

METHOD FOR PACKING CATALYST

BACKGROUND OF THE INVENTION

Field of the Invention

5 [0001]

The present invention relates to a method for packing a catalyst into a reaction tube of a reactor, particularly each reaction tube of a fixed-bed multi-tubular reactor used in an industrial scale.

10

Description of the Related Art

[0002]

It is common to use, as the method for packing solid particulates such as catalysts into a fixed-bed multi-tubular reactor, a method in which the solid particulates are packed by falling of the particulates from an upper opening of each reaction tube. The fixed-bed multi-tubular reactor used in an industrial scale includes several hundreds to several tens of thousands of reaction tubes.

20 There is required, as the method for packing a catalyst into each reaction tube, a method that has less variation in packing height and pressure loss of catalyst layers among the reaction tubes, and can facilitate the packing operation.

25 [0003]

JP2009-82865A discloses a method in which, when a catalyst for the production of an unsaturated aldehyde or a catalyst for the production of an unsaturated carboxylic acid prepared multiple times is packed into each reaction tube of a fixed-bed multi-tubular reactor, the variation in pressure loss in each reaction tube after packing the catalyst is satisfactorily suppressed and the catalyst is packed more simply and easily by weighing individually the catalyst for each reaction tube without depending on bulk density of the catalyst so that the weight of the catalyst packed into one reaction tube is within a range from 99 to 101% relative to an average value of each weight of the catalyst packed into each reaction tube, and then packing individually the catalyst into each reaction tube so that the packing rate of the catalyst into one reaction tube is within a range from 80 to 120% relative to an average value of each packing rate into each reaction tube.

Also, JP2009-82865A discloses a catalyst packing machine that can supply a catalyst to each reaction tube in a given supply rate by a conveyor and shorten the operation time required to supply a catalyst to the reaction tube, and also can reduce the worker's labor and suppress the variation in pressure loss in catalyst layers.

[0004]

However, the above conventional methods have a

problem that the amount of a catalyst packed must be weighed individually for each reaction tube, and it is difficult to adjust the height of a catalyst layer packed in each reaction tube to a predetermined height. Thus, it was difficult to solve the problems such as shortening of the operation time required to supply a catalyst to reaction tubes and reduction of the worker's labor, and variation in pressure loss in catalyst layers.

SUMMARY OF THE INVENTION

[0005]

An object of the present invention is to provide a method for packing a catalyst used mainly in a fixed-bed multi-tubular reactor, that can shorten the labor time required to supply a catalyst to reaction tubes and reduce the worker's labor, and also can suppress the variation in pressure loss in catalyst layers.

[0006]

The present inventors have intensively studied to solve the above problem. As a result, they have found that the above object can be achieved, in case a catalyst is packed into each reaction tube of a fixed-bed multi-tubular reactor, by inserting a diffuse-reflective type photoelectric sensor into the reaction tube up to a

predetermined height, detecting the height of the catalyst
by the photoelectric sensor, and packing the catalyst
individually into each reaction tube so that the packing is
stopped at the predetermined height, and thus the present
5 invention has been completed.

[0007]

That is, the method for packing a catalyst of the
present invention includes the following constitutions.

(1) A method for packing a solid catalyst into a reaction
10 tube from the upper side of the reaction tube, which
comprises:

disposing, in the reaction tube, a diffuse-reflective
type photoelectric sensor in which a white drawing paper is
used as a standard detection object, and a detection
15 distance as a maximum distance that enables detection of
the standard detection object is within a range from 90 to
1,000 mm; and

detecting a packing height of the catalyst by the
photoelectric sensor, and stopping the packing of the
20 catalyst when the packing height of the catalyst reaches a
predetermined value.

(2) The method for packing a catalyst according to (1),
wherein the packing of the catalyst is stopped using
control means that stops conveying means of the catalyst by
25 a detection signal output from the photoelectric sensor.

(3) The method for packing a catalyst according to (1) or (2), wherein control means is used that stops the packing of the catalyst into the reaction tube when detection light irradiated downwardly from the photoelectric sensor

5 reflects on a surface of the packed catalyst and the quantity of light received returning to a light receiving section of the photoelectric sensor exceeds a predetermined threshold value.

(4) The method for packing a catalyst according to any
10 one of (1) to (3), wherein the photoelectric sensor in the reaction tube is covered with a protective tube, and air, an inert gas, or a mixed gas thereof flows from the upper side toward the lower side in the protective tube.

[0008]

15 According to the present invention, in case a catalyst is packed into each reaction tube of a fixed-bed multi-tubular reactor used in an industrial scale, the height of a catalyst layer in each reaction tube after packing the catalyst can be set to a predetermined height
20 without previously measuring the weight of the catalyst, and the above catalyst can be packed more simply and easily. As a result, the variation in pressure loss in each reaction tube is satisfactorily suppressed when the reactor is used, and distribution of the catalyst in each reaction
25 tube tends to be identical. Accordingly, the present

method has the effect capable of preventing the difference of reaction state between reaction tubes, facilitating the temperature control for reaction tubes and reducing the cost of the catalyst using up the catalyst in each reaction tube until its life.

Also, when the photoelectric sensor in the reaction tube is covered with a protective tube, and air, an inert gas or a mixed gas thereof is supplied into the protective tube from the upper side, as described in (4), it is possible to prevent the reduction of sensitivity of a light receiving section and detection light of the photoelectric sensor by dust raising in the reaction tube when packing the catalyst. Thus, the present method has the effect capable of carrying out stable packing operation of the catalyst over a long period.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

Fig. 1 is an explanatory view showing an embodiment of the present invention.

Fig. 2 is a cross-sectional view showing an example of a protective tube in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0010]

The present invention will be described in more detail below with reference to the drawings. Fig. 1 is an explanatory view showing an embodiment of the present invention.

5 [0011]

As shown in the drawing, in the method for packing a catalyst according to the present invention, a diffuse-reflective type photoelectric sensor 1 is disposed in a cylindrical reaction tube 10 of a fixed-bed multi-tubular reactor, or inserted from the upper side into the fixed-bed multi-tubular reactor. Then, a solid catalyst 3 is conveyed from the upper side by a belt conveyor 4, and falls to the lower side of the reaction tube 10 thereby being packed in the tube.

15 The photoelectric sensor 1 detects a packing height of the catalyst 3. When the photoelectric sensor 1 detects a sign that the packing height of the catalyst reaches a previously set height, the packing of the catalyst is stopped.

20 [0012]

The photoelectric sensor 1 in the present invention refers to a so-called diffuse-reflective type photoelectric sensor in which light such as visible light and infrared light is used as a light source, and light from a detection section (irradiation section) is emitted as signal light,

25

and the light reflected from a detection object is detected at a light receiving section.

[0013]

By using such a photoelectric sensor 1, detection can
5 be carried out without contacting with a catalyst, and thus
neither the catalyst nor the sensor per se is not damaged.
Also, since detection is carried out by surface reflection
on the catalyst, there is an advantage that the packing
height of the catalyst can be precisely detected. There is
10 also an advantage that the sensor 1 has a long life and
hardly needs maintenance.

[0014]

The method for packing a catalyst is a method that
includes the steps of inserting the photoelectric sensor 1
15 into reaction tube 10 up to a predetermined height while a
detection section and a light receiving section face the
lower side of the reaction tube 10, initiating the packing
of the catalyst 3, detecting the height of the packed
catalyst 3 using the photoelectric sensor 1, and stopping
20 the packing of the catalyst when the height of the catalyst
3 reaches a predetermined packing height.

[0015]

In the photoelectric sensor 1, detection light
emitted from the sensor 1 reflects on the surface of a
25 detection object (catalyst) and returns to a light

receiving section of the sensor 1, and the light quantity returned (the quantity of light received) is converted into a numerical value. The numerical value increases or decreases depending on the increase or decrease of the quantity of light received, and it is possible to detect the distance between the sensor 1 and the detection object. Thus, when the distance between the sensor 1 and the detection object is large, since the quantity of light received is small, a small numerical value is presented.

To the contrary, as the distance between the sensor 1 and the detection object is closer, the light quantity returned to the light receiving section increases, and therefore, the numerical value becomes larger. By measuring previously the relation of an actual distance between the sensor 1 and the detection object to the numerical value representing the quantity of light received, it is possible to determine the distance between the sensor 1 and the detection object on the basis of the numerical value representing the quantity of light received. Also, it is possible to adjust the packing height of a catalyst in the packing of the catalyst by setting a threshold value on the numerical value representing the quantity of light received by the sensor 1. Thus, the packing height of the catalyst can be adjusted by determining an inserting position (L1) of the sensor 1, setting a threshold value on the numerical

value representing the quantity of light received by the sensor 1 on the basis of the distance between the catalyst and the sensor 1 in a target packing height of the catalyst, then commencing the packing of the catalyst, detecting the packing height of the catalyst by the numerical value representing the quantity of light received by the sensor 1, and stopping the packing of the catalyst when the packing height of the catalyst reaches a predetermined value. The threshold value can be optionally set depending on the packing height of the catalyst.

[0016]

It is possible to output a signal from the photoelectric sensor 1 when exceeding a predetermined threshold value depending on the above-mentioned packing height of the catalyst 3 in the photoelectric sensor 1. The workers may be informed of the completion of the packing of the catalyst by the signal, for example, by a blinking light or a warning tone, and they can stop the packing of the catalyst manually. Alternatively, the packing may be stopped by sending a stop signal from the photoelectric sensor 1 through control means to belt conveyor 4 conveying the catalyst 3.

[0017]

The detection distance between photoelectric sensor 1 and a detection object represents a distance (maximum

distance that enables detection of the detection object) at which detection starts, i.e., the quantity of light received starts to increase, when moving the detection section of the photoelectric sensor 1 closer to the detection object.

The distance detectable by the photoelectric sensor 1 may usually be 90 to 1,000 mm, preferably 100 to 500 mm, more preferably 100 to 300 mm, when a standard detection object is used as a detection object. For example, a white drawing paper (i.e., a white material: a material showing a reflectance of 90% or more in a visible light region) can be used as the standard detection object.

When the detection distance obtained using a standard detection object is shorter than 90 mm, a case in which a catalyst can not be detected until it reaches the proximity of the sensor (i.e., until the sensor is buried in the catalyst) may occur. Also, if the detection distance is longer than 1,000 mm, a case in which interference with the wall of a reaction tube occurs and detection of a precise position is impossible may occur.

[0018]

As the above-mentioned diffuse-reflective type photoelectric sensor 1, for example, an optical fiber type of photoelectric sensor manufactured by Omron Corp. (E32 series), a photoelectric sensor manufactured by Keyence

Corp. (PS/PZ series) and the like can be used with appropriate selection. In this case, the photoelectric sensor 1 may be either of a sensor with a built-in amplifier or a sensor with a separate amplifier.

5 [0019]

(Reaction Tube)

The reaction tube 10 used in the present invention is one used in a common fixed-bed multi-tubular reactor that is industrially used and includes usually several thousands
10 to several tens of thousands of reaction tubes. The outside diameter of such a reaction tube is usually from about 10 to 60 mm, the wall thickness of the reaction tube is usually from about 1 to 5 mm, and the length of the reaction tube is usually from about 0.3 to 10 m.

15 [0020]

(Catalyst)

The catalyst packed into the above reaction tube 10 in the present invention is not limited to a particular one as long as it is a catalyst for a reaction carried out
20 using a fixed-bed multi-tubular reactor. The catalyst is preferably a solid. This is because a large surface area can be ensured easily in the reaction tube.

Examples of the catalyst include a catalyst for the production of unsaturated aldehydes and unsaturated
25 carboxylic acids, a catalyst for the production of

unsaturated carboxylic acids, a catalyst for the production of unsaturated nitriles, a catalyst for hydrogenation treatment, a catalyst for the production of chlorine and the like. Among these catalysts, a catalyst for the production of unsaturated aldehydes and unsaturated carboxylic acids and a catalyst for the production of unsaturated carboxylic acids are preferable. Examples of the catalyst for the production of unsaturated aldehydes and unsaturated carboxylic acids include a catalyst for the production of acrolein and acrylic acid by vapor-phase contact oxidation of propylene with molecular oxygen, and a catalyst for the production of methacrolein and methacrylic acid by vapor-phase contact oxidation of isobutylene or tert-butyl alcohol with molecular oxygen. Examples of the catalyst for the production of unsaturated carboxylic acids include a catalyst for the production of acrylic acid by vapor-phase contact oxidation of propane with molecular oxygen, a catalyst for the production of acrylic acid by vapor-phase contact oxidation of acrolein with molecular oxygen, and a catalyst for the production of methacrylic acid by vapor-phase contact oxidation of methacrolein with molecular oxygen. Examples of the catalyst for the production of unsaturated nitriles include a catalyst for the production of acrylonitrile by vapor-phase contact ammoxidation of propylene or propane with molecular oxygen

and ammonia, and a catalyst for the production of methacrylonitrile by vapor-phase catalytic ammoxidation of isobutylene or tert-butyl alcohol with molecular oxygen and ammonia. Examples of the catalyst for hydrogenation

5 treatment include a catalyst for reacting sulfur compounds and/or nitrogen compounds contained in a petroleum fraction with hydrogen to remove or reduce the sulfur compounds and/or nitrogen compounds in the products and/or hydrogenolysis catalysts for lightening heavy oil.

10 Examples of the catalysts for the production of chlorine include a catalysts for the production of chlorine from hydrogen chloride and oxygen.

The shape of catalyst 3 is not particularly limited and, for example, may be in a cylindrical, spherical, or
15 ring form. Also, the bulk density of the above catalyst may be usually from 0.8 to 1.5 g/ml, and preferably from 0.8 to 1.3 g/ml.

[0021]

(Conveying Means of Catalyst)

20 In Fig. 1, in the present invention, there is used a method in which a catalyst 3 is conveyed by belt conveyor 4 and packed into a reaction tube 10 by falling from the upper side. However, the conveying means is not particularly limited. It is possible to replace the means,
25 for example, with an apparatus conveying a catalyst by

giving vibration to a conveying lane, or an apparatus such as a lift or a crane, and it is also possible to carry out the conveyance by hand. Among these, a method using an apparatus equipped with a belt conveyor 4 or an apparatus conveying a catalyst by giving vibration to a conveying lane is preferable from the viewpoint that it is easy to control a packing rate in the packing of a catalyst into each reaction tube 10. A catalyst is packed into each reaction tube of a fixed-bed multi-tubular reactor so that the packing rate in the packing of the catalyst into each reaction tube is constant, and the packing height of the catalyst in each reaction tube is uniformly set by photoelectric sensor 1. By packing a catalyst so that the packing rate in each reaction tube is constant, and setting the packing height of the catalyst uniformly as described above, it is possible to satisfactorily control the variation in pressure loss in each reaction tube after the packing the catalyst.

In the case of packing a catalyst using an apparatus equipped with a belt conveyor 4 or an apparatus for conveying a catalyst by giving vibration to a conveying lane, the packing rate is usually from 5 to 60 g/sec, and preferably from 5 to 40 g/sec.

[0022]

(Protective Tube for Photoelectric Sensor)

As shown in Fig. 2, a photoelectric sensor 1 may be used, if necessary, by inserting into a protective tube 5. In such a case, dry air, an inert gas or a mixed gas thereof may be fed from a tube 6 branching from the side of the protective tube 5, through a gap between the internal side of the protective tube 5 and the external side of photoelectric sensor 1, to the lower side of the protective tube 5, i.e., toward the photoelectric sensor 1. Examples of the inert gas include nitrogen, helium, argon and the like. The photoelectric sensor 1 may be inserted into a middle position of the reaction tube 5 or a position near the wall of the reaction tube 5. The shape of the protective tube 5 is not limited to a particular one.

The material of the protective tube 5 is not particularly limited and examples thereof include a stainless steel tube, a plastic tube, an aluminum tube, a rubber tube and the like. Also, the size of the protective tube 5 is not particularly limited, but it is preferable that its inside diameter provides the above gap so that dry air, an inert gas or a mixed gas thereof flows, and that its outside diameter is small as compared with the inside diameter of the reaction tube so that the packing of a catalyst is not prevented.

[0023]

When the falling distance of catalyst 3 in reaction

tube 10 is long, the inside of the reaction tube 10 becomes a circumstance containing a large amount of dust.

The above-mentioned protective tube 5 is inserted or disposed in the reaction tube 10 in a state including photoelectric sensor 1, and protects the photoelectric sensor 1 from dust generated upon the packing of a catalyst 3. Thus, it becomes possible to maintain the accuracy of the photoelectric sensor 1, and also to use the photoelectric sensor 1 in a maintenance-free manner over a long period.

[0024]

In this connection, it is preferable to insert the photoelectric sensor 1 from the upper side of reaction tube 10 without contacting with the reaction tube 10 in order to maintain the accuracy of detection light and a light receiving section, although the present invention is not limited to the particular fashion.

Examples

[0025]

The present invention will be described in more detail by way of Examples, but the present invention is not limited thereto.

[0026]

(Reference Example)

<Preparation of Catalyst>

As a catalyst, an acidic salt of a Keggin type of heteropolyacid containing phosphorus, molybdenum and vanadium (a cylindrical extrusion product having a diameter of 5 mm and a height of 5 mm) was prepared 20 times in total, on the basis of the method described in a Japanese Patent Application JP2004-188231A. The bulk density of the catalyst was measured for each production lot, and it has been found that the average value of the bulk density is 1.15 g/ml, the maximum value is 1.20 g/ml, and the minimum value is 1.09 g/ml.

The bulk density was measured according to the following method. Thus, about 190 ml of the catalyst was taken and the weight [W (g)] was measured. The weighted catalyst was then packed into a glass measuring cylinder having an inside diameter of 31 mm and a volume of 200 ml, and the measuring cylinder was tapped 40 times from a height of 20 mm on a rubber mat having a thickness of 2.5 mm. The packing volume [V (ml)] of the catalyst was read to an accuracy of 0.5 ml, and the bulk density (g/ml) was calculated by dividing W (g) by V (ml).

[0027]

(Example 1)

A packing test of the catalyst was carried out in a standard mode and at a threshold value of 3000, using E32-

D32L (Manufactured by Omron Corp.; reflection type: special beam type; detection distance in standard mode when a white drawing paper is used as a standard detection object = 150 mm) as a diffuse-reflective type photoelectric sensor 1 in which a threshold value was set at 3000, and using E3X-DA-21S (manufactured by Omron Corp.) as an amplifier unit.

Other conditions were as shown below.

In this connection, the measurement by the photoelectric sensor 1 used in the Examples can be carried out in three modes: a high speed mode, a standard mode, and a high accuracy mode. Then, the lag time from interruption of a light input to actuation or recovery of a control output is referred to as response time. The response time differs depending on the modes, and is 250 μ s in the high speed mode, 1 ms in the standard mode and 4 ms in the high accuracy mode.

Length of reaction tube = 1 m

Inside diameter of reaction tube = 25 mm

Insertion length of sensor (L1) (distance from the upper end of reaction tube to detection section of photoelectric sensor) = 300 mm

The photoelectric sensor was inserted into protective tube 5 (outside diameter: 8 mm, inside diameter: 6 mm) made of a stainless steel (SUS304), and dry air was introduced into a gap between the photoelectric sensor and the inside

wall of the protective tube in a constant flow rate so that the air flows from the upper side of the protective tube toward the detection section at the tip of the photoelectric sensor.

5 The packing of the catalyst was carried out by the falling of the catalyst from the upper side of reaction tube 10 using belt conveyor 4 at a speed of 20 g/s. When the catalyst supply from the belt conveyor 4 is stopped in response to a stop signal output from photoelectric sensor 10 1 by exceeding the threshold value, distance L2 (distance from detection section of photoelectric sensor to catalyst) is measured and a distance between the photoelectric sensor and the catalyst ($L2 - L1$) was calculated. The results are shown in Table 1.

15 [0028]

(Example 2)

 The packing of the catalyst was carried out under the same conditions as in Example 1, except that E32-D22L (manufactured by Omron Corp.; reflection type: special beam 20 type; detection distance in standard mode when a white drawing paper is used as a standard detection object = 130 mm) was used as a photoelectric sensor.

[0029]

(Example 3)

25 The packing of the catalyst was carried out under the

same conditions as in Example 1, except that E32-D12R
(manufactured by Omron Corp.; reflection type: standard
type; detection distance in standard mode when a white
drawing paper is used as a standard detection object = 170
5 mm) was used as a photoelectric sensor.

[0030]

(Comparative Example 1)

The packing of the catalyst was carried out under the
same conditions as in Example 1, except that E32-D22
10 (manufactured by Omron Corp.; reflection type: standard
type; detection distance in standard mode when a white
drawing paper is used as a standard detection object = 80
mm) was used as a photoelectric sensor.

[0031]

15 (Comparative Example 2)

The packing of the catalyst was carried out under the
same conditions as in Example 1, except that E32-D32
(manufactured by Omron Corp.; reflection type: special beam
type; detection distance in standard mode when a white
20 drawing paper is used as a standard detection object = 75
mm) was used as a photoelectric sensor.

[0032]

The results of these tests were shown in Table 1.

[Table 1]

	Detection	L2 (mm)	Distance between
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	distance (standard mode)		photoelectric sensor and catalyst (mm)
Example 1	150	317	17
Example 2	130	306	6
Example 3	170	310	10
Comparative Example 1	80	0	-
Comparative Example 2	75	0	-

As is apparent from Table 1, in Examples 1 to 3, the photoelectric sensor was not buried in the catalyst, and the catalyst could be packed into the reaction tube precisely up to a predetermined height. To the contrary, in Comparative Examples 1 and 2, the sensor could not detect the threshold value and was buried in the catalyst.

[0033]

(Example 4)

The packing of the catalyst was carried out in the same manner as in Example 1, except that the following conditions were used.

Photoelectric sensor: E32-D12R (above-described)
(detection distance in high accuracy mode when a white drawing paper is used as a standard detection object = 300 mm);

Mode: high accuracy mode

Threshold value: 3,000

The packing was carried out manually grain by grain.

Then, the threshold value was exceeded at a 10 mm (L2 - L1)

position from the tip of the sensor.

[0034]

(Example 5)

The packing of the catalyst was carried out in the same manner as in Example 1, except that a silica-alumina catalyst having the following shape (manufactured by Iwao Jiki Kogyo Co., Ltd.; a porous ceramic compact of silica-alumina) was used and the following conditions were used.

(1) Spherical compact (diameter: 6.35 mm)

(2) Ring compact (outside diameter: 6.5 mm, inside diameter: 3.5 mm, length 6.4 mm)

Photoelectric sensor: E32-D12R (above-described)

Mode: standard mode

Threshold value: 3,000

The packing was carried out manually grain by grain.

As a result, catalyst (1) exceeded the threshold value at a 10 mm ($L_2 - L_1$) position from the tip of the sensor and catalyst (2) exceeded the threshold value at an 8 mm ($L_2 - L_1$) position from the tip of the sensor.

In the above Examples, a single lane of a belt conveyor was used as belt conveyor 4. Also, the flow rate of dry air in the protective tube was 3 L/min.

Reference Signs List

[0036]

- 1: Photoelectric sensor
- 2: Signal
- 5 3: Catalyst
- 4: Belt conveyor
- 5: Protective tube
- 6: Branch tube
- 10: Reaction tube

What is claimed is:

1. A method for packing a solid catalyst into a reaction tube from the upper side of the reaction tube, comprising
5 the steps of:

disposing a diffuse-reflective type photoelectric sensor in the reaction tube, wherein a white drawing paper is used as a standard detection object and a detection distance as a maximum distance possible to detect the
10 standard detection object is within a range from 90 to 1,000 mm; and

detecting a packing height of the catalyst by the photoelectric sensor, and stopping the packing of the catalyst when the packing height of the catalyst reaches a
15 predetermined value.

2. The method for packing a catalyst according to claim 1, wherein the packing of the catalyst is stopped using control means for stopping conveying means of the catalyst
20 by a detection signal output from the photoelectric sensor.

3. The method for packing a catalyst according to claim 1 or 2, wherein control means is used to stop the packing of the catalyst into the reaction tube when detection light
25 irradiated downwardly from the photoelectric sensor

reflects on a surface of the packed catalyst and the quantity of light received returning to a light receiving section of the photoelectric sensor exceeds a predetermined threshold value.

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4. The method for packing a catalyst according to any one of claims 1 to 3, wherein the photoelectric sensor in the reaction tube is covered with a protective tube, and air, an inert gas or a mixed gas thereof flows from the
10 upper side toward the lower side in the protective tube.