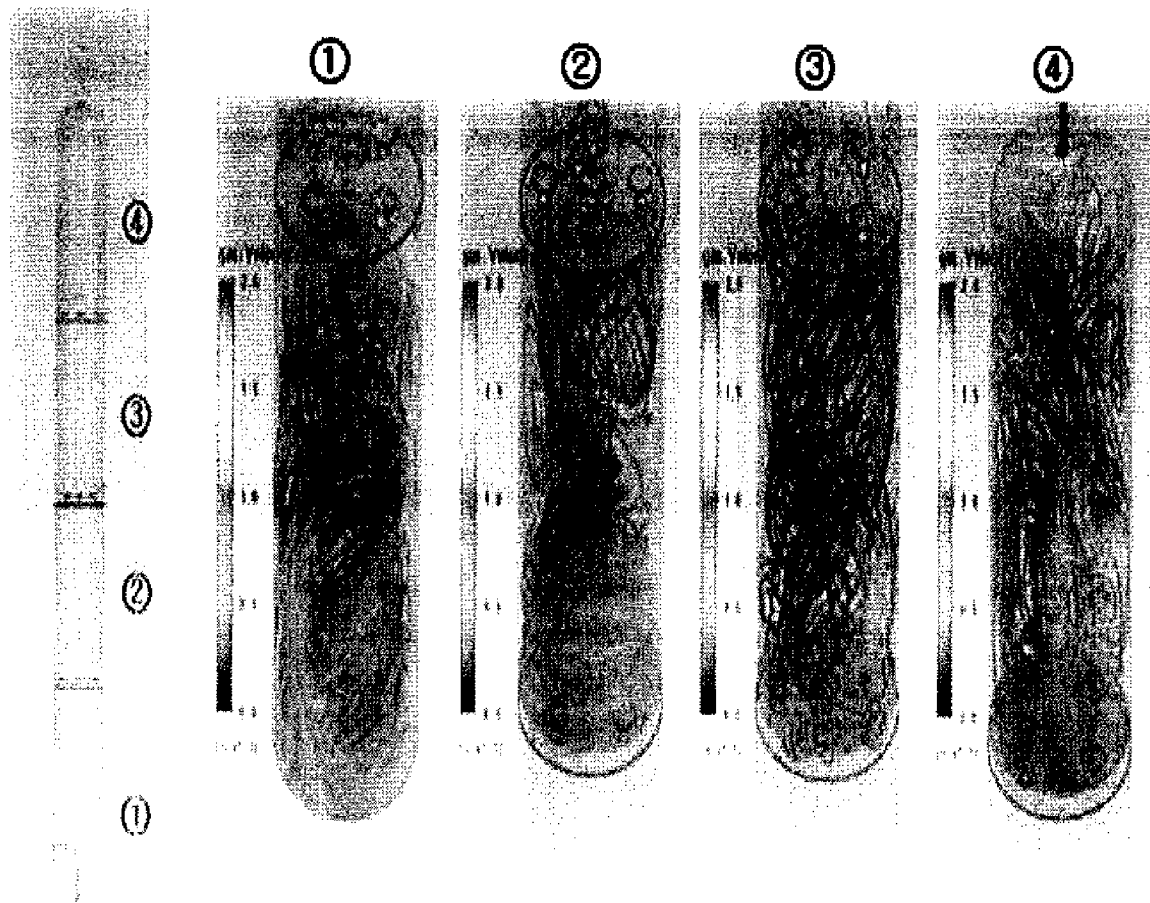
[Fig. 6]



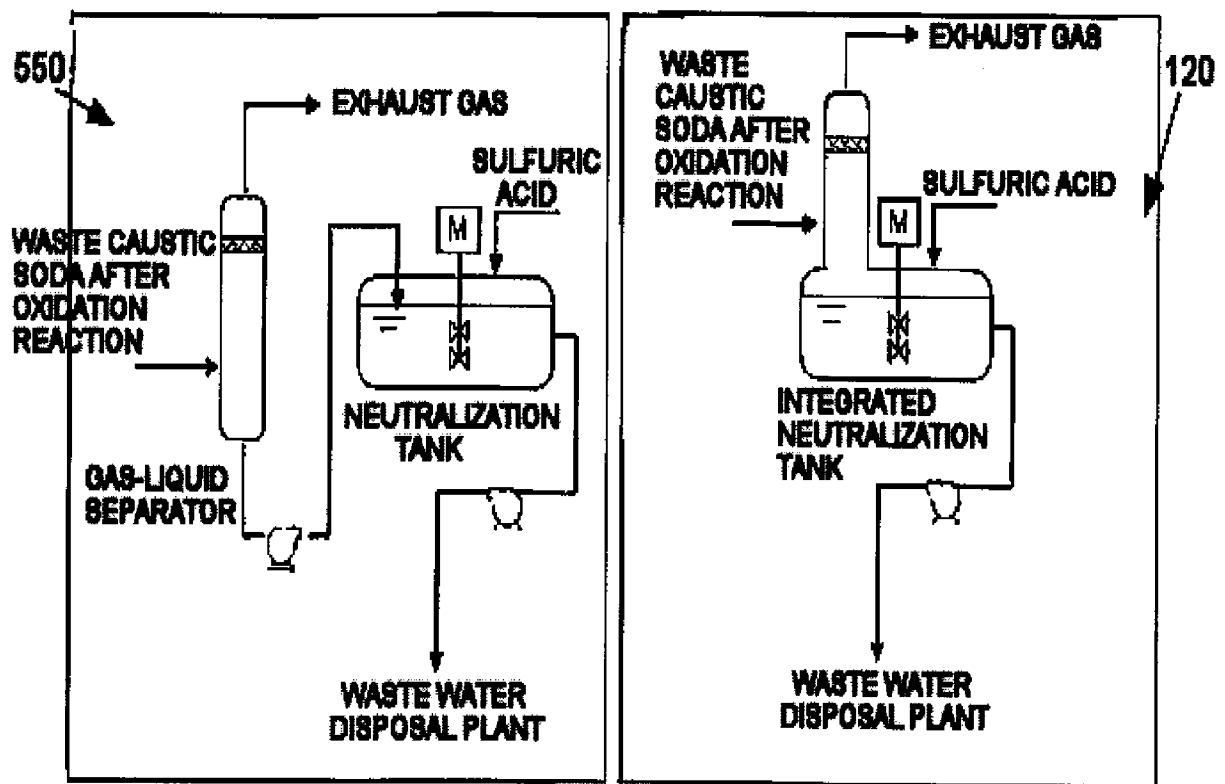
[Fig. 7]



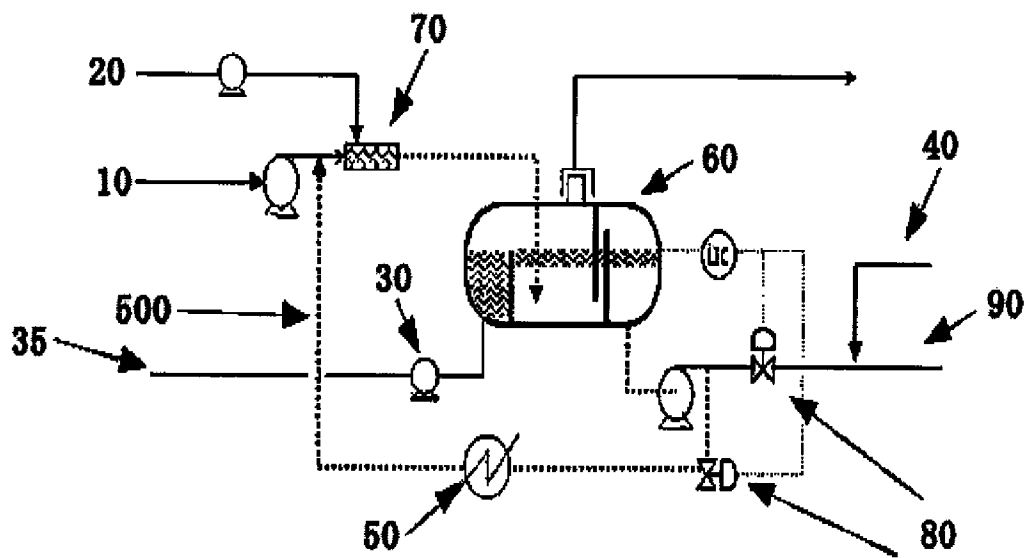
[Fig. 8]



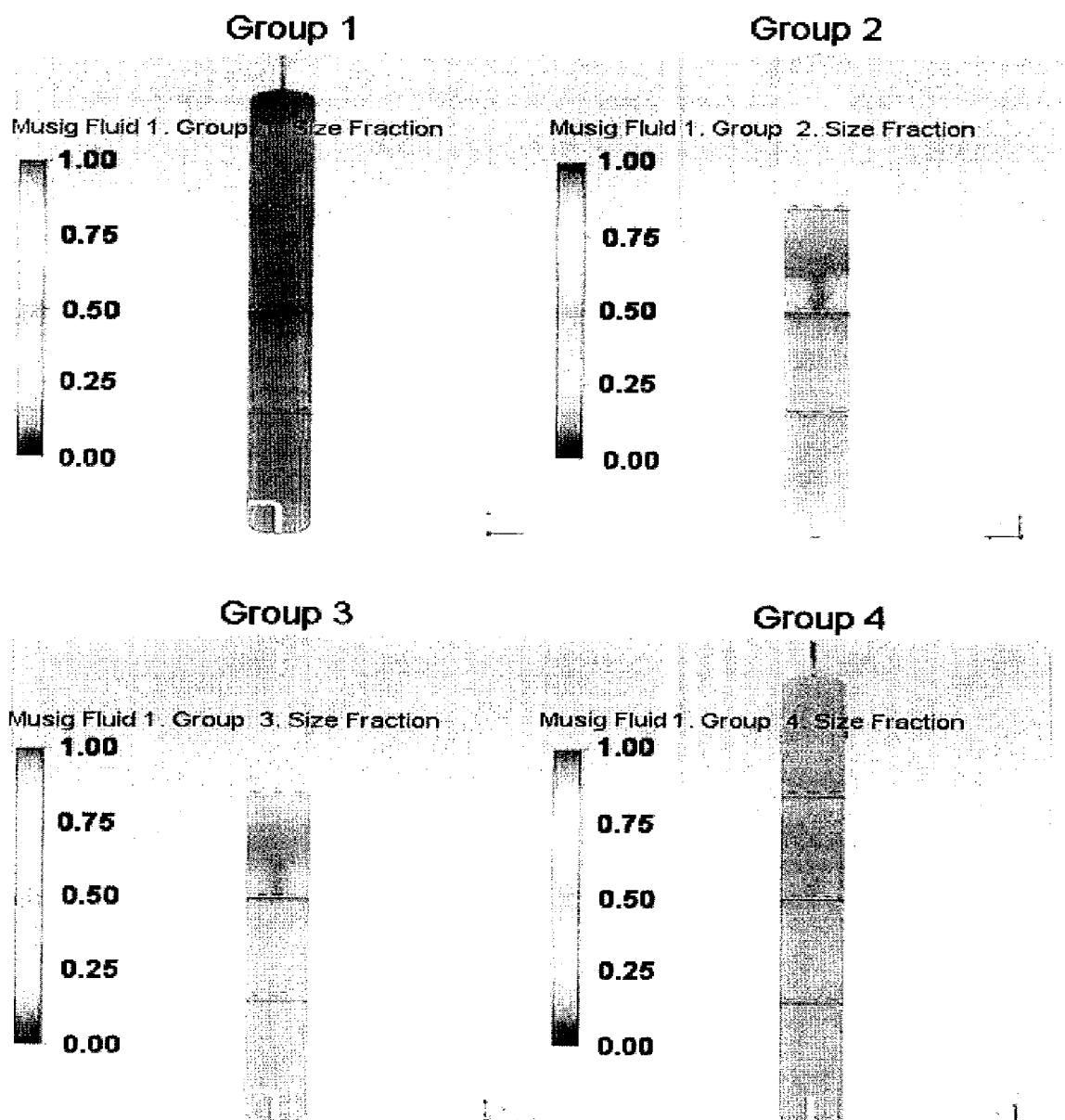
[Fig. 9]



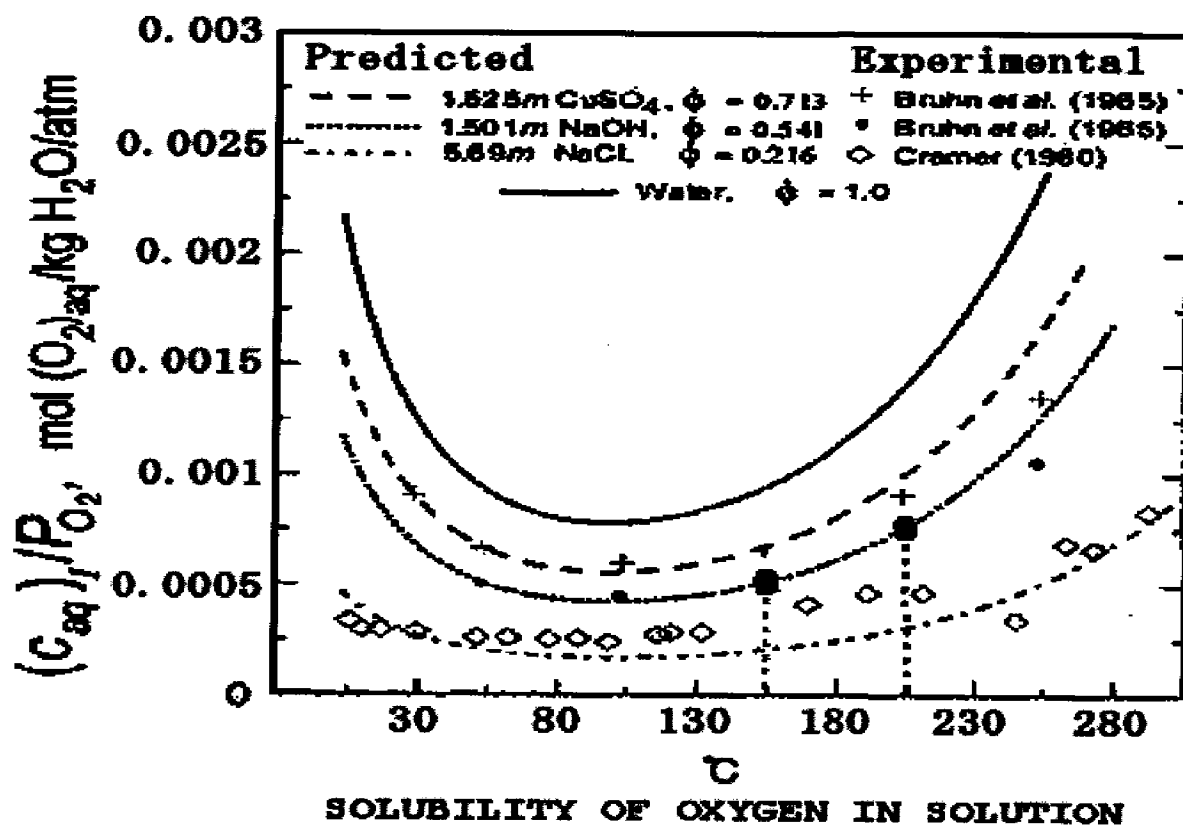
[Fig. 10]



[Fig. 11]



[Fig. 12]



A. CLASSIFICATION OF SUBJECT MATTER***C02F 11/08(2006.01)i, C02F 1/66(2006.01)i, B09B 5/00(2006.01)i***

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C02F 11/08; C01B 17/16; C02F 1/72; C07C 7/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: waste caustic soda(spent caustic), wet air oxidation, neutralizing

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Shih-Hsiung Sheu et al., "Treatment of olefin plant spent caustic by combination of neutralization and fenton reaction", Water Research, Vol.35, No.8, pp.1717-2021 (2001).	1-8
A	Claude E. Ellis, "Wet air oxidation of refinery spent caustic", Environmental Progress, Vol.17, No.1, pp.28-30 (1998).	1-8
A	KR 10-0704900 B1 (Samsung Total Petrochemicals CO., LTD) 09 April 2007 See abstract, claim 1 and figure 1.	1-8
A	US 5434329 A1 (LEHR; JAMES S.) 18 July 1995 See abstract, column 2, line 24 - column 5, line 26 and figure 1.	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

05 AUGUST 2010 (05.08.2010)

Date of mailing of the international search report

06 AUGUST 2010 (06.08.2010)

Name and mailing address of the ISA/KR

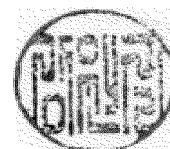
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2009/007678Patent document
cited in search reportPublication
datePatent family
member(s)Publication
date

KR 10-0704900 B1

09.04.2007

None

US 5434329 A1

18.07.1995

None