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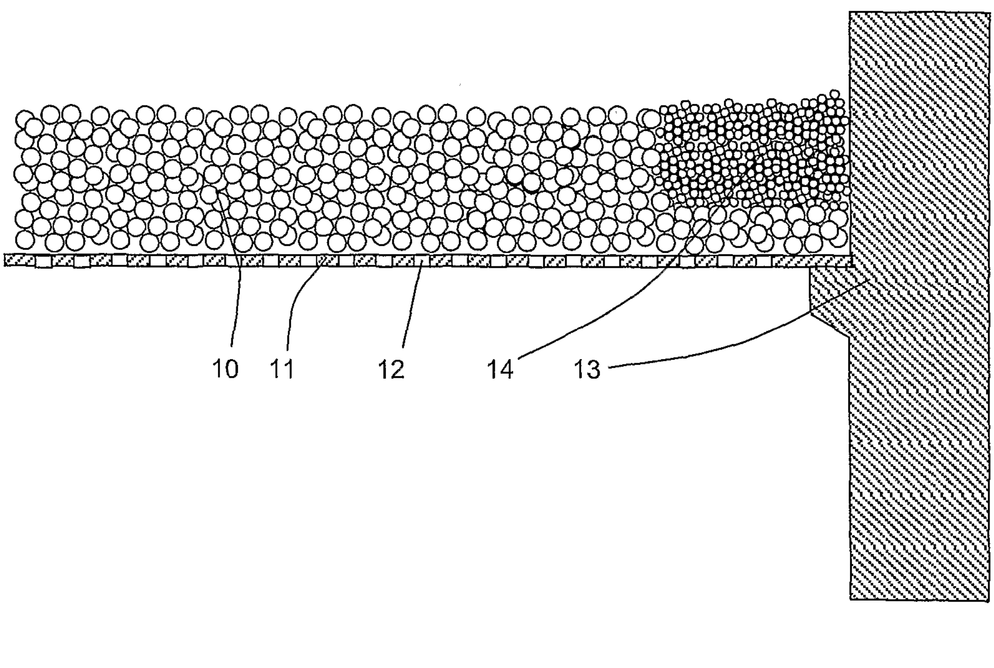
(54) Title: PARTICULATE BEDS




(57) Abstract: A fixed bed containing a catalyst or sorbent having at least one region of reduced permeability is described. The reduced permeability may be achieved for example by the use of smaller sized particles in the desired region. The regions improve the efficiency of the bed by preventing bypass of, e.g. ammonia through a bed of particulate ammonia oxidation catalyst.

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

Particulate beds

This invention relates to fixed beds of catalyst or sorbent and in particular means for providing regions of low permeability to increase the effectiveness of such beds.

Particulate beds such as fixed catalyst and sorbent beds generally comprise at least one layer of a catalyst or sorbent with optionally an inert material, in the form of particles such as extrudates, pellets or granules supported by a perforate member such as a perforate plate, grid or mesh. By the term "sorbent" we include both adsorbent and absorbent materials. To pass through the bed, a gas or liquid must flow through the interstices or voids between the particles and through any passages through the particles and the opposition to the flow causes a pressure drop to occur between one side of the bed and the other. A greater resistance to flow (i.e. lower permeability) for a given flow-rate produces a greater pressure drop or, for a given pressure drop, lower permeability produces a lower flow-rate. Generally, it is recognised that the pressure drop across the bed should be as low as possible and hence the permeability of the bed should be high whilst at the same time providing sufficient contact time between the particles and gas or liquid to efficiently perform the catalysis or sorption processes.

It is preferred that the flow of gas or liquid through the bed of catalyst or sorbent is uniform to provide consistent operation in terms of conversion in the case of a catalyst bed, or absorption in the case of an absorbent bed. To achieve this generally the size of the particles and thickness of the layer of particles is carefully controlled to achieve a uniform particle shape and size and a uniform permeability through the bed, through which the gas or liquid may flow.

It is known that the pressure drop and hence permeability through a fixed bed may be related to two independent variables arising from the size and shape of the particles: the voidage ($e$) and the equivalent diameter of the catalyst particle ($d_e$). (For example see the *Catalyst Handbook*, 2nd Edition, M. V. Twigg (ed.), Wolfe Publishing Ltd, London, 1989, page 101). Equivalent diameter may be defined by the following equation.

$$d_e = (6 \times \text{volume of particle}) / \text{surface area of particle}$$

Voidage is the fraction of the bed volume not taken up by solid. For particles without holes or passages therethrough it may simply be considered as the spaces between the particles through which the fluid is able to flow and may be calculated by the following equation

$$e = (\text{volume of bed} - \text{volume of solid}) / \text{volume of bed}$$

Hence a bed of small spheres will have the same voidage as a bed of large spheres (but the spheres have different equivalent diameters). Alternatively, a bed of particles having no holes therethrough will have a different (smaller) voidage than a bed of particles of the same size but having one or more passages therethrough. Voidage values generally range between 0.35 and 0.55 for most types of particle suitable for use in a catalyst or sorbent bed.

The relationship of pressure drop to voidage and equivalent diameter is provided by the well known Ergun equation (see S. Ergun, *Chem. Eng. Prog.*, 48 (2) 89 (1952)) which may be simplified to the following equation where $K$ is a constant depending on the gas density, height of catalyst bed and mass flow-rate for unit cross section of bed;

$$\text{Pressure drop} = K\,(1 - e) / (de \cdot e^3)$$

Thus pressure drop may increase when the equivalent diameter and/or the voidage becomes smaller.

A problem encountered with catalyst or sorbent particles disposed in fixed beds is that in the region where the particles make contact with the means for containing the bed and/or any member transecting the bed that is aligned with the flow of fluid through the bed, it has been found that the permeability is greater and hence the flow of gas or liquid through the bed is higher. In addition, a further problem encountered with fixed beds containing particles of catalyst or sorbent and in particular fixed beds subjected to high temperatures is that where the particles make contact with the means for containing the bed and/or any member transecting the bed, it has been found that the thermal expansion and contraction of the bed associated with start-up-shutdown procedures can result in a reduction in the bed depth in this region. Consequently, the permeability is greater and hence the flow of gas or liquid through the bed is higher through the region of decreased bed depth. This increase in flow through the bed reduces the contact time between fluid and catalyst or absorbent and may result in the problem of fluid by-pass. In the case of a catalytic process where 100% conversion is required, this can result in unreacted species entering the product stream and in the case of a sorbent bed, similarly requiring complete removal of contaminants, this can result in the undesirable presence of contaminants in the product.

We have found that by use of particles of catalyst or sorbent that provide lower permeability in regions where high permeability would normally result, the problem of by-pass may be reduced.

Accordingly the present invention provides a fixed bed containing a particulate catalyst or sorbent wherein a region of reduced permeability is provided adjacent to any fluid-impermeable surface aligned with the direction of fluid flow through the bed by means of particles of said catalyst or sorbent that provide a relative permeability factor of less than 0.8.

The relative permeability factor ($P_r$) expresses the reduction in permeability in the region of low permeability and is given by the following equation;

$$P_r = [(1 - e_r) \cdot (d_{eb} \cdot e_b^3)] / [(1 - e_b) \cdot (d_{er} \cdot e_r^3)]$$

where the subscripts, "r" and "b" relate to the voidage and equivalent diameter in the region of low permeability and the bulk of the bed respectively.

Preferably, $P_r$ is in the range 0.05 to 0.8 and most preferably 0.05 to 0.5.

In the present invention the beds may be subjected to axial and / or radial flow of the process fluid which may be a gas or liquid. Preferably, the beds of the present invention are subject to axial flow and may be disposed, for example, substantially horizontally in the vessel with gas or liquid passing substantially vertically through the bed.

The beds generally comprise particles of catalyst or sorbent supported by a perforate member such as perforate plates, meshes or grids having appropriately-sized holes to prevent passage of the particles therethrough. The bed is typically bounded by the vessel wall or a boundary member that extends from the perforate plate for at least the depth of the bed, and which may be attached to the perforate plate, vessel wall or other supporting means for the bed. Such edge members are generally impermeable to process fluid.

The beds may be of any shape necessary to provide the required task. Often the bed shape matches that of the cross-section of the vessel in which it is disposed. For example, the bed may be circular, oval, square, rectangular, hexagonal or octagonal. The cross-section width may vary in the range of 0.25 m to 6 m and is preferably 0.5 m to 3.5 m.

The present invention is of particular utility where the beds are relatively thin, i.e. having a depth less than the vessel diameter. Hence where the fixed catalyst bed is circular, the beds of the present invention have a depth (L) to diameter (d) ratio (L/d) of 0.001 to 0.2. Typical bed may have a thickness of between 5 and 500 mm and most preferably between 25 and 300 mm.

In the present invention one or more regions of reduced permeability are provided. The region or regions are provided in any parts of the bed where fluid impermeable surfaces are aligned with the flow of fluid through the bed, for example at the periphery of the bed and/or where the bed meets with a member that transects the bed. Thus in a circular bed, a region of reduced permeability is preferably provided in at least part of the circumferential region, or in a rectangular bed along at least part of the outer edge. If columns, pillars or other supporting means for the bed transect the bed, it may also be desirable to provide a region of low permeability around such means.

The size, i.e. volume occupied by the region of reduced permeability may be expressed as a percentage of the total volume of the bed. More than one region may be present and the combined size of the regions is preferably between 0.1 and 15 % of the volume of the bed and most preferably between 0.3 and 10 %. The region of reduced permeability may be between 5 and 100% of the thickness of the bed and have a width greater than 5% of the thickness of the bed. Preferably the region extends for at least 50% of the thickness of the catalyst or sorbent bed.

The particles used to provide the region of low permeability of the present invention comprise particles of catalyst or sorbent in the form of spheres, platelets, cubes, extrudates, cylindrical pellets, rings, granules or other regular or irregular shapes, preferably having an aspect ratio, i.e. the largest dimension divided by the smallest dimension, of less than 2. The reduced permeability may be achieved by any particle shape and/or size that provides for the region of reduced permeability, a relative permeability factor of less than 0.8. For example, reduced permeability may be provided by using smaller particles alone or in combination with larger particles of the same or different shape in layers, randomly or otherwise that provides, in the desired region, smaller interstices through which the gas or liquid has to flow. A particularly suitable method for providing a region of reduced permeability is to use smaller particles having a smaller equivalent diameter than those in the bulk of the bed. Alternatively, where the particles in the bulk of the bed posses passages through which fluid is able to flow, e.g. where the particles are rings, reduced permeability may be achieved by using particles of the same size but having no (or fewer or smaller) passages therethrough. However, although there is a desirable reduction in voidage in the latter case, there is also a reduction in the equivalent diameter as the surface area of the particle is increased relative to its volume. Consequently where particles with passages therethrough are used in the bulk of the bed it may be desirable to use smaller particles (having no, fewer or smaller passages) to provide the region of lower permeability.

The present invention has been found to be of particular utility for thin beds of catalyst or sorbent supported on, for example, substantially horizontal perforate plates, grids or meshes where the fluid flowing substantially vertically through the bed is able to by-pass the bed by flowing between the particles and substantially vertical members used to bound, support or monitor the bed. The present invention has also been found to be of particular utility where, the bed of catalyst or sorbent is subjected to elevated temperatures, for example temperatures greater than 200°C and in particular at temperatures greater than 500°C.

In a first embodiment, the fixed bed contains particles of a catalyst. The catalyst is preferably disposed in a thin bed and if desired may be supported by a layer of particles of an inert material such as a suitable alumina. Processes that can utilise catalysts in thin beds include for example, ammonia oxidation using, e.g. a particulate cobalt-based catalyst, hydrodesulphurisation using e.g. a cobalt- or nickel-molybdate hydrodesulphurisation catalyst, hydrogen cyanide manufacture, formaldehyde manufacture using a silver catalyst and partial oxidation reactions. Preferably the fixed bed contains particles of an ammonia oxidation catalyst and most preferably this bed is disposed beneath one or more platinum or platinum alloy catalyst meshes which may be woven or knitted. The region of reduced permeability is produced by particles of the said catalyst that provide a relative permeability factor of less than 0.8. This may be achieved for example by use of particles of a smaller equivalent diameter than those in the remainder of the bed, use of particles whose shape when random packed, naturally produces, for example a lower interstitial volume or, where the particles in the bed have passages therethrough, the use of similarly sized particles without any passages.

In a second embodiment, the fixed bed contains particles of a sorbent material. Any sorbent material suitable for the removal of sulphur, mercury or arsenic or compounds threreof, water or hydrogen chloride from hydrocarbons may be used. Examples of sorbents include basic zinc carbonate and copper and/or zinc oxides for e.g. sulphur removal, copper sulphide for e.g. mercury and arsenic removal and sodium aluminate or lead carbonate for e.g. hydrogen chloride removal. The region of reduced permeability may be produced in the same way as that for a catalyst bed.

The invention will now be described with reference to the accompanying drawings in which;

Figures 1 is a diagrammatic cross section of a fixed particulate bed in accordance with a first embodiment.

Figure 2 is a diagrammatic cross section of a fixed catalyst bed in accordance with a second embodiment.

Referring to the drawings, Figure 1shows a bed of a catalyst or sorbent particles (10) supported upon a perforate member (11) having orifices (12) present to allow the flow of gas or liquid substantially vertically through the bed. The perforate member is held in position by supporting means forming part of a vessel wall (13). A region of reduced permeability is provided at the periphery of the bed by a single layer of catalyst or sorbent particles (14), extending from the surface of the bed for approximately 67% of the thickness of the bed and having a width approximately 133% of the thickness of the bed; said particles in said region having a smaller equivalent diameter than the particles of catalyst or sorbent (10) in the bulk of the bed.

In a second embodiment shown in Figure 2, a catalyst bed for the oxidation of ammonia is provided by a layer of a cobalt-containing catalyst particles (20) on top of a layer of inert alumina support particles (21); said layers being of approximately equal thickness and supported on a perforate member (22) having orifices (23) to allow the flow of gases through the bed. Between 1 and 10 platinum-containing ammonia oxidation catalyst gauzes may optionally be disposed on top of the particulate catalyst (not shown). The perforate member is held by supporting means forming part of the vessel wall (24) to which is a attached a heat-shield (25) that extends substantially vertically from the vessel wall to the perforate member and bounds the bed such the particles are prevented from contacting said vessel wall. A region of low permeability is provided adjacent to where the particles contact with the heat-shield by a layer of particles of catalyst (26) having a smaller equivalent diameter than the particles of catalyst (20) forming the bulk of the bed.

In a preferred embodiment of the present invention, a catalyst bed of a cobalt-rare earth perovskite for the oxidation of ammonia as described in WO98/28073, disposed in a reactor of 0.5 - 6 m circular cross-section has a region of low permeability provided in the circumferential zone of width 1-20 cm. The catalyst particles are typically cylindrical pellets of equivalent diameter 1-3 mm and are present in the bed at a depth of 25 - 150 mm. They are supported on a layer of $\alpha$-alumina pellets of typically 3 - 10 mm equivalent diameter of depth 25 - 150 mm. The circumferential region comprises small particles of catalyst having an equivalent diameter in the range 0.5-2.9 mm; said particles extending between 10 and 100% of the thickness of the bed. The region of reduced permeability reduces the amount of unreacted ammonia in the product gas stream.

Claims.

1. A fixed bed containing a particulate catalyst or sorbent wherein a region of reduced permeability is provided adjacent to any fluid-impermeable surface aligned with the direction of fluid flow through the bed by means of particles of said catalyst or sorbent that provide a relative permeability factor of less than 0.8.

2. A fixed bed according to claim 1 wherein the region of reduced permeability has a relative permeability factor in the range 0.05 to 0.5.

3. A fixed bed according to claim 1 or claim 2 wherein the particulate catalyst or sorbent comprises spheres, platelets, cubes, extrudates, rings, cylindrical pellets or granules.

4. A fixed bed according to any one of claims 1 to 3 wherein the total volume occupied by the region of reduced permeability is between 0.1 and 15 % of the bed.

5. A fixed bed according to any one of claims 1 to 4 wherein the region of reduced permeability is provided at the periphery of the bed and comprises between 10 and 100% of the thickness of the bed.

6. A fixed bed according to any one of claims 1 to 5 wherein the bed is subjected to a temperature greater than 200°C.

7. The use of a fixed sorbent bed according to any one of claims 1 to 6 for the removal of materials containing sulphur, mercury or arsenic, water or hydrogen chloride from hydrocarbons.

8. The use of a fixed catalyst bed according to any one of claims 1 to 6 in an ammonia oxidation process employing a particulate cobalt-based ammonia oxidation catalyst.

9. The use according to claim 8 wherein the cobalt-based catalyst is disposed beneath one or more platinum or platinum alloy catalyst meshes,

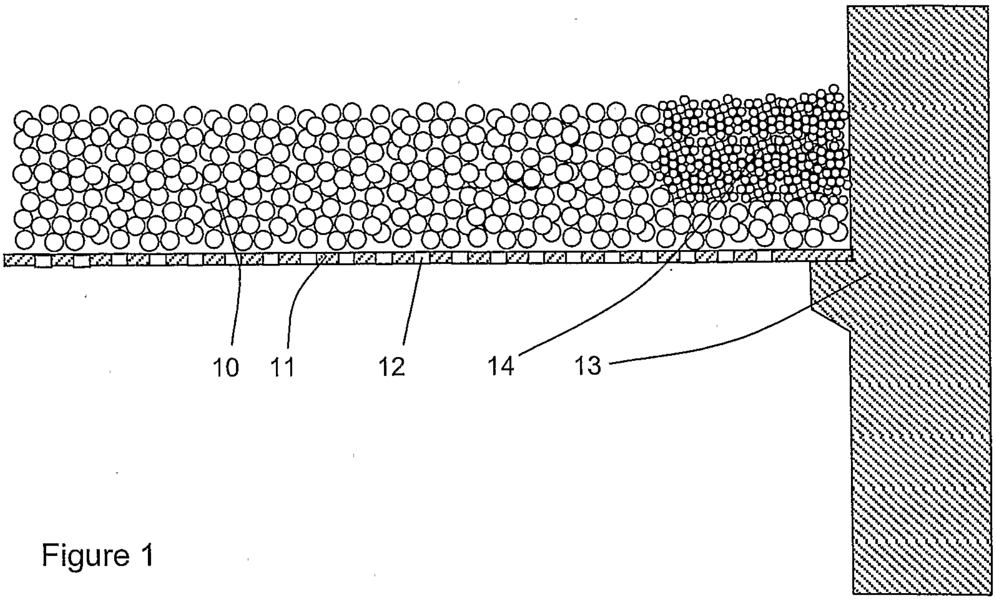


Figure 1

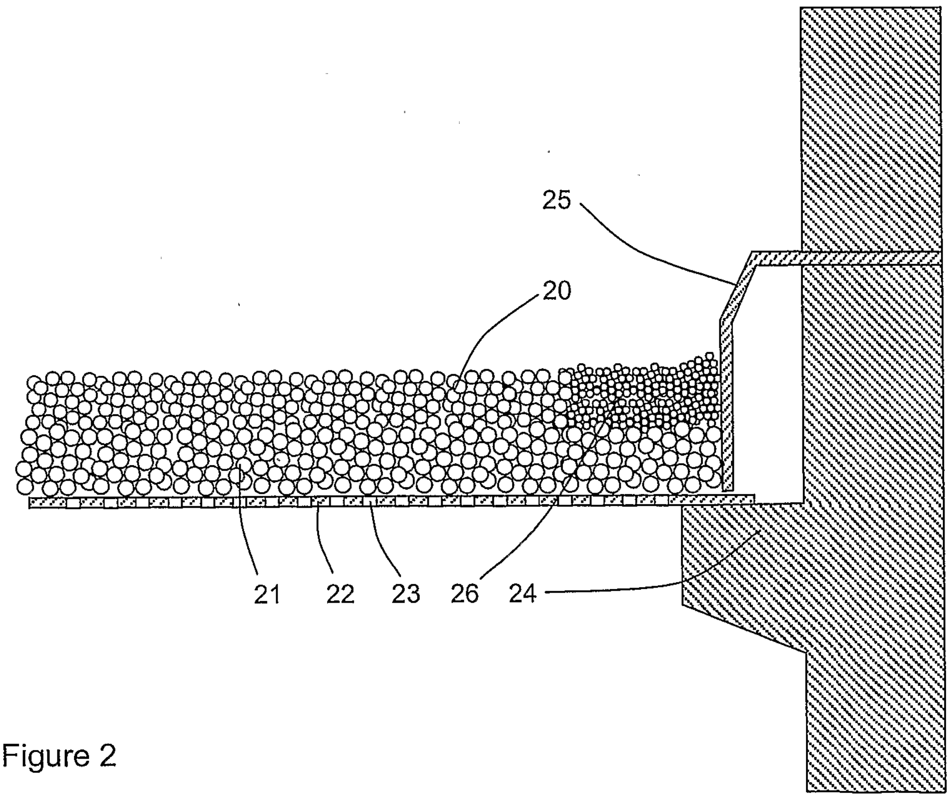


Figure 2

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/003522

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 B01J8/00 B01J8/04

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)
IPC 7 B01J

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

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

EPO-Internal, PAJ, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | US 6 548 029 B1 (VANDEN BUSSCHE KURT M ET AL) 15 April 2003 (2003-04-15) figure 1 | 1 |
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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| Date of the actual completion of the international search | Date of mailing of the international search report |
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| European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Vlassis, M |

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Information on patent family members

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