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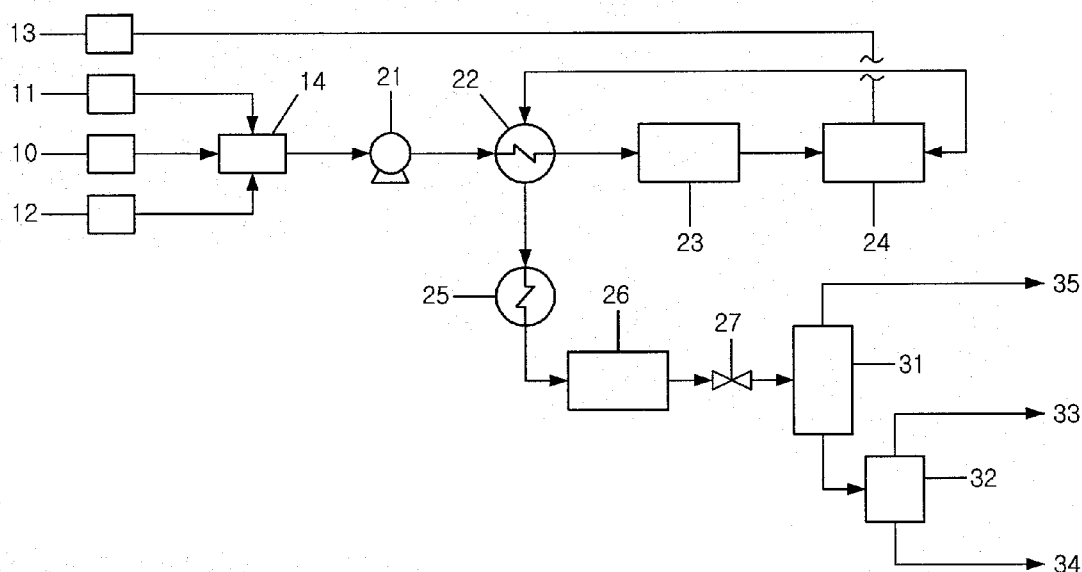
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(54) Title: METHOD FOR TREATING WASTES FROM TEREPHTHALIC ACID PROCESS



(57) Abstract: Disclosed herein is a method for treating waste byproducts from terephthalic acid processes, by homogeneously mixing the waste byproducts with water and an anti-corrosion agent to prepare a waste water, decomposing organic compounds of the waste water through oxidation reaction with an oxidant under the condition that the waste water is kept in a liquid state, and recovering catalyst particles from the liquid component. The method is of high industrial applicability as it allows organics to be decomposed with the waste byproducts maintained in a liquid state and can recover catalysts with high yield availability.

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METHOD FOR TREATING WASTES FROM TEREPHTHALIC ACID PROCESS

Technical Field

The present invention relates to a method for treating waste byproducts from terephthalic acid processes. More particularly, the present invention relates to a method for treating waste byproducts from terephthalic acid processes, to decompose organic compounds with the concomitant recovery of catalysts such as cobalt and manganese, by homogeneously mixing the waste byproducts with water and anti-corrosion agents and reacting the waste water with an oxidant under high temperature and pressure conditions, such that the waste byproducts are kept in a liquid state.

10 Background Art

Typically, terephthalic acid can be prepared through the partial oxidation of p-xylene in the presence of transition metal such as cobalt and manganese, with the concomitant production of by-products, such as benzoic acid, p-tolualdehyde, p-toluic acid, 4-carboxybenzaldehyde, 4-hydroxymethyl benzoic acid, etc. After terephthalic acid synthesis, the recovery of the produced terephthalic acid and the solvent acetic acid leaves the by-products, catalyst metals such as cobalt, manganese, and the co-catalyst hydrobromic acid (HBr), as waste materials.

It is very difficult to recover the expensive catalysts of cobalt and manganese from the waste byproducts generated upon the synthesis of terephthalic acid because the major components of waste byproducts are aromatic chemicals which are nearly solid state at room temperature. It might be very difficult to decompose the wastes since they could be nearly solid state when the acetic acid was recovered. Usually, these solid

wastes are treated through incineration. When the waste byproducts are incinerated, the catalysts, such as cobalt, manganese and so on, are discharged along with the resulting ash from the incinerator and then recovered from incinerator ash (U. S. Pat. Nos. 4,786,621 and 4,876,386). However, solid wastes are very difficult to continuously
5 feed into an incinerator. For this reason, the organic waste byproducts left after the recovery of the solvent acetic acid are mixed with combustible oil so as prevent the nozzle from clogging (Korean Pat. No. 0371231, Japanese Pat. No. 63040157). Nevertheless, incineration techniques suffer from problems in that it is difficult to recover catalyst metal from the ash and produce new waste byproducts and waste water
10 during the recovery. In addition, because they are fine, some of the catalyst metal particles fly away along with exhaust gas to thus make recovery impossible, and additional means of preventing environmental pollution, such as air pollution, are required.

Another technique for recovering catalysts from waste byproducts of
15 terephthalic acid processes has been disclosed (Chinese Pat. No. 1117163), in which a waste product from terephthalic acid processes is primarily neutralized to pH of 7.5 or higher with an alkali waste solution generated in an ethylene process and then adjusted to pH ranging from 8.5 to 9.5 using an aqueous sodium hydroxide solution, followed by associating polyacrylamide with cobalt to form precipitates. Although advantageous in
20 that the waste water from ethylene processes can be reused, this technique is disadvantageous in that the prevailing organics of the waste byproducts from terephthalic acid processes, such as benzoic acid, terephthalic acid, toluic acid, and the like, are not chemically decomposed, but are discharged as they are, to produce a high concentration of organic waste byproducts in large quantities. The organic waste solution generated
25 in the course of recovering the catalysts contains a lot of organics that require COD amounting to hundreds of thousands of ppm. Thus, the biological treatment of such

organic waste water is very difficult, and requires an enormous area for the construction of waste water-treatment facilities.

Disclosure of the Invention

Technical Problem

5 Leading to the present invention, research into the treatment of waste byproducts generated during the synthesis of terephthalic acid, conducted by the present inventors, aiming to solve the problems encountered in the prior art, resulted in the finding that using an anti-corrosion agent and maintaining temperature and pressure conditions for keeping the waste byproducts in a liquid state together enable continuous
10 decomposition of the waste byproducts as well as increasing the recovery rate of catalysts from the waste byproducts.

 Therefore, it is an object of the present invention to provide a method for treating waste byproducts from terephthalic acid processes, which is effective for the oxidative decomposition of organics and the recovery of catalysts from the waste
15 byproducts.

Technical Solution

 In accordance with the present invention, the object could be accomplished by providing a method for treating waste byproducts from a terephthalic acid process,
20 comprising: a) homogeneously mixing the waste byproducts with water and an anti-corrosion agent to prepare waste water, said waste byproducts containing catalysts for use in the synthesis of terephthalic acid; b) heating the waste water under pressure with the proviso that the waste water be in a liquid state; c) reacting the heated waste water with an oxidant to decompose organics contained therein and convert the catalysts into
25 metal oxides; d) cooling the hot treated water of step c); e) depressurizing the cooled

treated water and separating the depressurized treated water into gaseous and liquid effluents with the catalyst particles contained therein, to discharge the gaseous effluent; and f) recovering the catalyst particles from the liquid effluent, said catalyst particles including cobalt and manganese.

5

Advantageous Effect

Removal of the solvent acetic acid causes the waste byproducts to enter a near-solid state at room temperature and to lose fluidity, making it difficult to treat them. Even if used to continuously feed the waste byproducts into an incinerator, an organic
10 solvent causes another problem in the treatment thereof. Upon incineration, some of the fine cobalt and manganese catalyst particles fly away along with exhaust gas to thus lower the recovery yield. Upon recovery from exhaust ash, dissolution and neutralization with strong acid and alkali, which aims to increase the recovery yield, produces new waste water and environmental pollution.

15 However, the present invention can decompose organics of the waste byproducts without the problems encountered in the conventional incineration method, and exhibits high catalyst recovery yield, enabling the terephthalic acid process to be carried out effectively.

Brief Description of the Drawings

20 FIG. 1 is a schematic view illustrating a process for treating waste byproducts from terephthalic acid process in accordance with an embodiment of the present invention.

FIG. 2 is a schematic view illustrating a process for treating waste byproducts from terephthalic acid process in accordance with another embodiment of the present
25 invention, which is suitable for the high content of organics that results from the

production of a large volume of gas.

FIG. 3 is a graph showing a particle size distribution of the catalyst particles recovered from waste byproducts generated during the synthesis of terephthalic acid according to an embodiment of the present invention.

5 ※ Description of Numerals for Main Parts ※

- | | | |
|----|--|------------------------------|
| 10 | 10 : Waste byproducts from terephthalic acid process | |
| | 11 : water | |
| | 12 : Anti-corrosion agent | 13 : oxidant |
| | 14 : Mixing tank | 21 : Waste water pump |
| 10 | 22 : Heat Exchanger | 23 : Heater |
| | 24 : Reactor | 25 : Cooler |
| | 26 : Pressure Reducer | 27 : Pressure reducing valve |
| | 31 : Gas-Solid Separator | 32 : Solid-Liquid separator |
| | 33 : Discharged water | 34 : Recovered catalyst |
| 15 | 35 : Discharged gas | 126 : Gas discharger |
| | 127 : Liquid level controlling valve | |

Best Mode for Carrying Out the Invention

Below, a detailed description will be given of the present invention with reference to the accompanying drawings wherein the same reference numerals will be used throughout the drawings and the description to refer to the same or like parts.

Consisting largely of organic acids with large molecular weights, as mentioned above, the waste byproducts from terephthalic acid processes are not readily dissolved in water, but are in a slurry state. Hydrobromic acid (HBr), acting as a co-catalyst in the synthesis of terephthalic acid, is highly corrosive, and thus an anti-corrosion agent is needed in order to prevent the corrosion of the facilities during the oxidation of organics.

Accordingly, an increase in the solubility of the organics is useful for treating the waste byproducts and the addition of a proper alkaline component is required for preventing the corrosion of hydrobromic acid.

In accordance with the present invention, the waste of terephthalic acid processes is added to water in a suitable concentration and increased in aqueous solubility, followed by the addition of an agent preventing corrosion due to hydrobromic acid.

Using a high-pressure pump, the resulting waste solution is pressurized to 41.5-250 bar so that it can be maintained at a reaction temperature at which it is a solution that can be continuously fed into treatment facilities. The waste solution is heated to a reaction temperature ranging from 250 to 370°C by means of a heat exchanger and a heater, and is fed with an oxidizing agent (e.g., oxygen, air, etc.) to decompose the organics into carbon dioxide and water. In accordance with the present invention, the waste is preferably mixed in an amount from 0.1 to 30 wt% with water.

During the oxidation process, the organic components are decomposed into carbon dioxide and water while the catalysts, such as cobalt, manganese, etc., are converted into metal oxide particles which form a slurry. After decomposition of the organic compounds to a desired extent, the mixture containing the catalytic particles is cooled and subjected to a vacuum, and the catalytic metal particles are separated therefrom to be recycled.

With reference to FIG. 1, the treatment of waste byproducts from terephthalic acid processes is illustrated in accordance with an embodiment of the present invention.

In FIG. 1, a waste 10 occurring during the synthesis of terephthalic acid is in a solid state at room temperature and contains not only un-recovered terephthalic acid, but also large-molecular weight aromatics, such as benzoic acid, p-tolualdehyde, p-toluic acid, 4-carboxybenzaldehyde, 4-hydroxymethylbenzoic acid and so on, which are

produced in side reactions and exist as solids at room temperature in the absence of the solvent acetic acid. To be effectively oxidized, accordingly, the organic waste must be homogeneously dispersed in water. However, a homogeneous dispersion of the waste in water is very difficult to achieve due to the low solubility of most of the organic compounds in water. Fortunately, because they consist largely of organic acids, the waste products produced during the synthesis of terephthalic acid can have increased solubility in water when they are converted into organic salts by mixing with basic components.

As illustrated in FIG. 1, the waste 10 from the terephthalic acid processes is mixed with water 11 to form a slurry. In order to dissolve the waste in water and neutralize the co-catalyst hydrobromic acid, an anti-corrosion agent 12 is added to the slurry, and the resulting homogeneous waste water is stored in a mixing tank 14.

Examples of the anti-corrosion agent (or a corrosion resistant) functioning to increase the solubility of the waste and neutralize hydrobromic acid to a salt include sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium hydrogen carbonate (NaHCO_3), potassium hydroxide (KOH), potassium carbonate (K_2CO_3) and combinations thereof. In the absence of the anti-corrosion agent, hydrobromic acid corrosion proceeds to an excessive extent with hydrobromic acid. On the other hand, if too much anti-corrosion agent is used, the pH of the waste solution increases, incurring alkaline corrosion. Therefore, the anti-corrosion agent is preferably added so as to adjust the pH of the waste solution to 4 ~ 7.

After being sufficiently mixed in the mixing tank 14, the aqueous waste solution is pressurized and introduced into a treatment process with the aid of a pump 21. According to the present invention, the pressure in the treatment process is increased to the point at which no steam occurs at the treatment temperature, that is, the point higher than the vapor pressure at the maximum reaction temperature, so as not to vaporize the

reactants. When the pressure of the reactants is lower than the vapor pressure, the reactant mixture is vaporized into steam. If too much steam is generated, a hammering phenomenon occurs, causing the process to operate irregularly and unstably. Upon the production of steam therefrom, the liquid sharply decreases in density so that the residence time period necessary for the reaction is not guaranteed, making it difficult to decompose the organics suitably. Therefore, the waste water is preferably fed at an operational pressure from 41.5 to 250 bar, with the oxidative reaction temperature varying within the range from 250 to 370 °C.

Pressurized by the pump 21, the water waste proceeds to a heat exchanger 22. The heat exchanger 22 is advantageous to the process in terms of energy because it can utilize the thermal energy of the hot treatment water effluent from the reactor 24 after the oxidative reaction. Particularly, when the waste water has a COD of 80,000mg O₂/ℓ, the energy from the oxidative exothermic reaction of the organic compounds is large enough to heat the waste water, flowing in to the heat exchanger, to the reaction temperature.

The waste water primarily heated during the passage of the heat exchanger 22 is allowed to enter a heater 23 in which it is finally heated to the oxidative reaction temperature. After being heated to the reaction temperature of 250 to 370°C in the heater 23, the waste water is introduced into the reactor 24. When the temperature of the waste water is increased to a point as high as or higher than the reaction temperature during the passage of the heat exchanger 22, it is not additionally provided with thermal energy in the heater 23, but is allowed to proceed immediately into the reactor 24. In the presence of an oxidant 13, the organics of the waste water are oxidized into carbon dioxide and water in the reactor 24.

In accordance with the present invention, the oxidant is an oxygen-containing fluid selected from among an oxygen gas, air, a gas mixture containing oxygen, an ozone

gas, a mixture of oxygen and water, hydrogen peroxide, and a combination thereof. The oxidant is fed in an excessive amount, 1 to 50 mol% more than the theoretical value necessary to decompose the organic compounds. Particularly, when the waste water has a high concentration of organic compounds, the oxidant must be carefully chosen lest the temperature of the reactor exceed 374 °C, at which temperature supercritical water is formed. Preferably, water is fed in combination with oxygen as an oxidant, functioning to cool the reactor, heated during the oxidative decomposition of the organic compounds. In addition, the oxidant may be fed in an aliquot manner into many locations in the reactor, for example, may be distributed between an inlet and a middle location of the reactor.

Preferably, the waste water is allowed to stay in the reactor for 2 to 30 min so that the organic compounds are sufficiently oxidized to the decomposition.

Although heat is exchanged with the influent into the heat exchanger 22, the effluent from the reactor 24 is too hot to be discharged outside. For this reason, the effluent from the reactor 24 is directed to a cooler 25 in which its temperature is decreased to a range from 25 to 100°C, suitable for discharge to the outside. The cooled waste water is depressurized while passing through a pressure reducer 26 and a pressure reducing valve 27.

The primary pressure reducer 26 is an apparatus for depressurizing the cooled waste water which is in a pressurized state as high as or higher than its vapor pressure. The decomposition of the waste water produces water and gaseous components such as carbon dioxide and oxygen with the concomitant precipitation of catalysts such as cobalt and manganese. If the gas, liquid and solid components are mixed in the course of depressurization, the mixture can seriously wear the pressure reducing valve 27, thereby reducing the longevity thereof. Accordingly, the installation of the pressure reducer prior to the pressure reducing valve 27 prevents abrasion of the valve 27. A capillary

pressure reducing apparatus, for which a tube with a small diameter is provided, is representative of the pressure reducer 27.

According to the present invention, while the cooled waste water passes through the pressure reducer 26, its pressure decreases from 41.5~250 bar to atmospheric pressure to 20 bar, thereby retarding the abrasion rate of the pressure reducing valve 27. After passing through the pressure reducing valve 27, the mixture is introduced into a gas-liquid separator 31, where the gaseous components 35, including carbon dioxide, generated upon the decomposition of the organic compounds, excessively fed oxygen, etc., are discharged into the air. Meanwhile, the liquid containing catalyst particles 34 are sent to a solid-liquid separator 32 where the catalyst particles 34 in the form of metal oxide are recovered while the remaining treated water 33 is drained outside.

Functioning to remove the particles from a mixture containing water and catalyst particles, the solid-liquid separator 32 may be operated in the manner of separation through settling, centrifugation and/or filtration. It takes a lot of time to separate the cobalt and manganese catalyst particles through settling because they are as fine as ones of μm in diameter. Therefore, the separator is preferably equipped with a centrifuge and a filter.

When the waste water has a high concentration of organic compounds, an excess amount of an oxidant is needed, leading to an increase in the production of oxygen and carbon dioxide. Under these circumstances, there occurs unstable operation in the course of reducing the pressure in the pressure reducer. In this case, therefore, it is preferred that the pressure reduction follow rather than precede the removal of gaseous components.

With reference to FIG. 2, a process of treating waste water having a high content of organic compounds is illustrated in accordance with another embodiment of the present invention, in which the removal of gaseous components precedes the pressure

reduction. In the reactor 24, the carbon dioxide produced upon the decomposition of organic compounds is partly dissolved in the water within the equilibrium concentration and partly exists as a gas. Additionally, an excess amount of oxygen, which is fed in an amount 1~50 mol% more than the COD, is not reacted, but is drained from the reactor

5 24. In the condition where a large volume of gas components exists, the direct introduction of the waste water into the capillary pressure reducer 26 as in FI. 1 causes the formation of a slug flow in a gas-slurry state. Due to the large difference between frictional coefficients of gas and slurry, the slug flow makes the pressure fluctuate greatly, incurring extreme abrasion in the pressure control valve.

10 In the case where a large volume of gaseous components exists, accordingly, the waste water effluent from the reactor 24 exchanges heat with the waste water flowing into the heat exchanger 22, cooled in the cooler 25, and is then fed into the gas-liquid separator 31, in which gas is separated from liquid containing catalyst particles. The pressure of the gas-liquid separator 31 is adjusted with a gas pressure reducing valve 126
15 installed on the side of the gas outlet, thereby adjusting the pressure of the entire treatment process. After being deprived of gas, the mixed slurry of the catalyst particles and water in a high pressure state is discharged from the gas-liquid separator 31 as an automatic liquid level controlling valve 127 is opened by a liquid level controller for controlling the liquid level of the slurry when the liquid level reaches a
20 predetermined point.

In order to prevent the valves (e.g., pressure reducing valve 27) from being abraded, a pressure reducer 26 is provided behind the automatic valve 127. With passage through the pressure reducer 26, as described in FIG. 1, the high pressure fluid decreases in pressure from 41.5-250 bar to atmospheric pressure to 20 bar, thereby
25 retarding the abrasion rate of the pressure reducing valve 27. Following passage through the pressure reducing valve 27, the mixture is introduced into a solid-liquid

separator 32 where catalyst particles 34 are recovered while the remaining treated water is drained outside.

As described above, the present invention provides a method of effectively recovering catalyst components in the form of metal oxide particles from waste byproducts generated during the synthesis of terephthalic acid, as well as decomposing the organics.

Modes for Invention

A better understanding of the present invention may be obtained through the following examples which are set forth to illustrate, but are not to be construed as the limit of the present invention.

EXAMPLE 1

Composition of Waste from Terephthalic Acid Process

After being completely deprived of the solvents acetic acid and water, waste byproducts of terephthalic acid processes were analyzed for organic compounds and catalyst components. A typical composition of the waste taking place in the course of synthesizing terephthalic acid is given in Table 1, below.

In a waste from terephthalic acid process, as seen in Table 1, terephthalic acid and benzoic acid are prevalent, amounting to 85% in total. Isophthalic acid and p-toluic acid are also contained in small amounts, along with impurities.

TABLE 1

Composition of Waste from Terephthalic Acid Process

Components	Contents (wt%)
Terephthalic acid	15.0
Benzoic Acid	70.0
Isophthalica acid	8.3

p-Toluic acid	4.2
Other organic impurities	1.5
Co	0.5
Mn	0.2
Br	0.3

EXAMPLE 2

Decomposition of Waste from Terephthalic Acid Process

5 As described above, the waste produced during the synthesis of terephthalic acid was a mixture of organics and catalyst components. The waste was mixed with water, increased in solubility with NaOH, and subjected to a treatment process with some particles remaining undissolved.

The waste water influent to the process was found to have a COD (chemical
10 oxygen demand) of 82,300 mg O₂/ℓ, and was adjusted to a pH of 6.0 by adding 1.786 wt% of NaOH. The reactor used in the treatment process was a tubular type, and was designed to initiate the oxidation reaction at 298°C at the inlet with a temperature gradient gradually increasing to 361°C at the outlet. In the reactor, a pressure of 250bar was maintained and the reactant remained for 4.3 min. Oxygen was supplied in an
15 amount 20% more than the COD. After oxidative decomposition, the resulting waste water was measured to have a pH of 7.2, which was higher than that of the original waste water, and to have a COD of 3,570 mg O₂/ℓ, thus showing a decomposition rate of 95.7%.

20 EXAMPLE 3

Decomposition Rate of Organics According to Reaction Time

Waste from a terephthalic acid process was mixed with water and sodium hydroxide to give primary waste water which had a COD of 84,000mg O₂/ℓ and was adjusted to a pH of 5.5. A pressure of 250 bar was maintained throughout the process before being reduced, and oxygen was fed in an amount 20% greater than the amount of
 5 COD. The treated water was measured for COD and decomposition rate according to reaction condition and the results are given in Table 2, below.

As seen in Table 2, it is preferred that the waste water flowing in to the reactor be maintained at 250°C or higher. A higher reaction temperature or a longer residence time assured a greater organic decomposition rate. If the temperature of the waste
 10 water influent into the reactor is lower than 250°C, the initial reaction rate is too slow to obtain a sufficient organic decomposition rate because it is difficult to increase the temperature to 250°C, at which the oxidative reaction starts, although the residence time is extended.

15

TABLE 2
Treatment of Waste Water

Temp. at Reactor Inlet(°C)	Temp. at Reactor Outlet(°C)	Residence Time(min)	COD of Treated Water (mg O ₂ /l)	COD Decomposition Rate(%)
231	350	21	11,000	86.9
250	364	30	120	99.9
256	365	20	235	99.7
300	370	7.5	190	99.8

EXAMPLE 4

Change of Treated Water in Metal Content with Anti-corrosion agent

20

Consisting mainly of hydrobromic acid and organic acids, such as terephthalic acid, benzoic acid, p-toluic acid, etc., the waste from a terephthalic acid process is acidic

in water. Due to the low extent of dissociation of the organic acids, the waste does not dissolve well in water, but forms slurry. In order to prevent the corrosion attributable to hydrobromic acid(HBr) and solve the problem of the low extent of dissociation of the organic acids leading to the formation of slurry, an alkali selected from among sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium hydrogen carbonate (NaHCO_3), potassium hydroxide (KOH), potassium carbonate (K_2CO_3) and combinations thereof is fed as an anti-corrosion agent to the waste. When mixed with an alkali in water, the waste is dissolved to a significant extent so as to yield waste water in which some particles remain undissolved. The waste water can be readily fed to the treatment process for oxidative decomposition, and is additionally non-corrosive.

The waste water was analyzed for corrosion resistance in conjunction with various anti-corrosive agents. This analysis was carried out with a tubular reactor which was maintained at 360°C at the outlet and at 250 bar throughout with a designed residence time of 4.5~5 min. Oxygen was supplied in an amount 20% more than the COD of the waste water, 84,000 mg O_2/l .

The waste was decomposed by adding thereto water and an alkaline solution of sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium hydrogen carbonate (NaHCO_3), potassium hydroxide (KOH), and/or potassium carbonate (K_2CO_3) and the resulting waste water was analyzed for the content of four metals, Fe, Ni, Cr, and Mo, the main components of the nickel alloy I-625 from which the reactor and the test apparatus were made. The high contents of these metal components in the waste water implied that the process apparatuses such as the reactor, the heat exchanger, etc. underwent corrosion to higher degrees.

As is apparent from the data of Table 3, the use of anti-corrosion agents for maintaining the waste water at a pH from 4~7 remarkably reduces the corrosion of the apparatus while significant corrosion proceeds in the absence of an anti-corrosion agent.

TABLE 3

Change of Waste Water in Metal Content with Anti-Corrosion Agent

Anti-Corrosion Agent	Waste Water pH	Content of Metal in Treated Water[ppm]			
		Fe	Ni	Cr	Mo
none	2.0	30	550	220	460
NaOH	12.3	15	90	33	28
NaOH+NaHCO ₃	9.8	18	4	6	5
NaOH	6.0	-	-	2.3	1.5
NaOH+NaHCO ₃	5.0	-	1.5	-	-
NaOH+Na ₂ CO ₃	5.5	1.0	1.0	0.5	-
KOH+NaHCO ₃	5.8	0.8	1.5	0.5	-
KOH+K ₂ CO ₃	4.5	1.5	2.0	-	-

5 EXAMPLE 5

Size Distribution of Recovered Catalyst Particles

Waste byproducts from terephthalic acid processes were mixed with water, sodium hydroxide and sodium hydrogen carbonate, and subjected to oxidative reaction at 360°C. Catalyst particles contained in the treated water were analyzed for size distribution, and the results are depicted in FIG. 3. By volume, the particles were measured to have a size of $d(0.1) = 1.175 \mu\text{m}$, $d(0.5) = 3.005 \mu\text{m}$, and $d(0.9) = 18.324 \mu\text{m}$.

EXAMPLE 6

15 Catalyst Recovery

The oxidative decomposition of the waste byproducts was conducted at 360°C under a pressure of 250 bar while a combination of sodium hydroxide and sodium

- hydrogen carbonate was used as an anti-corrosion agent to control the pH of the waste water. The contents of cobalt and manganese catalysts in the waste water were quantitatively analyzed using ICP-MS so as to calculate the amounts of the catalysts used. To recover the catalysts, the waste water was allowed to settle and filtered.
- 5 Amounts of the catalysts fed and recovered are summarized in Table 4, below. Taken together, the data of Table 4 demonstrate that the method according to the present invention is superior in catalyst recovery yield.

TABLE 4

Catalyst Recovery Yield

Anticorrosive	Amount of Catalyst Recovered(g)		Amount of Catalyst Fed(g)		Recovery Yield(%)	
	Co	Mn	Co	Mn	Co	Mn
NaOH	23.0	8.5	25.1	11.0	91.6	77.3
NaOH	22.3	15.1	33.9	18.6	65.8	81.2
NaOH NaHCO ₃	18.7	9.3	20.2	11.2	92.6	83.0
NaOH K ₂ CO ₃	22.5	10.5	24.8	13.0	90.7	80.8
NaHCO ₃ Na ₂ CO ₃	25.7	15.8	28.8	17.2	89.2	91.9

Claims

1. A method for treating waste byproducts from terephthalic acid process, comprising:
- a) homogeneously mixing the waste byproducts with water and an anti-
 - 5 corrosion agent to prepare waste water, said waste byproducts containing catalysts for use in the synthesis of terephthalic acid;
 - b) heating the waste water under pressure with the proviso that the waste water be in a liquid state;
 - c) reacting the heated waste water with an oxidant to decompose organics
 - 10 contained therein and convert the catalysts into metal oxides;
 - d) cooling the hot treated water of step c);
 - e) depressurizing the cooled treated water and separating the depressurized treated water into gaseous and liquid effluents with the catalyst particles contained therein, to discharge the gaseous effluent; and
 - 15 f) recovering the catalyst particles from the liquid effluent, said catalyst particles including cobalt and manganese.
2. The method as set forth in claim 1, wherein the waste water in step a) contains organics in an amount from 0.1 to 30 wt%.
- 20
3. The method as set forth in claim 1, further comprising the step of separating the cooled treated water into gaseous and liquid effluents and depressurizing the separated effluents, instead of step e).
- 25
4. The method as set forth in claim 1, wherein the anti-corrosion agent is

selected from a group consisting of sodium hydroxide, sodium hydrogen carbonate, sodium carbonate, potassium hydroxide, potassium carbonate, and combinations thereof.

5 5. The method as set forth in claim 1, wherein the anti-corrosion agent is used to maintain the waste water at pH 4~7.

6. The method as set forth in claim 1, wherein the steps b) and c) are performed at 250~370°C under a pressure from 41.5 to 250 bar.

10 7. The method as set forth in claim 1, wherein the oxidant is selected from a group consisting of oxygen, air, an oxygen-containing gas mixture, ozone, a hydrogen peroxide solution, oxygen-dissolved water, and combinations thereof.

15 8. The method as set forth in claim 1, wherein the oxidant is used in an amount 1 mol%~50 mol% more than a theoretical value necessary to decompose the organic compounds completely.

20 9. The method as set forth in claim 1, wherein the waste water is chilled to 25~100°C in step d).

10. The method as set forth in claim 1 or 3, wherein the waste water was depressurized to a range from atmospheric pressure to 20 bar in step e).

25 11. The method as set forth in claim 1 or 3, wherein step e) is performed in a capillary tube.

12. The method as set forth in claim 1, wherein step f) is performed in a solid-liquid separator equipped with a device selected from a group consisting of a precipitator, a centrifuge, a filter and combinations thereof.

FIGURE

FIG. 1

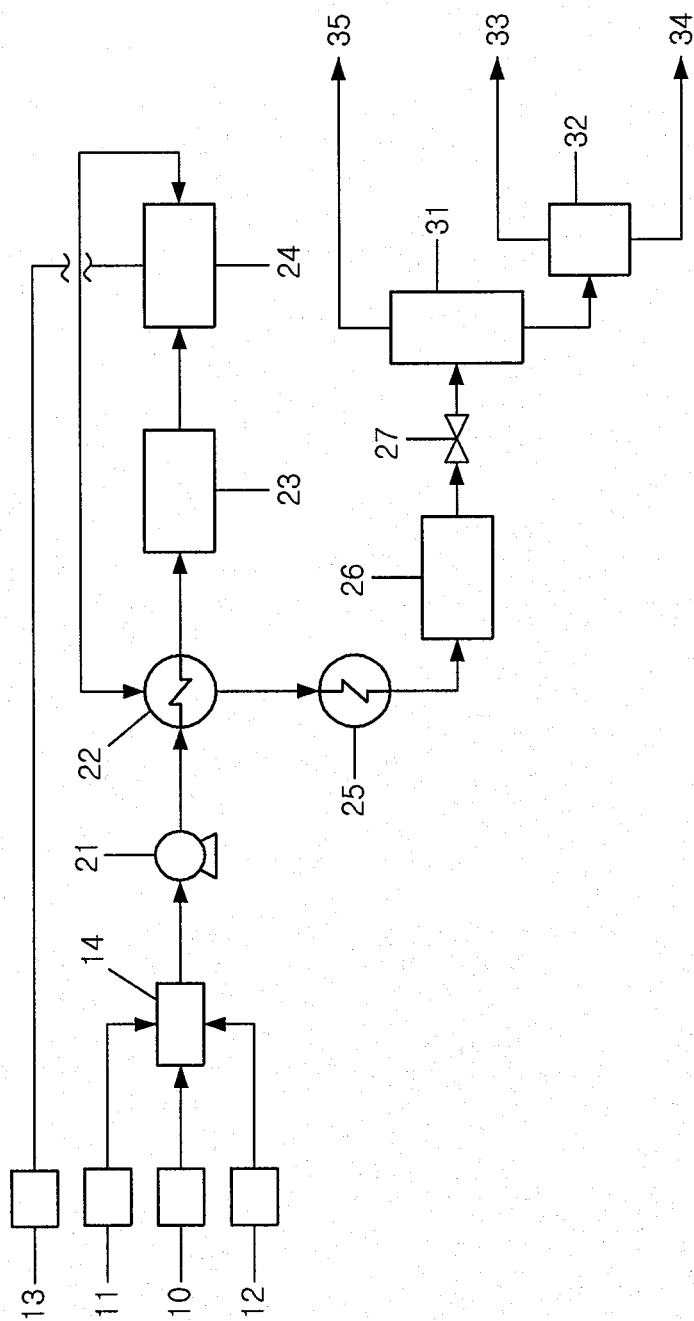


FIG. 2

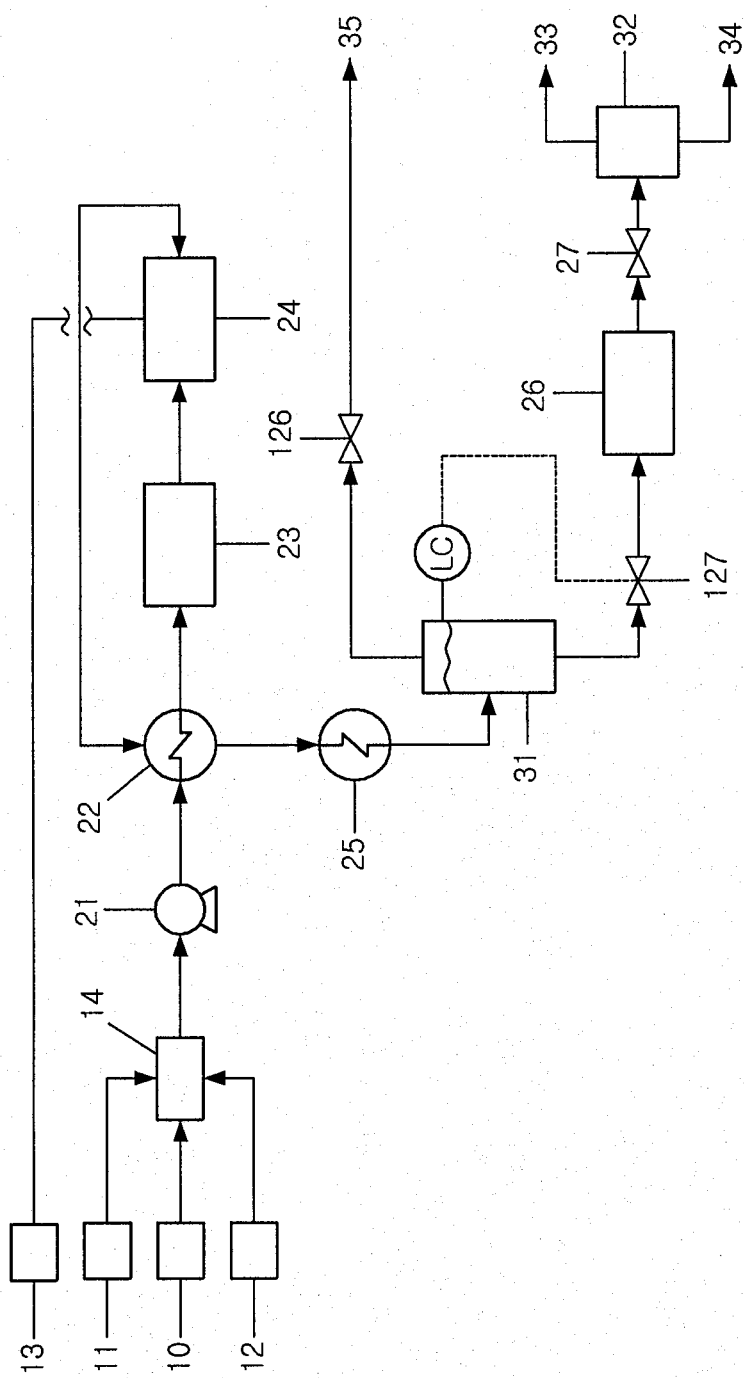
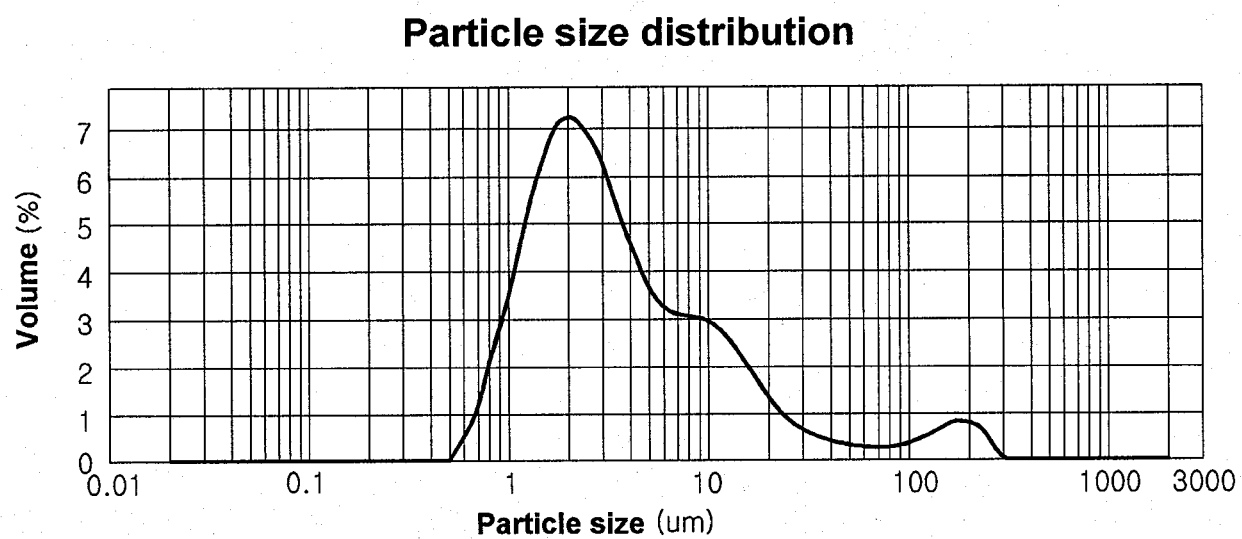


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2006/003515**A. CLASSIFICATION OF SUBJECT MATTER*****B01J 31/40(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)

B01J, B01D, C07C

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

Korean Patents and applications for inventions since 1975

Korean Utility models and applications for Utility models since 1975

Japanese Utility models and application for Utility models since 1975

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

eKIPASS in KIPO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-1979-000412 A (MATSUYAMA PETROCHEMICALS INC) 14 May 1979 See examples and claim	1 - 12
A	US 04939297 A (EASTMAN KODAK CO) 3 July 1990 See claim 1 and example	1 - 12
A	US 2004/0245176 A1 (KENNY UANDOLPH PARKER) 9 December 2004 See [0014]-[0033] and claims	1 - 12
A	JP 11-165079 A (TORAY IND INC) 22 June 1999 See [0015]-[0019] and example	1 - 12
A	JP 10-015390 A (MITSUBISHI GAS CHEM CO INC etc) 20 January 1998 See [0007], [0013], [0018]	1 - 12
A	US 4410449 A (DYNAMIT NOBEL) 18 October 1983 See abstract and claims	1 - 12
A	US 4250330 A (MONTEDESON S.P.A.) 10 February 1981 See example 1 and claims	1 - 12

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

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

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

"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

"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

07 DECEMBER 2006 (07.12.2006)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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