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(54) Title: METHOD FOR REGENERATING COS CONVERSION CATALYST

(54) 発明の名称: C O S 転換触媒の触媒再生方法

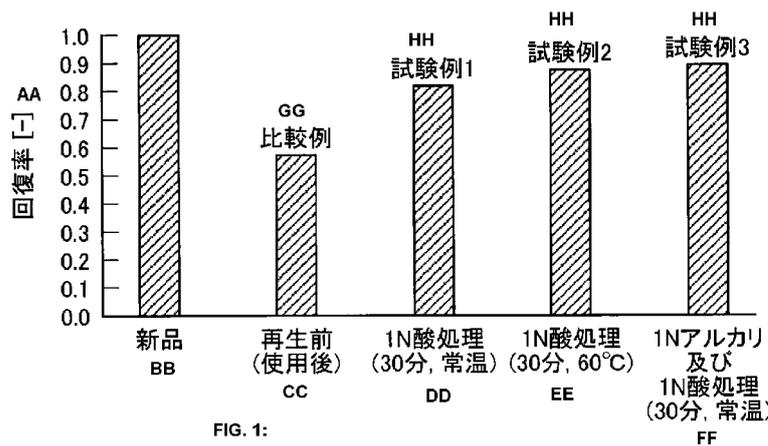


FIG. 1:
 AA Recovery rate [-]
 BB Fresh
 CC Before regeneration (after use)
 DD Treatment with 1N acid (30min, ordinary temperature)
 EE Treatment with 1N acid (30min, 60°C)
 FF Treatment with 1N alkali and 1N acid (30min, ordinary temperature)
 GG Comparative example
 HH Test example

(57) Abstract: A method for regenerating a carbonyl sulfide (COS) conversion catalyst for hydrolyzing COS which is contained in a gas obtained by gasifying a carbon material, comprising: immersing a spent COS conversion catalyst in an acid solution for a prescribed time; thereby removing poisoning substances adhering to the surface of the COS conversion catalyst; and thus regenerating the COS conversion catalyst.

(57) 要約: 本発明にかかるC O S 転換触媒の再生方法は、炭素原料をガス化してガス化ガス中の硫化カルボニル (C O S) を加水分解するC O S 転換触媒の再生方法であって、使用済のC O S 転換触媒を、酸溶液中に所定時間浸漬処理することにより、C O S 転換触媒の表面に付着した被毒物質を除去し、C O S 転換触媒を再生することができる。

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— 国際調査報告 (条約第 21 条(3))

METHOD FOR REGENERATING COS HYDROLYSIS CATALYST

TECHNICAL FIELD

[0001]

The present invention relates to a method for regenerating a COS hydrolysis catalyst.

BACKGROUND ART

[0002]

In recent years, there has been a demand for the effective utilization of low-quality fuels such as coal or heavy oil from the perspective of diversification so as to actively use low-quality fossil fuels in addition to high-quality fossil fuels. In addition, integrated coal gasification combined cycle (IGCC), in which gas turbines using gas fuel and steam turbines are used in combination, and power generation by means of introducing hydrocarbon gas into fuel cells are also becoming widespread from the perspective of improving power generation efficiency in the field of thermal power generation. Therefore, there is research and development underway to gasify low-quality fuels and use them for such power generation.

[0003]

Incidentally, a low-quality fuel typically contains a large amount of sulfur compounds, and when a gas obtained by gasifying this fuel is combusted directly, the sulfur compounds are discharged from the chimney into the atmosphere as sulfur oxides, which become a source of environmental pollution such as acid rain. Therefore, in ordinary thermal power generation, a method of installing an exhaust gas desulfurizer on the downstream side of the boiler so as to remove sulfur compounds as gypsum, for example, has been put into practical application. However, in combined cycle power generation, the inlet temperature of a gas turbine is higher than the boiler temperature in ordinary thermal power generation, so the corrosion of the material is substantial. Therefore, it is necessary to protect the material by removing various impurities such as sulfur compounds on the upstream side rather than the downstream side of the gas turbine. For example, when installing a fuel cell power generator, it is essential to secure power generation efficiency and durability by protecting the material, and various impurities must be similarly removed on the upstream side of the fuel cell.

[0004]

A so-called wet gas purification process, wherein water-soluble components are removed with a water scrubber and hydrogen sulfide (H₂S) is removed with an aqueous amine solution, has been put into practical application as such a method for removing impurities. However, although hydrogen sulfide (H₂S) can be removed with an aqueous amine solution, carbonyl sulfide (COS) cannot be removed. Therefore, a hydrolysis reaction expressed by formula (1) is performed using a COS hydrolysis catalyst so as to accelerate a reaction for converting the substance into the form of hydrogen sulfide (H₂S) which can be removed with an aqueous amine solution.



[0005]

Here, examples of known COS hydrolysis catalysts include catalysts containing titania, catalysts containing alumina, a group IV metal and barium, and catalysts containing an alkali metal, chromium oxide, and alumina (Patent Document 1).

[0006]

Incidentally, in integrated coal gasification combined cycle (IGCC), there is a problem in that when a COS hydrolysis catalyst is used continuously for COS in a gasified gas, so-called catalyst poisoning occurs, wherein the dust content (for example, sulfides) in the gasified gas covers the surface of the COS hydrolysis catalyst, which causes a decrease in catalyst performance.

The catalyst with reduced performance as a result of poisoning is reused by means of regeneration treatment.

[0007]

A method of performing heat treatment on a catalyst and then re-supporting sodium carbonate, for example, has been proposed as such a catalyst regeneration method (Patent Document 2).

CITATION LIST

Patent Literature(s)

[0008]

Patent Document 1: Japanese Unexamined Patent Application Publication No. 2004-75712A

Patent Document 2: Japanese Unexamined Patent Application Publication No. 2001-162174A

SUMMARY OF INVENTION

Technical Problem

[0009]

A method for regenerating a COS catalyst according to conventional technology has a problem in that since the active component of the catalyst is once again supported, the cost of relatively expensive chemicals such as potassium carbonate and sodium carbonate increases.

[0010]

Therefore, there is a demand for the emergence of a method for regenerating a COS hydrolysis catalyst without using relatively expensive chemicals, whereby catalyst regeneration is inexpensive.

[0011]

In light of the problem described above, the present invention seeks to provide a method for inexpensively regenerating a COS hydrolysis catalyst.

Solution to Problem

[0012]

In order to solve the problem described above, a first invention of the present invention is a method for regenerating a Ba/TiO₂ carbonyl sulfide (COS) hydrolysis catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material, wherein a spent Ba/TiO₂ COS hydrolysis catalyst is immersed in an acid solution for a prescribed amount of time.

[0013]

With the present invention, by immersing a spent, degraded Ba/TiO₂ COS hydrolysis catalyst in an acid solution, poisoning components such as sulfides adhering to the catalyst surface are removed, which makes it possible to regenerate the catalyst.

[0014]

A second invention is a method for regenerating a Ba/TiO₂ carbonyl sulfide (COS) hydrolysis catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material, wherein a spent Ba/TiO₂ COS hydrolysis catalyst is immersed in an alkali solution for a prescribed amount of time and then immersed in an acid solution for a prescribed amount of time.

[0015]

With the present invention, by immersing a spent, degraded Ba/TiO₂ COS hydrolysis catalyst in an alkali solution and then immersing the catalyst in an acid solution so as to neutralize the solution, poisoning components such as sulfides adhering to the catalyst surface are removed, which makes it possible to regenerate the catalyst.

[0016]

A third invention is a method for regenerating a Ba/TiO₂ carbonyl sulfide (COS) hydrolysis catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material, wherein a spent Ba/TiO₂ COS hydrolysis catalyst is immersed in an acid solution for a prescribed amount of time and then immersed in an alkali solution for a prescribed amount of time.

[0017]

With the present invention, by immersing a spent, degraded Ba/TiO₂ COS hydrolysis catalyst in an acid solution and then immersing the catalyst in an alkali solution so as to neutralize the solution, poisoning components such as sulfides adhering to the catalyst surface are removed, which makes it possible to regenerate the catalyst.

[0018]

A fourth invention is the method for regenerating a Ba/TiO₂ COS hydrolysis catalyst according to one of the first through third inventions, wherein the immersion is performed in a prescribed heated state (for example, 60°C to 80°C).

[0019]

With the present invention, by immersing a spent, Ba/TiO₂ degraded COS hydrolysis catalyst in an acid solution in a heated state, poisoning components such as sulfides adhering to the catalyst surface are removed, which makes it possible to regenerate the catalyst.

Advantageous Effects of Invention

[0020]

With the present invention, poisoning components adhering to a Ba/TiO₂ COS hydrolysis catalyst can be removed by performing chemical washing with an acid, an alkali, or the like, which makes it possible to reuse the substance.

Brief Description of Drawing(s)

[0021]

FIG. 1 illustrates the results of testing the catalyst recovery rate under various conditions.

FIG. 2 illustrates the relationship between the change in temperature of a COS hydrolysis catalyst and the COS conversion rate.

Description of Embodiments

[0022]

The following is a detailed description of preferred embodiments with reference to the attached drawings. Note that the invention is not limited by the embodiments, and when a plurality of embodiments are present, the invention is intended to include a configuration combining these embodiments. In the following, reference to COS hydrolysis catalyst and spent COS hydrolysis catalyst refers to Ba/TiO₂ COS hydrolysis catalyst.

Embodiment 1

[0023]

The method for regenerating a COS hydrolysis catalyst according to Embodiment 1 will be described.

The method for regenerating a COS hydrolysis catalyst according to Embodiment 1 is a method for regenerating a carbonyl sulfide (COS) hydrolysis catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material such as coal, for example, wherein a spent COS hydrolysis catalyst is immersed in an acid solution for a prescribed amount of time.

[0024]

The procedure of the method for regenerating a catalyst according to Embodiment 1 will be described hereinafter.

(1) First, a COS hydrolysis catalyst with which a COS conversion device of a coal gasification power plant has been filled is extracted.

(2) The dust content adhering to the extracted COS hydrolysis catalyst is removed by a gas spraying device such as an air blower.

(3) Next, a prescribed amount of an acid solution is placed in an immersion vessel, and the air-blown COS hydrolysis catalyst is immersed in the acid solution. Here, the amount of the acid solution is at least an amount which allows the COS hydrolysis catalyst to be sufficiently hidden. More preferably, the amount is such that the volume ratio of the acid solution/COS hydrolysis catalyst is at least 3.

As the acid solution, sulfuric acid (H₂SO₄), hydrochloric acid (HCl), nitric acid (HNO₃), or the like with a concentration of at least 0.1 N and approximately 1 N can be used.

In this chemical treatment, when the chemical solution is heated (for example, 60 to 80°C), the removal efficiency of adhering sulfides or the like improves.

(4) The substance is left and immersed for approximately 15 to 60 minutes in this immersed state.

(5) The immersed COS hydrolysis catalyst is then immersed and water-washed in water (for example, ion-exchanged water) prepared in a separate vessel. Here, the amount of the water washing solution is at least an amount

which allows the COS hydrolysis catalyst to be sufficiently hidden. More preferably, the amount is such that the volume ratio of water/COS hydrolysis catalyst is at least 3.

(6) The substance is left and water-washed for approximately 15 to 60 minutes, for example, in this immersed state.

(7) After water washing, the COS hydrolysis catalyst is taken out and dried after excess liquid in the catalyst is removed.

Drying may be performed by means of natural drying or heat drying. Here, in the case of heat drying, the temperature is preferably from 80°C to 200°C and particularly preferably from 110°C to 150°C.

[0025]

By performing chemical washing with an acid in this way, poisoning components adhering to a COS hydrolysis catalyst can be removed, which makes it possible to reuse the substance.

[0026]

Here, the dust removal by means of air blowing in step (2) can be omitted depending on the amount of dust adhering to the catalyst.

Embodiment 2

[0027]

The method for regenerating a COS hydrolysis catalyst according to Embodiment 2 will be described.

The method for regenerating a COS hydrolysis catalyst according to Embodiment 2 is a method for regenerating a carbonyl sulfide (COS) hydrolysis catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material such as coal, for example, wherein a spent COS hydrolysis catalyst is immersed in an alkali solution for a prescribed amount of time.

[0028]

The procedure of the method for regenerating a catalyst according to Embodiment 2 will be described hereinafter.

(1) First, a catalyst with which a COS conversion device of a coal gasification power plant has been filled is extracted.

(2) The dust content adhering to the extracted COS hydrolysis catalyst is removed by a gas spraying device such as an air blower.

(3) Next, a prescribed amount of an alkali solution is placed in an immersion vessel, and the air-blown COS hydrolysis catalyst is immersed in the alkali solution. Here, the amount of the alkali solution is at least an amount which allows the COS hydrolysis catalyst to be sufficiently immersed. More

preferably, the amount is such that the volume ratio of the alkali solution/COS hydrolysis catalyst is at least 3.

As the alkali solution, sodium hydroxide (NaOH), ammonia water (NH₄OH), sodium carbonate (Na₂CO₃), or the like with a concentration of at least 0.1 N and approximately 1 N can be used.

In this chemical treatment, when the chemical solution is heated (for example, 60 to 80°C), the removal efficiency of adhering sulfides or the like improves.

(4) The substance is left and immersed for approximately 15 to 60 minutes, for example, in this immersed state.

(5) The immersed COS hydrolysis catalyst is then immersed and water-washed in water (for example, ion-exchanged water) prepared in a separate vessel. Here, the amount of the water washing solution is at least an amount which allows the COS hydrolysis catalyst to be sufficiently hidden. More preferably, the amount is such that the volume ratio of water/COS hydrolysis catalyst is at least 3.

(6) The substance is left and water-washed for approximately 15 to 60 minutes, for example, in this immersed state.

(7) After water washing, the COS hydrolysis catalyst is taken out and dried after excess liquid in the catalyst is removed.

Drying may be performed by means of natural drying or heat drying. In addition, the substance may also be calcined.

[0029]

By performing chemical washing with an alkali in this way, poisoning components adhering to a COS hydrolysis catalyst can be removed, which makes it possible to reuse the substance.

Embodiment 3

[0030]

The method for regenerating a COS hydrolysis catalyst according to Embodiment 3 will be described.

The method for regenerating a COS hydrolysis catalyst according to Embodiment 3 is a method for regenerating a carbonyl sulfide (COS) hydrolysis catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material such as coal, for example, wherein a spent COS hydrolysis catalyst is immersed in an alkali solution for a prescribed amount of time and then immersed in an acid solution for a prescribed amount of time.

[0031]

The procedure of the method for regenerating a catalyst according to Embodiment 3 will be described hereinafter.

(1) First, a catalyst with which a COS conversion device of a coal gasification power plant has been filled is extracted.

(2) The dust content adhering to the extracted COS hydrolysis catalyst is removed by a gas spraying device such as an air blower.

(3) Next, a prescribed amount of an alkali solution is placed in an immersion vessel, and the air-blown COS hydrolysis catalyst is immersed in the alkali solution. Here, the amount of the alkali solution is at least an amount which allows the COS hydrolysis catalyst to be sufficiently hidden. More preferably, the amount is such that the volume ratio of the alkali solution/COS hydrolysis catalyst is at least 3.

As the alkali solution, sodium hydroxide (NaOH), ammonia water (NH₄OH), sodium carbonate (Na₂CO₃), or the like with a concentration of at least 0.1 N and approximately 1 N can be used.

In this chemical treatment, when the chemical solution is heated (for example, 60 to 80°C), the removal efficiency of adhering sulfides or the like improves.

(4) The substance is left and immersed for approximately 15 to 60 minutes, for example, in this immersed state.

(5) Next, a prescribed amount of an acid solution is placed in a separate immersion vessel, and the alkali-treated COS hydrolysis catalyst is immersed in the acid solution. Here, the amount of the acid solution is at least an amount which allows the COS hydrolysis catalyst to be sufficiently hidden. More preferably, the amount is such that the volume ratio of the acid solution/COS hydrolysis catalyst is at least 3.

As the acid solution, sulfuric acid (H₂SO₄), hydrochloric acid (HCl), nitric acid (HNO₃), or the like with a concentration of at least 0.1 N and approximately 1 N can be used.

In this chemical treatment, when the chemical solution is heated (for example, 60 to 80°C), the removal efficiency of adhering sulfides or the like improves.

(6) Further, the immersed COS hydrolysis catalyst is then immersed and water-washed in water (for example, ion-exchanged water) prepared in a separate vessel. Here, the amount of the water washing solution is at least an amount which allows the COS hydrolysis catalyst to be sufficiently hidden. More preferably, the amount is such that the volume ratio of water/COS hydrolysis catalyst is at least 3.

(7) The substance is left and water-washed for approximately 15 to 60 minutes, for example, in this immersed state.

(8) After water washing, the COS hydrolysis catalyst is taken out and dried after excess liquid in the catalyst is removed.

Drying may be performed by means of natural drying or heat drying. In addition, the substance may also be calcined.

[0032]

By performing chemical washing with an alkali and then neutralizing the substance with an acid in this way, poisoning components adhering to a COS hydrolysis catalyst can be removed, which makes it possible to reuse the substance.

Embodiment 4

[0033]

The method for regenerating a COS hydrolysis catalyst according to Embodiment 4 will be described.

Embodiment 4 is a method for regenerating a carbonyl sulfide (COS) hydrolysis catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material such as coal, for example, wherein a spent COS hydrolysis catalyst is immersed in an acid solution for a prescribed amount of time and then immersed in an alkali solution for a prescribed amount of time.

[0034]

The procedure of the method for regenerating a catalyst according to Embodiment 4 will be described hereinafter.

(1) First, a catalyst with which a COS conversion device of a coal gasification power plant has been filled is extracted.

(2) The dust content adhering to the extracted COS hydrolysis catalyst is removed by a gas spraying device such as an air blower.

(3) Next, a prescribed amount of an acid solution is placed in an immersion vessel, and the air-blown COS hydrolysis catalyst is immersed in the acid solution. Here, the amount of the acid solution is at least an amount which allows the COS hydrolysis catalyst to be sufficiently hidden. More preferably, the amount is such that the volume ratio of the acid solution/COS hydrolysis catalyst is at least 3.

As the acid solution, sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), or the like with a concentration of at least 0.1 N and approximately 1 N can be used.

In this chemical treatment, when the chemical solution is heated (for example, 60 to 80°C), the removal efficiency of adhering sulfides or the like improves.

(4) The substance is left and immersed for approximately 15 to 60 minutes, for example, in this immersed state.

(5) Next, a prescribed amount of an alkali solution is placed in a separate immersion vessel, and the acid-treated COS hydrolysis catalyst is immersed in the alkali solution. Here, the amount of the alkali solution is at least an amount which allows the COS hydrolysis catalyst to be sufficiently hidden. More preferably, the amount is such that the volume ratio of the alkali solution/COS hydrolysis catalyst is at least 3.

As the alkali solution, sodium hydroxide (NaOH), ammonia water (NH₄OH), sodium carbonate (Na₂CO₃), or the like with a concentration of at least 0.1 N and approximately 1 N can be used.

In this chemical treatment, when the chemical solution is heated (for example, 60 to 80°C), the removal efficiency of adhering sulfides or the like improves.

(6) Further, the immersed COS hydrolysis catalyst is then immersed and water-washed in water (for example, ion-exchanged water) prepared in a separate vessel. Here, the amount of the water washing solution is at least an amount which allows the COS hydrolysis catalyst to be sufficiently hidden. More preferably, the amount is such that the volume ratio of water/COS hydrolysis catalyst is at least 3.

(7) The substance is left and water-washed for approximately 15 to 60 minutes, for example, in this immersed state.

(8) After water washing, the COS hydrolysis catalyst is taken out and dried after excess liquid in the catalyst is removed.

Drying may be performed by means of natural drying or heat drying. In addition, the substance may also be calcined.

[0035]

By performing chemical washing with an acid and then neutralizing the substance with an alkali in this way, poisoning components adhering to a COS hydrolysis catalyst can be removed, which makes it possible to reuse the substance.

[0036]

[Test Examples]

Next, test examples illustrating the effect of the present invention will be described, but the present invention is not limited to these test examples.

[0037]

In Test Example 1, a spent COS hydrolysis catalyst is immersed in 1 N sulfuric acid for 30 minutes at room temperature and then washed with water for 30 minutes.

In Test Example 2, a spent COS hydrolysis catalyst is immersed in 1 N sulfuric acid for 30 minutes while heating (60°C) and then washed with water for 30 minutes.

In Test Example 3, a spent COS hydrolysis catalyst is immersed in a 1 N sodium hydroxide aqueous solution for 30 minutes at room temperature, and the alkali-treated COS hydrolysis catalyst is then neutralized by means of immersion in 1 N sulfuric acid for 30 minutes at room temperature and then washed with water for 30 minutes.

[0038]

The COS hydrolysis catalyst used in these tests is a Ba/TiO₂ honeycomb-type catalyst, and the temperature at which the COS conversion rate of the regenerated product was measured was 300°C.

[0039]

The recovery rate was determined from K/K_0 . Here, K is a reaction rate constant of the COS hydrolysis catalyst after regeneration, and K_0 is a reaction rate constant of a fresh COS hydrolysis catalyst.

[0040]

In these tests, the substances prior to regeneration (immediately after use) were used as comparative examples.

Using a fresh substance prior to use as a criterion of "1", the results of testing the catalyst recovery rate under various conditions are shown in FIG. 1.

[0041]

As illustrated in FIG. 1, in both acid treatment alone and treatment with both an alkali and an acid, an improvement in the catalyst recovery rate was confirmed in comparison to the catalysts prior to regeneration.

In particular, in acid treatment, a greater improvement in the catalyst recovery rate was confirmed when treatment was performed while heating than when treatment was performed at room temperature.

[0042]

According to these tests, the recovery rate is at least 80%, so in contrast to conventional cases in which a catalyst component is newly re-supported with a chemical, it was possible to establish a method for inexpensively regenerating a COS hydrolysis catalyst.

[0043]

FIG. 2 illustrates the relationship between the change in temperature of a COS hydrolysis catalyst and the COS conversion rate.

Using the regenerated COS hydrolysis catalyst of Test Example 1, the COS conversion rates at catalyst treatment temperatures (250°C, 300°C, and 350°C) were measured and shown in FIG. 2.

As illustrated in FIG. 2, it was confirmed that the substances of Test Example 1 (acid-treated products) always have a higher COS conversion rate than a catalyst prior to regeneration.

In particular, it was confirmed that the acid-treated products have a higher COS conversion rate than a fresh product from a temperature range exceeding approximately 270°C.

[0044]

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

[0045]

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for regenerating a Ba/TiO₂ carbonyl sulfide (COS) conversion catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material, wherein a spent Ba/TiO₂ COS hydrolysis catalyst is immersed in an acid solution for a prescribed amount of time.
2. A method for regenerating a Ba/TiO₂ carbonyl sulfide (COS) hydrolysis catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material, wherein a spent Ba/TiO₂ COS hydrolysis catalyst is immersed in an alkali solution for a prescribed amount of time;
and then immersed in an acid solution for a prescribed amount of time.
3. A method for regenerating a Ba/TiO₂ carbonyl sulfide (COS) hydrolysis catalyst by hydrolyzing COS which is contained in a gas obtained by gasifying a carbon raw material, wherein a spent Ba/TiO₂ COS hydrolysis catalyst is immersed in an acid solution for a prescribed amount of time;
and then immersed in an alkali solution for a prescribed amount of time.
4. The method for regenerating a Ba/TiO₂ carbonyl sulfide (COS) hydrolysis catalyst according to any one of claims 1 to 3, wherein the immersion is performed in a prescribed heated state.

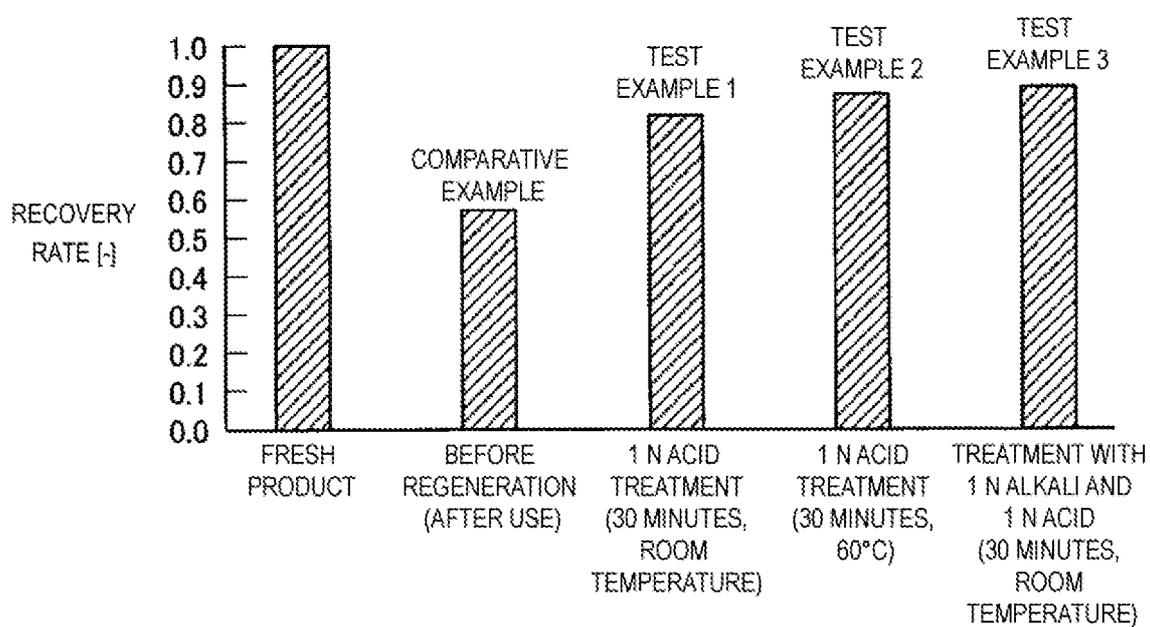


FIG. 1

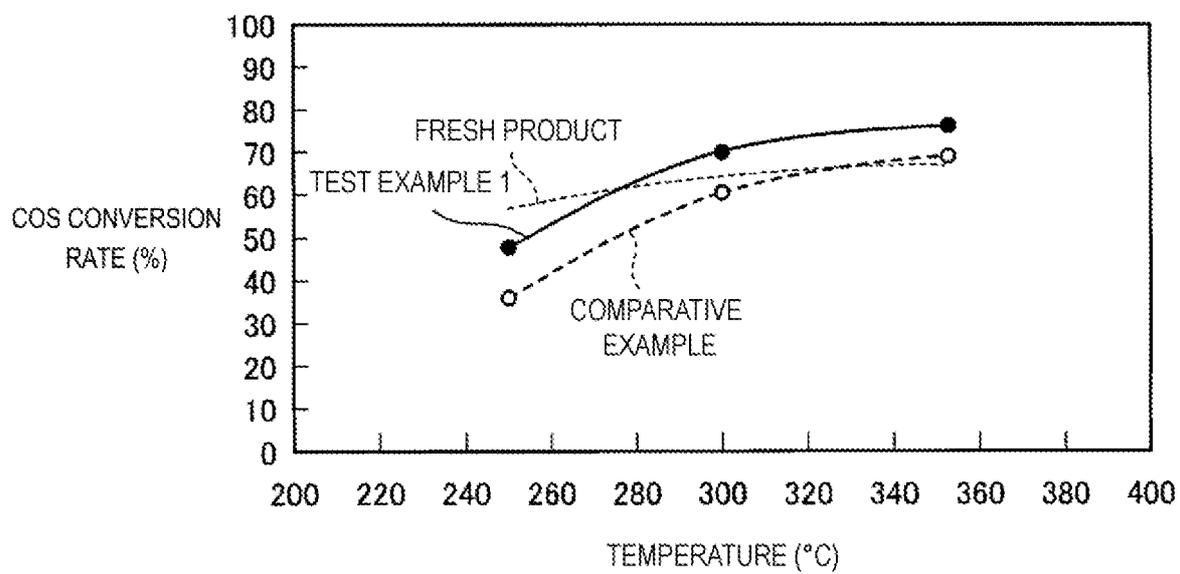


FIG. 2