



(51) International Patent Classification:

B01J 19/24 (2006.01) **C01B 21/087** (2006.01)
B01J 23/42 (2006.01) **B01J 35/04** (2006.01)
C01B 21/26 (2006.01) **B01J 35/06** (2006.01)
C01B 21/28 (2006.01)

(21) International Application Number:

PCT/GB2009/051206

(22) International Filing Date:

17 September 2009 (17.09.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0819096.9 20 October 2008 (20.10.2008) GB

(71) Applicant (for all designated States except US): **JOHNSON MATTHEY PLC** [GB/GB]; 40-42 Hatton Garden, London EC1N 8EE (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **ROE, Stephen, Philip** [GB/GB]; 51 Bedale Avenue, Billingham, Cleveland TS23 1AU (GB).

(74) Agent: **RIDLAND, John**; Johnson Matthey Catalysts, PO Box 1, Belasis Avenue, Billingham, Cleveland TS23 1LB (GB).

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

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

Published:

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

(54) Title: PRECIOUS METAL GAUZE ASSEMBLY

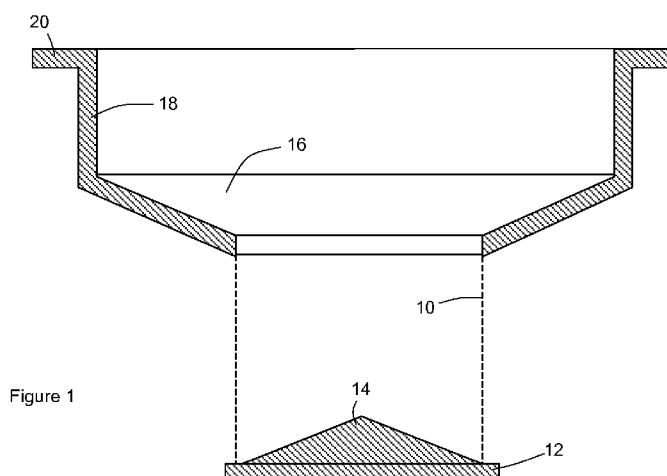


Figure 1

(57) Abstract: A precious metal gauze assembly, suitable for use in an ammonia oxidation vessel is described, comprising a precious metal gauze in the form of a tube mounted between process fluid-impermeable end members, wherein one end member provides a closed end to the tube and the other end member extends radially from the tube thereby providing an open end through which gases may enter or exit the unit, and suspending means attached to one or both end members by which the assembly may be secured within a reactor. The assembly may be suspended below a conventional precious metal ammonia oxidation gauze pack.



Precious metal gauze assembly

This invention relates to apparatus for supporting precious metal gauzes, particularly catalyst and catchment gauzes used in ammonia oxidation vessels, and processes using such apparatus.

Ammonia oxidation is carried out industrially with air to generate nitric oxide, which used to make nitric acid (the Ostwald Process) or with air and methane to generate hydrogen cyanide (the Andrussov Process). In both processes, the reactant gases are mixed and passed at elevated temperature and pressure through a reaction vessel in which is placed a pack of platinum/rhodium gauzes that catalyse the oxidation reactions. The gauzes are typically circular and are supported on a frame or basket that holds them perpendicular to the flow of gases through the reactor. The catalyst pack may also comprise one or more palladium-rich gauzes, known as "catchment gauzes" that act to capture volatilised platinum.

In conventional arrangements the gauze pack can give rise to unacceptable pressure drop thereby increasing compression costs. There is also the possibility of enhanced side reactions due to increased contact time with the catalyst structure. Furthermore there is a desire to increase the amount of catchment gauze used in order to more effectively capture the volatilised platinum, but this is limited by the increased pressure drop this would cause. Therefore there is a need to provide a catalyst arrangement that overcomes these problems.

Accordingly the invention provides a precious metal gauze assembly, suitable for use in an ammonia oxidation vessel, comprising a precious metal gauze in the form of a tube mounted between process fluid-impermeable end members, wherein one end member provides a closed end to the tube and the other end member extends radially from the tube thereby providing an open end through which gases may enter or exit the assembly, and suspending means attached to one or both end members by which the assembly may be secured within a reactor.

The precious metal gauze assembly therefore provides a means for passing gases radially through the precious metal gauze. Radial flow reactors are known, however, to our knowledge none comprise a precious metal gauze assembly wherein an end member serves as suspending means by which the unit is secured within a reactor. Moreover, to our knowledge, radial flow catalyst structures have not heretofore been used in ammonia oxidation vessels. The radial flow arrangement allows for a reduced pressure drop for the same gauze volume or an increase in the amount of gauze for the same pressure drop, thus offering the operator increased operational flexibility and reduced compression costs.

In the present invention, the precious metal gauze to be formed into a tube may comprise one or more platinum catalyst gauzes and/or one or more palladium catchment gauzes.

Precious metal gauzes may be formed by weaving or knitting or otherwise forming precious metal filaments into a gauze-like structure. Such catalyst gauzes are well established and may consist of platinum or platinum alloy filaments of thickness from 0.02 to 0.15 mm woven to provide rectangular interstices, knitted to provide a regular looped structure or simply agglomerated to provide a non-woven irregular structure. Herein the term 'filament' is meant to include wires that have a substantially circular cross-section and also wires that are flattened or otherwise shaped and thereby have a non-circular cross section. Woven gauzes are well established and typically comprise 0.076 mm diameter wire, woven to provide 1024 apertures per square centimetre and prepared to a specific weight per unit area dependant upon the wire composition. Knitted gauzes offer a number of advantages in terms of catalyst physical properties, catalyst activity and lifetime. Knitted gauzes comprise a regular looped structure and may be formed using wire with diameters in the same range as woven materials, in a variety of shapes and thicknesses using variety of stitches such as tricot, jacquard, satin stitch (smooth sunk loops) and raschel. EP-B-0364153, page 3, line 5 to line 56 describes knitted gauzes of particular use in the present invention. Non-woven gauzes are described for example in GB 2064975 and GB 2096484.

The precious metal ammonia oxidation catalyst is preferably platinum (Pt) or a platinum alloy, such as an alloy of platinum with rhodium (Rh) and/or palladium (Pd) containing $\geq 85\%$ preferably $\geq 90\%$ Pt by weight. Alloys used in ammonia oxidation in the production of nitric acid or hydrogen cyanide include 10% Rh 90% Pt, 8% Rh 92% Pt, 5% Pd 5% Rh 90% Pt and 5% Rh 95% Pt. Alloys containing upto about 5% of iridium (Ir) may also be used in the present invention. The precious metal catalyst may desirably be formulated to reduce nitrous oxide by-product formation, and may thus have an increased rhodium (Rh) content, or may contain other components such as cobalt (Co).

Catchment gauzes based on palladium are desirably used in ammonia oxidation plants to act as so-called "getters" or collectors of 'vaporised' platinum lost by chemical action, evaporation or mechanical losses from the precious metal catalyst. Such catchment gauzes may be in the form of woven or knitted gauzes or agglomerated non-woven gauzes akin to those described above for the precious metal catalysts. Any palladium present in a gauze will be able to catch vapourised platinum passing over it, hence the palladium content of the catchment gauze may be from 10 to $\geq 95\%$ wt, preferably $>40\%$, more preferably $>70\%$. One or more palladium based catchment gauzes may be used. The catchment gauzes may be knitted, e.g. according to the aforesaid EP-B-0364153. Alternatively the palladium-based guard material may be woven or knitted into a precious metal ammonia oxidation catalyst gauze by using it as a

filament in the weaving or knitting process. Palladium-based guard materials suitable for weaving or knitting into gauze structures are palladium or palladium alloys with nickel (Ni), cobalt (Co) or gold (Au). For example a catchment gauze may be fabricated from a 95:5% wt Pd:Ni alloy. In addition the palladium-based guard material may desirably be formulated to
5 reduce nitrous oxide by-product formation, and may thus preferably contain a small amount, e.g. <5% rhodium (Rh). In particular, palladium gauzes containing amounts of platinum and rhodium may be used. Such gauzes may comprise, for example >92% wt palladium, 2-4% wt rhodium and the remainder platinum, or alternatively comprise 82-83% wt palladium, 2.5-3.5% wt rhodium and the remainder platinum. Ceramic fibres comprising an inert refractory
10 material, such as alumina, zirconia or the like, may also be woven or knitted into catchment gauzes in addition to the palladium-based materials.

Where catalyst and catchment gauzes are combined it is desirable that they are arranged in the tube wall so that the gases contact first with the catalyst gauzes and then catchment
15 gauzes.

The number of gauzes employed depends on the pressure at which the process is operated. For example in a plant operating at low pressure, e.g. up to about 5 bar abs., typically <10, often 3 to 6 gauzes may be employed, while at higher pressures, e.g. up to 20 bar abs., a
20 greater number of gauzes, typically >20, often 35-45, may be employed. If adjacent woven gauzes are present, to facilitate replacement, they are preferably arranged so that their warps or wefts are at an angle of 45° to each other. Angular displacement, suitably at 90°, may also be used between adjacent woven gauzes to reduce opportunities for gas channelling.

25 In order to increase the strength of the assembly, the tube may further comprises a steel mesh. By the term "steel" we mean suitable high-temperature stable alloys, including non-Fe-based alloys such as Ni-based materials.

The cross section of the tube may be circular, oval, or polygonal, e.g. having between 3 and 50
30 sides. Tubular arrangements have the advantage over conventional circular-cut gauzes in that that the gauze may be formed into a tube from the square or rectangular form in which it was woven or knitted, thereby reducing waste during fabrication.

Cylindrical tubes are preferred. Where the precious metal gauze tube is cylindrical, the closed
35 end member may be circular with a diameter at least that of the tube, and the open end member may be ring shaped with a central hole of diameter at most equal to that of the tube. The end members are suitably fabricated from steel sheet.

The suspending means may be attached to one or both end members. Preferably the suspending means are provided by extending the end member forming the open end of the assembly. When the assembly is placed in a reactor, the end members may also be inclined to direct the flow of gases through the gauze in the desired manner. Additionally, baffles may
5 also be provided on the assembly to direct the flow of gases radially through the gauze. For example a conical baffle may be placed on the closed end member.

The flow of gases through the assembly may be radially inwards, i.e. from the periphery of the unit towards its centre, or may be radially outwards, i.e. from the central region outwards to
10 wards the periphery. For simplicity of design, outward radial flow is preferred. In this case it may be desirable to include a baffle that acts as a heat shield and prevents the hot gases exiting the assembly from contacting directly with the inside wall of the ammonia oxidation vessel.

15 The flow through the vessel may be upflow or downflow.

Whereas the precious metal gauze assembly may be placed in a reaction vessel as a stand-alone unit, it is possible that the assembly may be used in combination with a conventional circular precious metal ammonia oxidation catalyst. Accordingly, the invention further provides
20 a catalyst combination comprising a circular precious metal ammonia oxidation catalyst gauze on a supporting framework and a tubular precious metal catalyst gauze in the assembly of the present invention.

One or more catchment gauzes may also be provided under the circular precious metal
25 catalyst gauzes but this is less preferred where the tubular gauze assembly comprises catchment gauzes.

The circular precious metal catalyst and catchment gauzes may be the same or different from the tubular precious metal catalyst and catchment gauzes disposed in the precious metal
30 gauze assembly.

The supporting framework for the circular gauzes may be any currently in use and includes simple girder support arrangements that extend across the ammonia oxidation vessel and so-called "baskets" in which the circular precious metal gauzes are supported on the base of a
35 cylindrical unit suspended within the ammonia oxidation vessel.

The tubular precious metal gauze assembly may be separate from the supporting framework for the circular precious metal gauzes, but in a preferred embodiment, the tubular precious metal gauze assembly is suspended from the circular precious metal catalyst-supporting

framework using the suspending means. In a particularly preferred arrangement, the tubular precious metal gauze assembly is suspended from a precious metal catalyst basket.

The precious metal gauze assembly according to the present invention may be installed in any ammonia oxidation vessel having a suitable space to accommodate it. Alternatively, the vessel
5 may be adapted to make a suitable space available. Ammonia oxidation vessels vary in size but are typically domed cylindrical vessels with internal diameters in the range 0.5-6 metres.

The precious metal gauze assembly may be fabricated to fit within these reactors. For example, in a 1.5 m diameter vessel, the wall thickness of the tube may be 180 mm by 700-750 mm in height.

10

The precious metal gauze assembly may be placed below the circular precious metal gauzes so that the gases enter the ammonia oxidation vessel through an inlet in the top, then pass vertically (i.e. axially) downwards through the precious metal catalyst layer, enter the open end of the precious metal gauze assembly then pass radially through the precious metal gauze
15 walls of the tube and then out of the base of the unit and exit the ammonia oxidation vessel via an outlet in the base. The arrangement may be reversed in an upflow vessel.

20

In cases where a combination of circular precious metal gauze and tubular precious metal catalyst is used, the invention further provides a method of retrofitting an ammonia oxidation vessel comprising suspending a precious metal gauze assembly beneath the circular precious metal catalyst. This is desirably accomplished by fixing a precious metal gauze assembly to the existing precious metal catalyst gauze support frame.

25

The invention further provides an ammonia oxidation process comprising the step of passing a gas mixture comprising ammonia, an oxygen containing gas such as air and optionally a methane containing gas through a tubular precious metal catalyst gauze catalyst disposed in the precious metal gauze assembly.

30

In one embodiment, the process comprises passing a gas mixture comprising ammonia, an oxygen containing gas such as air and optionally a methane containing gas through a circular precious metal catalyst gauze on a supporting framework and a tubular precious metal gauze catalyst disposed in the precious metal gauze assembly.

35

In the oxidation of ammonia to nitric oxide for the manufacture of nitric acid, the oxidation process may be operated at temperatures of 750-1000°C, particularly 850-950°C, pressures of 1 (low pressure) to 15 (high pressure) bar abs., with ammonia in air concentrations of 7-13%, often about 10%, by volume. In the oxidation of ammonia with air in the presence of methane for the manufacture of hydrogen cyanide, the Andrussov Process, the operating conditions are similar. The present invention is particularly suited to processes and ammonia oxidation

reactors operated at pressures in the range 6-15 bar abs, particularly 7-15 bar g (so-called high pressure plants) because the tubular precious metal gauze assembly may readily be placed in the vessel without having to move or adjust heat recovery means commonly found just below the gauzes in medium pressure and atmospheric plants.

5

Hence for a low-pressure ammonia oxidation process, the catalyst assembly of the present invention may comprise 2-10 platinum oxidation gauzes and 2-5 palladium catchment gauzes formed into a tube, optionally with one or more steel meshes to act as a strengthening material. Alternatively a catalyst combination may be used comprising 1 or 2 circular precious metal ammonia oxidation catalyst gauzes followed by one or more gauzes of palladium catchment in a conventional arrangement, followed by a radial flow arrangement of tubular precious metal ammonia oxidation catalyst and/or further catchment gauzes. Alternatively the catalyst assembly may comprise between 2 and 10 circular platinum catalyst gauzes without catchment and the precious metal gauze assembly used only for catchment gauzes. Likewise in a high-pressure plant, there may be less than 15, e.g. 10 precious metal ammonia oxidation catalyst gauzes followed by the tubular catchment gauzes.

10

15

The invention is further illustrated by reference to the drawings in which:

20

Figure 1 is a cut-away side elevation of a precious metal gauze assembly according to a first embodiment with the end members arranged to provide outwards radial flow,

Figure 2 is a cut-away side elevation of a precious metal gauze assembly according to a second embodiment with the end members arranged to provide inwards radial flow,

Figure 3 is a cut-away side elevation of an ammonia oxidation vessel containing a precious metal gauze assembly arranged to provide outwards radial flow, and

25

Figure 4 is a cut-away side elevation of an ammonia oxidation vessel containing a catalyst combination comprising a precious metal gauze supported in a basket and precious metal gauze assembly suspended from said basket with the end members arranged to provide outwards radial flow.

30

In Figure 1 the precious metal gauze assembly comprises a vertical tube 10 formed from one or more precious metal gauzes, mounted on a circular steel sheet 12 that extends horizontally across the width of the tube 10, thereby forming a closed end. On the upper surface of sheet 12 and within the tube 10 is placed a conical baffle 14 that acts to direct gas radially through the gauzes. A ring-shaped steel end member 16 having a central hole corresponding to the internal diameter of the tube 10 is mounted on the other end of the gauzes, thereby forming an open end. The end member 16 is angled upwards from the tube at about 45 degrees.

35

Suspending arm 18 is formed by vertically extending the edge of the ring member 16. The suspending arm 18 has a flange 20 at its extremity to permit installation of the assembly into a reactor.

In use, gases enter the assembly via the central hole in the ring-shaped end member 16, pass through meshes 10, and then out of the assembly.

In Figure 2, the precious metal gauze assembly comprises a vertical tube 30 mounted on a
5 ring-shaped steel end member 32, having a central hole corresponding to the internal diameter of the tube, thereby forming an open end. At the other end of the tube 30, the assembly has a circular steel sheet end member 34 mounted horizontally on the tube and extending across its width thereby providing a closed end. On the upper surface of sheet 34 and extending across its width is a conical baffle 36. Suspending arm 36 is formed by extending the sides of the ring
10 end member 32 horizontally then vertically from the tube to above the end member 34. Providing the suspending means in this manner provides a peripheral annular void 38 through which gases may flow to the precious metal gauzes. The suspending arm 36 has a flange 40 at its extremity to permit installation of the assembly into a reactor.

15 In use, gases enter the assembly via the annular void 38, pass through the walls of tube 30, and then out of the assembly via the central hole in ring end member 32.

In Figure 3, a cylindrical ammonia oxidation vessel comprises a domed upper portion 50 with inlet 52 and a domed lower portion 54 with outlet 56. A flanged joint 58 joins the upper and
20 lower portions. Suspended from this joint 58 within the vessel is a catalyst containment unit as depicted in Figure 1 in which the walls of tube 10 are fabricated from multiple layers of platinum ammonia oxidation gauze with one or more layers of palladium catchment gauze on the outer (vessel wall-facing) surface.

25 In use, a mixture of ammonia and air, optionally containing methane, is passed at elevated temperature and pressure through the inlet 52, passes downwards and is deflected by member 16 to pass through the open end of the precious metal gauze assembly. The gases then pass radially, with the assistance of baffle 20, through the catalyst and catchment gauzes where the ammonia oxidation reaction takes place. The reacted gases then exit the unit and are
30 deflected downwards to the lower portion 54 of the vessel and then out of the vessel via outlet 56.

In Figure 4, a cylindrical ammonia oxidation vessel comprises a domed upper portion 60 with inlet 62 and a domed lower portion 64 with outlet 66. A flanged joint 68 joins the upper and
35 lower portions. Suspended from this joint 68 within the vessel is a precious metal gauze-support 70 in the form of a steel-frame basket containing a circular precious metal gauze pack 72 made up of a plurality of platinum/rhodium ammonia oxidation gauzes and optionally one or more palladium catchment gauzes. Suspended from basket 70 is a precious metal gauze assembly as depicted in Figure 1 in which the tube is made up of a plurality of palladium

catchment gauzes and the flange 20 on the suspending means 18 is attached to limbs 74 extending from the underside of basket 70.

5 In use, a mixture of ammonia and air, optionally containing methane, is passed at elevated temperature and pressure through the inlet 62 and distributed over the surface of the catalyst gauze pack 72 by means of distribution means (not shown). The gases pass downwards (axially) through the gauze pack where the ammonia oxidation reactions take place. The hot gas mixture then passes downwards and is deflected by member 16 to pass through the open end of the precious metal gauze assembly. The gases then pass radially, with the assistance of baffle 20, through the catchment gauzes where volatilised platinum is captured. The reacted 10 gases then exit the assembly and are deflected downwards to the lower portion 64 of the vessel and then out of the vessel via outlet 66.

Claims.

1. A precious metal gauze assembly, suitable for use in an ammonia oxidation vessel, comprising a precious metal gauze in the form of a tube mounted between process fluid-impermeable end members, wherein one end member provides a closed end to the tube and the other end member extends radially from the tube thereby providing an open end through which gases may enter or exit the unit, and suspending means attached to one or both end members by which the unit may be secured within a reactor.
2. A precious metal gauze assembly according to claim 1 wherein the precious metal gauze comprises one or more platinum catalyst gauzes and/or one or more palladium catchment gauzes.
3. A precious metal gauze assembly according to claim 1 or claim 2 wherein the tube further comprises a steel mesh.
4. A precious metal gauze assembly according to any one of claims 1 to 3 wherein the cross section of the tube is circular, oval, or polygonal.
5. A precious metal gauze assembly according to any one of claims 1 to 4 wherein the tube is cylindrical, the closed end member is circular with a diameter at least that of the tube, and the open end member is ring shaped with a central hole of diameter at most equal to that of the tube.
6. A precious metal gauze assembly according to any one of claims 1 to 5 wherein the suspending means are provided by extending the end member forming the open end of the unit.
7. A precious metal gauze assembly according to any one of claims 1 to 6 wherein baffles are provided on the unit to direct the flow of gases radially through the assembly.
8. A catalyst combination comprising a circular precious metal ammonia oxidation catalyst gauze on a supporting framework and a precious metal catalyst disposed in the precious metal gauze assembly according to any one of claims 1 to 7.
9. A catalyst combination according to claim 8 wherein a palladium catchment gauze is provided underneath the circular precious metal catalyst.

10. A catalyst combination according to claim 8 or claim 9 wherein the supporting framework for the circular gauzes comprises a girder support arrangement or is a basket in which the precious metal gauzes are supported on the base of a cylindrical support structure.
11. A catalyst combination according to any one of claims 8 to 10 wherein the precious metal gauze assembly is separate from the supporting framework for the circular precious metal gauzes, or is fixed to the supporting framework for the circular precious metal gauzes.
12. An ammonia oxidation process comprising the step of passing a gas mixture comprising ammonia, an oxygen containing gas such as air and optionally a methane containing gas through a tubular precious metal catalyst disposed in the precious metal gauze assembly according to any one of claims 1 to 8.
13. An ammonia oxidation process according to claim 12 wherein the gas mixture is passed through a catalyst combination according to any one of claims 9 to 11.
14. An ammonia oxidation process according to claim 12 or claim 13 comprising passing a gas mixture comprising ammonia, an oxygen containing gas such as air and optionally a methane containing gas through a circular precious metal catalyst gauze on a supporting framework and then through a tubular precious metal catalyst disposed in the precious metal gauze assembly.
15. An ammonia oxidation process according to any one of claims 12 to 14 operated at temperatures of 750-1000°C, pressures of 1 to 15 bar abs., with ammonia in air concentrations of 7-13% by volume.
16. A process according to any one of claims 12 to 15 operated at pressures in the range 6-15 bar abs.
17. A method of retrofitting an ammonia oxidation vessel comprising suspending a precious metal gauze assembly according to any one of claims 1 to 8 beneath an existing precious metal catalyst gauze support frame.
18. A method according to claim 17 comprising fixing a precious metal gauze assembly according to any one of claims 1 to 8 to the existing precious metal catalyst gauze support frame.

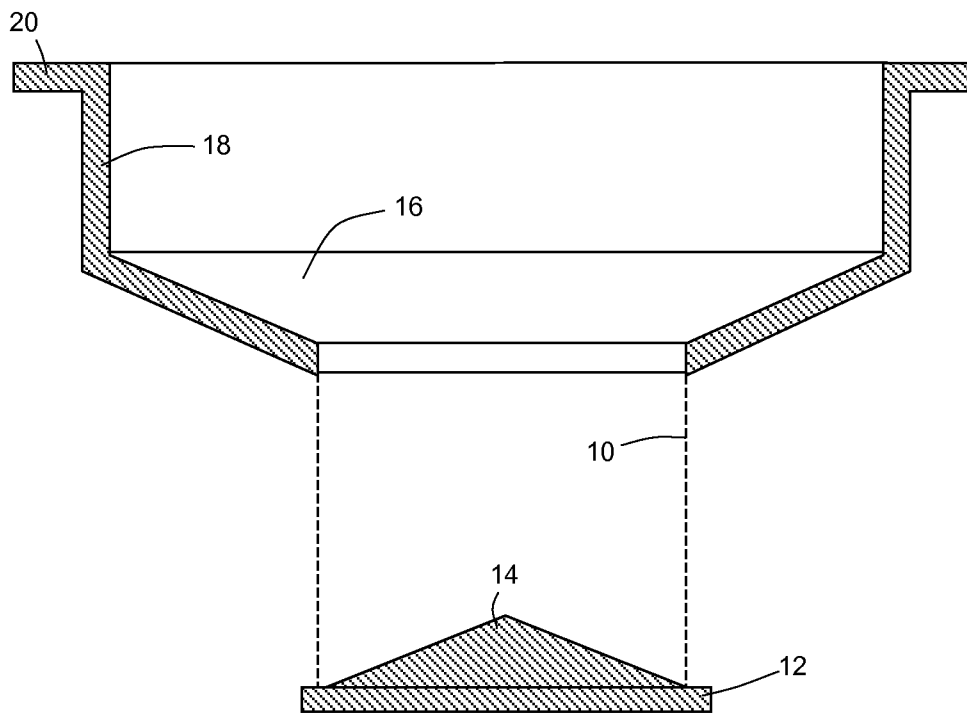


Figure 1

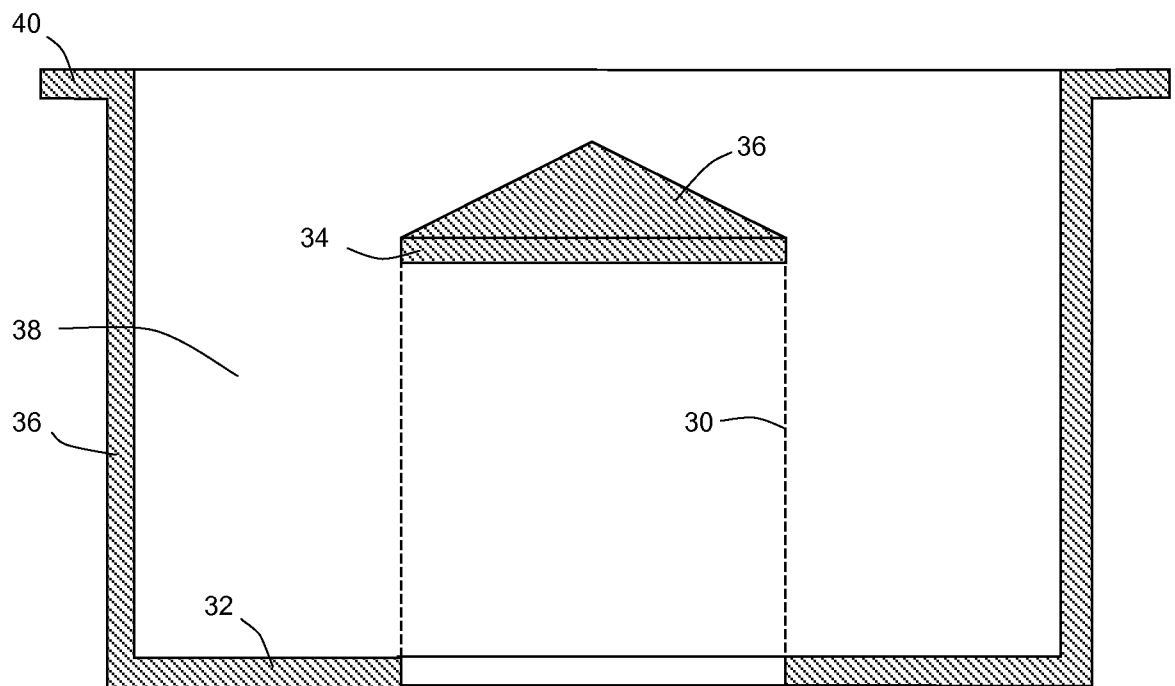


Figure 2

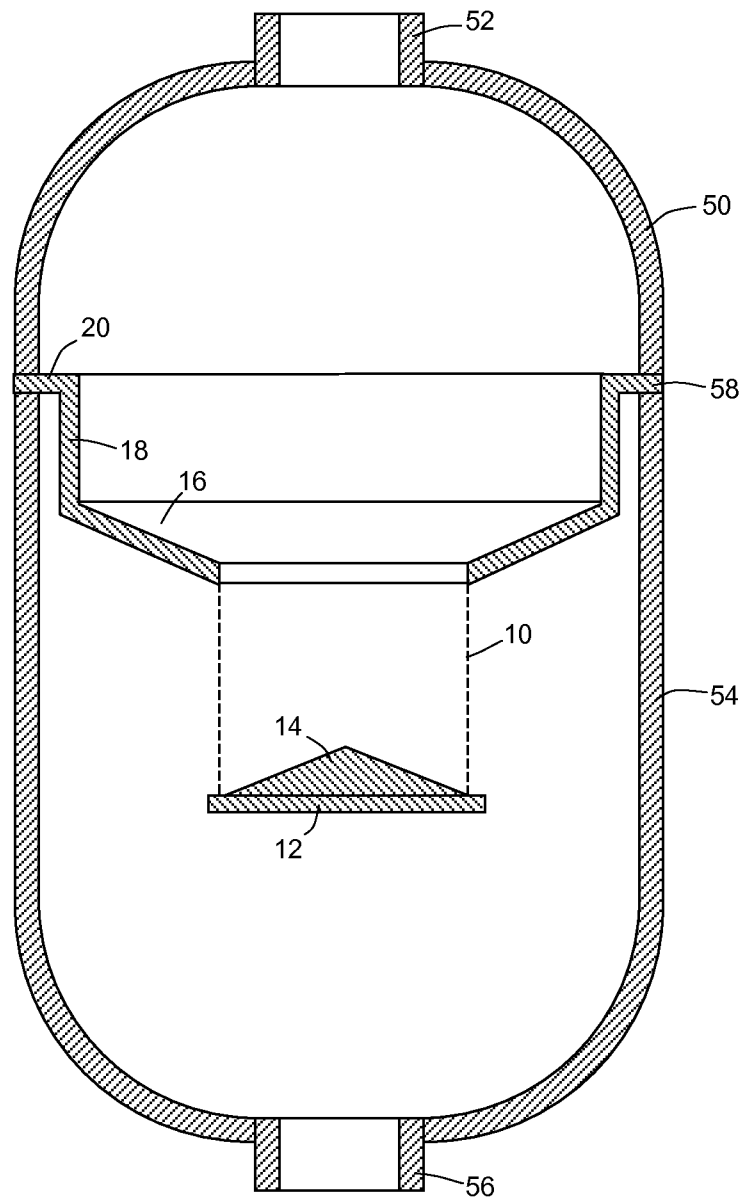


Figure 3

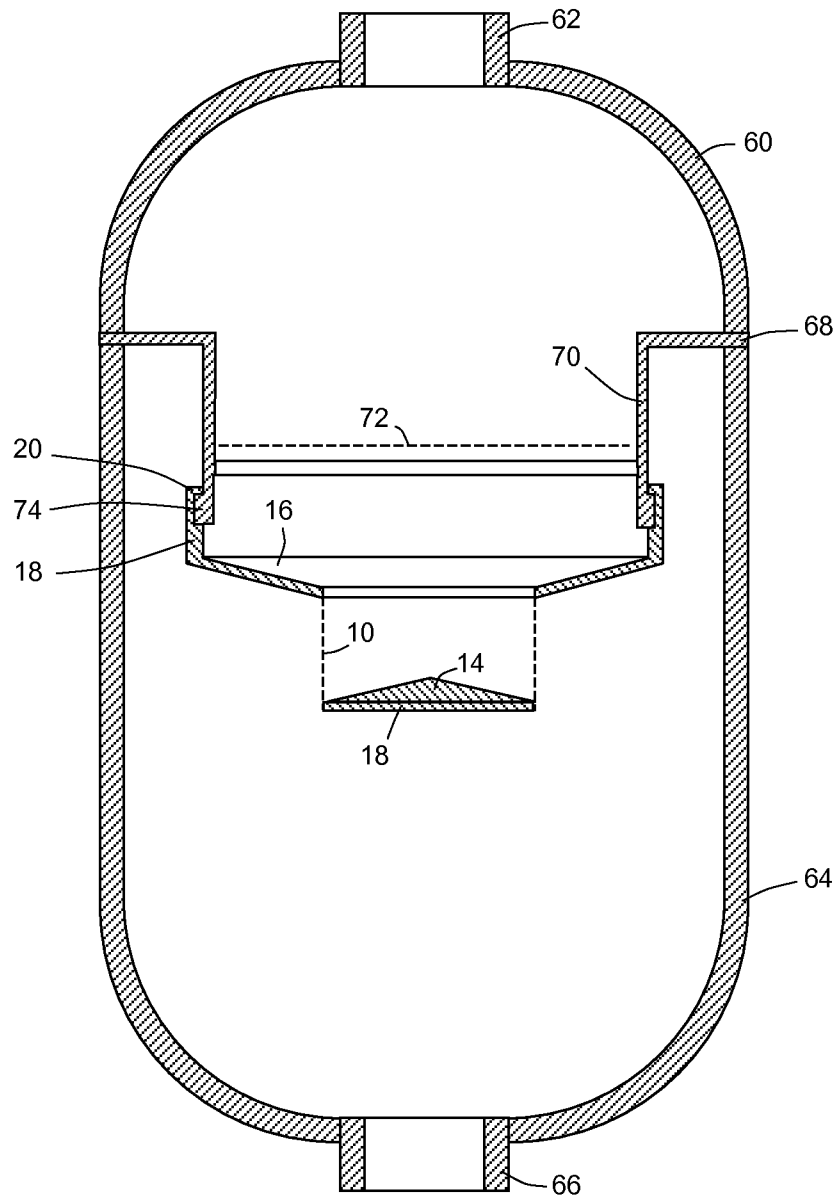


Figure 4

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2009/051206

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J19/24 B01J23/42 C01B21/26 C01B21/28 C01B21/087
B01J35/04 B01J35/06

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 C01B B01D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 627 497 A (KLEIN LOUIS A ET AL) 14 December 1971 (1971-12-14)	1,2,4-7, 12,15
Y	the whole document	3,8-11, 13,14, 17,18
Y	US 4 022 581 A (RUDORFER HERMANN ET AL) 10 May 1977 (1977-05-10) column 1, lines 40-56 column 4, lines 37-49 column 4, line 65 - column 5, line 6 figures 2a,2b,4a,4b claims; example 1	8-18

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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.

G document member of the same patent family

Date of the actual completion of the international search

26 January 2010

Date of mailing of the international search report

03/02/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Goebel, Matthias

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2009/051206

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 057 138 A (HUXSTER FREDERICK G) 9 October 1962 (1962-10-09) column 1, line 71 - column 2, line 29 column 4, line 14 - column 5, line 73 claims 1-3; figures -----	1-8, 10-16
Y	US 2 730 189 A (HERMANN HOLZMANN) 10 January 1956 (1956-01-10) the whole document -----	1-18
Y	US 2003/124046 A1 (GORYWODA MAREK [DE] ET AL) 3 July 2003 (2003-07-03) the whole document -----	1-18
X	WO 03/078054 A (DU PONT [US]) 25 September 2003 (2003-09-25) figures 3-5,7 page 3, lines 15-37 page 6, lines 12-22 page 6, line 31 - page 7, line 6 page 10, line 16 - page 11, line 14 claims 1,3,5,10-14,16,21,23-27; examples 2-8,17-26 -----	1-7,12, 15
A	BUSBY J A ET AL: "Catalytic Processes in Nitric Acid Manufacture" PROCEEDINGS OF THE FERTILIZER SOCIETY, vol. 169, 1978, pages 5-39, XP001473486 pages 26-29 -----	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2009/051206

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3627497	A	14-12-1971	NONE
US 4022581	A	10-05-1977	NONE
US 3057138	A	09-10-1962	NONE
US 2730189	A	10-01-1956	FR 1031790 A 26-06-1953 GB 706696 A 07-04-1954
US 2003124046	A1	03-07-2003	AT 284838 T 15-01-2005 AU 767406 B2 06-11-2003 AU 6593801 A 26-11-2001 BR 0106434 A 16-04-2002 CA 2374950 A1 22-11-2001 CN 1380874 A 20-11-2002 CZ 20020103 A3 12-06-2002 DE 50104839 D1 20-01-2005 DK 1284927 T3 24-01-2005 WO 0187771 A1 22-11-2001 EP 1284927 A1 26-02-2003 ES 2234844 T3 01-07-2005 JP 3965053 B2 22-08-2007 JP 2003533351 T 11-11-2003 MX PA01012930 A 31-07-2002 NO 20020122 A 28-02-2002 PL 351821 A1 16-06-2003 RU 2205151 C1 27-05-2003 UA 70376 C2 15-04-2002 ZA 200200296 A 29-04-2003
WO 03078054	A	25-09-2003	AT 429974 T 15-05-2009 AU 2003222264 A1 29-09-2003 CN 1652868 A 10-08-2005 EP 1480740 A1 01-12-2004 ES 2324776 T3 14-08-2009 JP 2005519832 T 07-07-2005 RU 2339576 C2 27-11-2008 TW 275415 B 11-03-2007 US 2003175196 A1 18-09-2003