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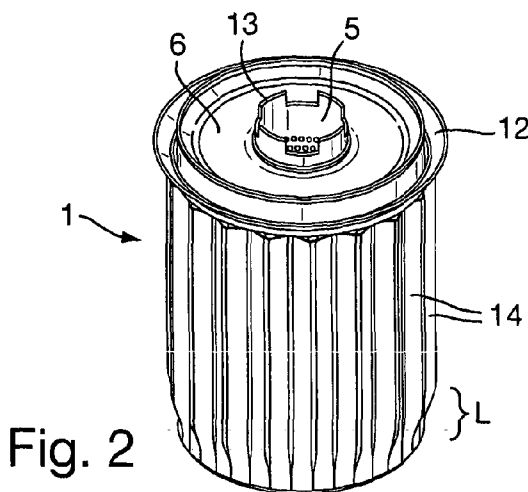
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(54) Title: PROCESS FOR THE PRODUCTION OF ANHYDRIDES



(57) Abstract: A process for the production of anhydrides by contacting a gaseous feed stream with a particulate catalyst, said process being carried out in a tubular reactor having an inlet and an outlet, said outlet being located downstream of the inlet, said reactor comprising one or more tubes having located therein one or more carriers for said particulate catalyst and cooling medium in contact with said tubes; wherein said catalyst carrier comprises: an annular container for holding catalyst in use, said container having a perforated inner wall defining a tube, a perforated outer wall, a top surface closing the annular container and a bottom surface closing the annular container; a surface closing the bottom of said tube formed by the inner wall of the annular container; a skirt extending upwardly from the perforated outer wall of the annular container from a position at or near the bottom surface of said container to a position below the location of a seal; and a seal located at or near the top surface and extending from the container by a distance which extends beyond an outer surface of the skirt; said process comprising: (a) introducing the gaseous reactants through the inlet; (b) passing said reactants downwardly through said at least one tube to the upper surface of the, or the first catalyst carrier where they pass into the passage defined by the inner perforated wall of the container before passing radially through the catalyst bed towards the perforated outer wall; (c) allowing reaction to occur as the gas contacts the catalyst; (d) passing unreacted reactant and product out of the container through the perforated outer wall and then upwardly between the inner

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surface of the skirt and the outer wall of the annular container until they reach the seal where they are directed over the end of the skirt and caused to flow downwardly between the outer surface of the skirt and the inner surface of the reactor tube where heat transfer takes place; (e) repeating steps (b) to (d) at any subsequent catalyst carrier; and (f) removing product from the outlet.

PROCESS FOR THE PRODUCTION OF ANHYDRIDES

The present invention relates to a process for the oxidation of hydrocarbons in the presence of a catalyst to form anhydrides. More particularly it relates to a process for the catalytic oxidation of butane or benzene to maleic anhydride or the oxidation of o-xylene, naphthalene or mixtures thereof to phthalic anhydride.

Processes for the oxidation of hydrocarbons such as butane and benzene to maleic anhydride are well known in the art. For about 50 years, the main process route to maleic anhydride has been the oxidation of benzene in the vapour phase and this remains a commercial route accounting for around 15 to 20 % of global capacity. However, high benzene costs mean that the process is becoming less attractive from an economic standpoint.

As the chemistry of the reactions are very similar, many of the old plants intended to utilise benzene as a starting material have been retrofitted to enable n-butane to be used as the starting material. Whichever starting material is used, the reaction is very exothermic. However, as discussed in more detail below, the energy released from the reaction in which n-butane is the starting material exceeds that where benzene is the starting material and this is reflected in the steam co-product.

It should be understood that there are a number of side reactions. In particular, there are mechanisms that result in small amounts of acetic acid and acrylic acid being formed in addition to carbon oxides.

The chemistry for the oxidation of butane and benzene to maleic anhydride are very similar as are the catalysts used in the reaction. Typical commercial catalysts are based on unsupported vanadium phosphorus oxide (VPO). These are conventionally used in fixed bed reactors. Promoters such as those selected from lithium, zinc and molybdenum may also be used. Recent research has suggested that magnesium, calcium and barium ions may also be effective promoters with the potential to generate higher conversion, yield, and selectivity than the unmodified VPO catalyst.

The ratio of phosphorous to vanadium in the catalyst determines the activity of the catalyst and hence the life. Catalyst activity is greater at high phosphorous:vanadium ratios, but the catalyst life is sacrificed as the activity increases. A phosphorous:vanadium ratio of 1.2 has been suggested to provide the optimal balance between activity and catalyst life.

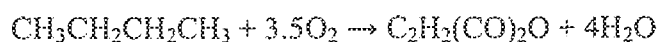
The process for the production of maleic anhydride is illustrated schematically in Figure 1. In this process, feed is prepared in section A. Here the benzene or n-butane feed is vaporised and mixed with compressed air in a controlled manner generally using static in-line mixers. If a catalyst promoter, such as trimethyl phosphate, is to be used, it will be added at this stage. The prepared feed is then passed to section B where the oxidation reaction takes place.

The oxidation will generate a substantial amount of heat which must be removed. Careful control of the reactor is required to prevent the hydrocarbon/oxygen composition breaching combustion limits.

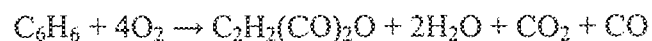
The product of the oxidation reaction is then removed from section B and passed to section C where recovery of the crude product occurs. Here more heat is removed from the reaction off-gas and then an aqueous or solvent based recovery system is generally employed to obtain the crude maleic anhydride stream. This crude stream is then passed to section D where product purification occurs. This is typically a two-step distillation approach involving light ends removal and the separation of a heat cut. This separation is generally vacuum assisted.

Energy recovery is a key factor in achieving an economic process for the production of maleic anhydride. Some or all of the reactor off-gases, post maleic anhydride recovery, non-condensables from vacuum systems, tank vent gases, and waste hydrocarbon rich liquids may all be utilised in energy recovery in section E. Generally these are incinerated to recover energy as super-heated steam. The steam can be used to supply energy to the process or to supply energy to integrated processes.

Specifically, the oxidation of n-butane to maleic anhydride is a complex reaction in which the catalytic system abstracts 8 hydrogen atoms and inserts 3 oxygen atoms giving an exothermic heat release of 297 kcal/g-mol of butane, with the main side reaction of butane oxidation to carbon oxides releasing a further 500 kcal/g-mol of heat. These reactions are shown by the equations below:



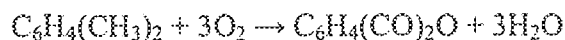
For the oxidation of benzene to maleic anhydride the heat releases are 352 kcal/g-mol and 555 kcal/g-mol:



However, it should be understood that the ratio of carbon monoxide to carbon dioxide is not fixed

On-going development work to improve the maleic anhydride production process centres on identifying more active catalysts and obtaining an increase in yield. However, the benefit of more active catalysts can be difficult to realise in, for example, fixed bed reactors unless the specific reaction rate can be increased. Such increases in productivity generate larger amounts of heat which must be removed at a rate that maintains a stable operating temperature.

Similar processes are used for the oxidation of o-xylene, naphthalene or mixtures thereof to phthalic anhydride. These processes are also well known in the art. The catalyst used will generally be similar to those used in the production of maleic anhydride or may be modifications thereof based on a vanadium-titania mixture. For the oxidation of o-xylene there is a significant heat release of 265 kcal/g-mol, as well as there being heat released when naphthalene is oxidised (467 kcal/g-mol):



Generally the reactions are carried out in specialised reactors which include devices to provide cooling. Generally fixed bed or fluid bed reactors will be used. However, it is difficult to realise the benefits of more active catalysts unless the specific reaction rate can also be increased.

Currently the best heat removal to catalyst ratio for a fixed bed system is delivered by an axial tubular reactor. In this arrangement, catalyst pellets are loaded inside tubes of an axial reactor. Cooling medium, such as vaporising water, is supplied around the tubes. Reactant gases are then passed through the tubes where they contact the catalyst and the oxidation reaction takes place. The heat evolved is transferred through the tube wall to the surrounding cooling medium. In view of the need to control the heat within the tube, the size of the tubes is limited to allow the heat to pass readily from the centre of the tubes to the walls where heat exchange occurs. Generally therefore the tubes have a diameter of less than about 40 mm to ensure the required level of heat transfer and to prevent the catalyst located towards the centre of the tube overheating and thermal runaway occurring. The small size of the tubes contributes to the high cost of construction of these reactors since the number and hence weight of the tubes in the reactor required to contain a specific catalyst volume is limited.

Even at the small tube size the catalyst particles have to be relatively small in order to ensure reasonable mixing and heat transfer. In addition careful selection of conditions such as superficial velocity and gas hourly space velocity has to be made in order to maintain the required heat transfer and manage the conversion of the reactant gases at a reasonable overall pressure drop.

The issue of pressure drop is critical for the oxidation reaction in that mass transfer limitation is thought to occur in catalyst pellets leading to excess carbon dioxide

production in the pores of the catalyst. Whilst this problem can be alleviated by ensuring that the active sites are only present near the surface of the catalyst particle, this can deleteriously affect productivity as the active sites that are available have to be worked hard to deliver a reasonable overall productivity.

Various approaches have been suggested for addressing the problems of these reactors. One proposal is to use multizone catalyst beds. Here the fixed bed is packed with catalysts of different activities. Generally the least active catalyst will be used at the feed point with the most active catalyst being located at or near the exit. Whilst this allows for staged heat release, packing of the catalyst into the tubes becomes a more complex, and hence more costly, procedure.

A second alternative that has been suggested is to operate with variable temperature zones within the same catalyst bed. In this arrangement the same catalyst bed is subjected to different temperature regimes. This is achieved by employing heat removal techniques. However, the engineering of the reactor required to achieve this is complex and costly.

An alternative approach is to carry out the reaction in a fluid bed reactor. This does offer some advantages. In particular these reactors will have an energy balance that provides export of high-pressure steam as a result of operating with less than half the air rate required for a fixed bed system. In this arrangement, small catalyst particles are suspended in the hydrocarbon product and are agitated by the injection of reaction gas at the bottom of the reactor. The gas becomes highly dispersed throughout the reactor and so in theory the mass transfer area from gas to catalyst is very large. Additionally, as the catalyst diameter is low, the mass transfer and heat transfer resistances within the catalyst particle are also low. Since the catalyst surface area is relatively large the heat transfer from catalyst particle to fluid is high so that the particles can be maintained at approaching fluid temperature conditions. The high heat evolution in the reaction can be managed with internal or external coils in which water is vaporised. Thus in theory, carrying out the process in a bubble slurry reactor offers various advantages.

However, problems can be encountered if the necessary particle size distribution in the reactor cannot be maintained while utilizing an economical amount of catalyst make-up.

An alternative approach has been to use a transport bed reactor. These reactors are also known as circulating-fluidized-bed reactors. However, these reactors still suffer from various drawbacks and disadvantages.

Thus it will be understood that whilst the various approaches to carrying out the reactions for the production of anhydrides such as maleic anhydride and phthalic anhydrides each offer some advantages, they also each have their own disadvantages. There is therefore still a need to provide an improved process which addresses one or more of the problems of prior art arrangements.

According to the present invention there is provided a process for the production of anhydrides by contacting a gaseous feed stream with a particulate catalyst, said process being carried out in a tubular reactor having an inlet and an outlet, said outlet being located downstream of the inlet, said reactor comprising one or more tubes having located therein one or more carriers for said particulate catalyst and cooling medium in contact with said at least one tube;

wherein said catalyst carrier comprises:

- an annular container holding catalyst, said container having a perforated inner wall defining a tube, a perforated outer wall, a top surface closing the annular container and a bottom surface closing the annular container;

- a surface closing the bottom of said tube formed by the inner wall of the annular container;

- a skirt extending upwardly from the perforated outer wall of the annular container from a position at or near the bottom surface of said container to a position below the location of a seal; and

- a seal located at or near the top surface and extending from the container by a distance which extends beyond an outer surface of the skirt; said process comprising:

- (a) introducing the gaseous reactants through the inlet;

- (b) passing said reactants downwardly through said at least one tube to the upper surface of the, or the first, catalyst carrier where they pass into the

- passage defined by the inner perforated wall of the container before passing radially through the catalyst bed towards the perforated outer wall;
- (c) allowing reaction to occur as the gas contacts the catalyst;
 - (d) passing unreacted reactant and product out of the container through the perforated outer wall and then upwardly between the inner surface of the skirt and the outer wall of the annular container until they reach the seal where they are directed over the end of the skirt and caused to flow downwardly between the outer surface of the skirt and the inner surface of the reactor tube where heat transfer takes place;
 - (e) repeating steps (b) to (d) at any subsequent catalyst carrier; and
 - (f) removing product from the outlet.

The catalyst carrier is described in detail in PCT/GB2010/001931 filed on 19th October 2010 which is incorporated herein by reference.

For the avoidance of doubt, any discussion of orientation, for example terms such as upwardly, below, lower, and the like have, for ease of reference been discussed with regard to the orientation of the catalyst carrier as illustrated in the accompanying drawings. However, where the tubes, and hence the catalyst carrier, are used in an alternative orientation, the terms should be construed accordingly.

The catalyst container will generally be sized such that it is of a smaller dimension than the internal dimension of the reactor tube into which it is placed. The seal is sized such that it interacts with the inner wall of the reactor tube when the catalyst carrier of the present invention is in position within the tube. The seal need not be perfect provided that it is sufficiently effective to cause the majority of the flowing gas to pass through the carrier.

Generally, a plurality of catalyst carriers will be stacked within the reactor tube. In this arrangement, the reactants/products flow downwardly between the outer surface of the skirt of a first carrier and the inner surface of the reactor tube until they contact the upper surface and seal of a second carrier and are directed downwardly into the

tube of the second carrier defined by the perforated inner wall of its annular container. The flow path described above is then repeated.

The catalyst carrier may be formed of any suitable material. Such material will generally be selected to withstand the operating conditions of the reactor. Generally, the catalyst carrier will be fabricated from carbon steel, aluminium, stainless steel, other alloys or any material able to withstand the reaction conditions.

The wall of the annular container can be of any suitable thickness. Suitable thickness will be of the order of about 0.1 mm to about 1.0 mm, preferably of the order of about 0.3 mm to about 0.5 mm.

The size of the perforations in the inner and outer walls of the annular container will be selected such as to allow uniform flow of reactant(s) and product(s) through the catalyst while maintaining the catalyst within the container. It will therefore be understood that their size will depend on the size of the catalyst particles being used. In an alternative arrangement the perforations may be sized such that they are larger but have a filter mesh covering the perforations to ensure catalyst is maintained within the annular container. This enables larger perforations to be used which will facilitate the free movement of reactants without a significant loss of pressure.

It will be understood that the perforations may be of any suitable configuration. Indeed where a wall is described as perforated all that is required is that there is means to allow the reactants and products to pass through the walls. These may be small apertures of any configuration, they may be slots, they may be formed by a wire screen or by any other means of creating a porous or permeable surface.

Although the top surface closing the annular container will generally be located at the upper edge of the, or each, wall of the annular container, it may be desirable to locate the top surface below the upper edge such that a portion of the upper edge of the outer wall forms a lip. Similarly, the bottom surface may be located at the lower edge of the, or each, wall of the annular container or may be desirable to locate the bottom

surface such that it is above the bottom edge of the wall of the annular container such that the wall forms a lip.

The bottom surface of the annulus and the surface closing the bottom of the tube may be formed as a single unit or they may be separate pieces connected together. The two surfaces may be coplanar but in a preferred arrangement, they are in different planes. In one arrangement, the surface closing the bottom of the tube is in a lower plane than the bottom surface of the annular container. This serves to assist in the location of one carrier on to a carrier arranged below it when a plurality of containers are to be used. It will be understood that in an alternative arrangement, the surface closing the bottom of the tube may be in a higher plane than the bottom surface of the annular container.

Whilst the bottom surface will generally be solid, it may include one or more drain holes. Where one or more drain holes are present, they may be covered by a filter mesh. Similarly a drain hole, optionally covered with a filter mesh may be present in the surface closing the bottom of the tube. Where the carrier is to be used in a non-vertical orientation, the drain hole, where present will be located in an alternative position i.e. one that is the lowest point in the carrier when in use.

One or more spacer means may extend downwardly from the bottom surface of the annular container. The, or each, spacer means may be formed as separate components or they may be formed by depressions in the bottom surface. Where these spacer means are present they assist in providing a clear path for the reactants and products flowing between the bottom surface of the first carrier and the top surface of a second lower carrier in use. The spacer may be of the order of about 4 mm to about 15 mm or about 6 mm deep. Alternatively, or additionally, spacer means may be present on the top surface.

The top surface closing the annular container may include on its upper surface means to locate the container against a catalyst carrier stacked above the container in use. The means to locate the container may be of any suitable arrangement. In one

arrangement it comprises an upstanding collar having apertures or spaces therein to allow for the ingress of reactants.

The upwardly extending skirt may be smooth or it may be shaped. Any suitable shape may be used. Suitable shapes include pleats, corrugations, and the like. The pleats, corrugations and the like will generally be arranged longitudinally along the length of the carrier. The shaping of the upstanding skirt increases the surface area of the skirt and assists with the insertion of the catalyst carrier into the reaction tube since it will allow any surface roughness on the inner surface of the reactor tube or differences in tolerances in tubes to be accommodated.

Where the upwardly extending skirt is shaped, it will generally be flattened to a smooth configuration towards the point at which it is connected to the annular container to allow a gas seal to be formed with the annular container. The upstanding skirt will generally be connected to the outer wall of the annular container at or near the base thereof. Where the skirt is connected at a point above the bottom of the wall, the wall will be free of perforations in the area below the point of connection. The upstanding skirt may be flexible.

Generally, the upstanding skirt will stop at about 0.5 cm to about 1.5 cm, preferably about 1 cm, short of the top surface of the annular container.

Without wishing to be bound by any theory, it is believed that the upstanding skirt serves to gather the reactants/products from the perforated outer wall of the annular container and direct them via the shapes towards the top of the catalyst carrier collecting more reactants/products exiting from the outer wall of the annular container as they move upwardly. As described above, reactants/products are then directed down between the tube wall and the outside of the upstanding skirt. By this method the heat transfer is enhanced down the whole length of the carrier but as the heat exchange is separated from the catalyst, hotter or colder as appropriate heat exchange fluid can be used without quenching the reaction at the tube wall and at the same time ensuring that the temperature of the catalyst towards the centre of the carrier is appropriately maintained.

The seal may be formed in any suitable manner. However, it will generally be sufficiently compressible to accommodate the smallest diameter of the reactor tube. The seal will generally be a flexible, sliding seal. In one arrangement, an O-ring may be used. A compressible split ring or a ring having a high coefficient of expansion could be used. The seal may be formed of any suitable material provided that it can withstand the reaction conditions. In one arrangement, it may be a deformable flange extending from the carrier. The flange may be sized to be larger than the internal diameter of the tube such that as the container is inserted into the tube it is deformed to fit inside and interact with the tube.

In the present invention, the annular space between the outer surface of the catalyst container and the inner surface of the tube wall is small, generally of the order of from about 3 mm to about 10 mm. This narrow gap allows a heat transfer coefficient to be achieved such that an acceptable temperature difference of the order of about 10 ° to about 40 °C between the cooled exit gas and the coolant to be achieved.

The size of the annulus between the skirt and the catalyst wall and the skirt and the tube wall will generally be selected to accommodate the gas flow rate required while maintaining high heat transfer and low pressure drop. Thus the process of the present invention may additionally include the step of selecting the appropriate size of the annulus to meet these criteria.

The process of the present invention enables relatively large reactor tubes to be used. In particular, tubes having diameters in the region of from about 75 mm to about 130 mm or even about 150 mm can be used compared to diameters of less than about 40 mm used in conventional systems. The larger diameter tubes will allow an increase in capacity of about 25,000 tonnes to about 250,000 tonnes a year for the same length reactor tube.

As discussed above the highly exothermic nature of the reactions in which anhydrides are formed is a major factor in the design of a reactor in which the reaction can be carried out. The use of the catalyst carrier in the process of the present invention,

allows tubes comprising a plurality of catalyst carriers to become, in effect, a plurality of adiabatic reactors with inter-cooling.

Any suitable catalyst may be used in the process of the present invention. Powdered, foamed, structured, or other suitable forms may be used.

One benefit of the process of the present invention is that the carrier allows for the deployment of small diameter catalysts to be used such as those having diameters of from about 100 μm to about 1 mm. Since these are used in a fixed bed, the mass transfer resistances can be greatly reduced over prior art arrangements. This will lead to improved selectivity to the required products.

Further, as these small catalysts have a high surface area and are located in the direct flow of the reacting gas, they are maintained at a temperature which is very similar to that of the flowing gas. This will reduce the tendency to by-product formation.

In one alternative arrangement, a monolith catalyst may be used. In this arrangement, the structure of the catalyst container may be modified. Full details of a catalyst container suitable for use with a monolith catalyst is described in GB patent application no 1105691.8 filed 4th April 2011 the contents of which are incorporated herein by reference.

Thus according to a second aspect of the present invention there is provided a process for the production of anhydrides by contacting a gaseous stream with a monolith catalyst, said process being carried out in a tubular reactor having an inlet and an outlet, said outlet being located downstream of the inlet, said reactor comprising one or more tubes having located therein one or more carriers for said monolith catalyst and cooling medium in contact with said tubes;

wherein said catalyst carrier comprises:

a container holding a monolith catalyst, said container having a bottom surface closing the container and a skirt extending upwardly from the bottom surface of said container to a position below the location of a seal and spaced therefrom, said skirt

being positioned such that there is a space between an outer surface of the monolith catalyst and the skirt; and

a seal located at or near a top surface of the monolith catalyst and extending from the monolith catalyst by a distance which extends beyond an outer surface of the skirt; said process comprising:

- (a) introducing the gaseous reactants through the inlet;
- (b) passing said reactants downwardly through said at least one tube to the upper surface of the, or the first, monolith catalyst where they pass through the monolith catalyst;
- (c) allowing reaction to occur as the gas contacts the catalyst;
- (d) passing unreacted reactant and product out of the catalyst and then upwardly between the inner surface of the skirt and the outer surface of the monolith catalyst until they reach the seal where they are directed over the end of the skirt and caused to flow downwardly between the outer surface of the skirt and the inner surface of the reactor tube where heat transfer takes place;
- (e) repeating steps (b) to (d) at any subsequent catalyst carrier; and
- (f) removing product from the outlet.

In one arrangement, the monolith catalyst is a solid, in that there is substantially no space within the body of the monolith that is not occupied by catalyst. When the monolith is in use in a vertical reactor with downflow, the reactant(s) flow downwardly through the reactor tube, the reactant(s) first contacts the upper face of the monolith catalyst and flows therethrough in a direction parallel to the axis of the cylinder. The seal of the container prevents the reactant(s) from flowing around the monolith and assists the direction of the reactants into the catalyst. Reaction will then occur within the monolith catalyst. The product will then also flow down through the monolith in a direction parallel to the axis of the cylinder.

Once the reactant(s) and product reach the bottom surface of the catalyst carrier they are directed towards the skirt of the carrier. To facilitate this flow, feet may be provided within the carrier on the upper face of the bottom surface such that, in use, the catalyst monolith is supported on the feet and there is a gap between the bottom of

the catalyst monolith and the bottom surface of the catalyst carrier. The upwardly extending skirt then directs the reactant(s) and product upwardly between the inner surface of the skirt and the outer surface of the monolith catalyst until they reach the underside of the seal. They are then directed, by the underside of the seal, over the end of the skirt and they then flow downwardly between the outer surface of the skirt and the inner surface of the reactor tube where heat transfer takes place.

In one alternative arrangement, the monolith catalyst has a channel extending longitudinally therethrough. Generally the channel will be located on the central axis of the monolith catalyst. Thus where the reactor tube is of circular cross-section, the monolith catalyst of this arrangement will be of annular cross-section. In this arrangement, in use, in a vertical reactor with downflow, reactant(s) flow downwardly through the reactor tube and thus first contacts the upper surface of the monolith catalyst. The seal blocks the passage of the reactant(s) around the side of the catalyst. Since the path of flow of reactant(s) is impeded by the catalyst, it will generally take the easier path and enter the channel in the monolith. The reactant(s) then enters the annular monolith catalyst and passes radially through the catalyst towards the outer surface of the catalyst monolith. During the passage through the catalyst monolith reaction occurs. Unreacted reactant and product then flow out of the monolith catalyst through the outer surface thereof. The upwardly extending skirt then directs reactant and product upwardly between the inner surface of the skirt and the outer wall of the monolith catalyst until they reach the seal. They are then directed, by the underside of the seal, over the end of the skirt and flow downwardly between the outer surface of the skirt and the inner surface of the reactor tube where heat transfer takes place.

In the arrangement in which the monolith catalyst includes the channel, the catalyst carrier may include a top surface which will extend over the monolith catalyst but leave the channel uncovered. This top surface serves to ensure that the reactant(s) do not enter the catalyst monolith from the top but are directed into the channel for radial flow.

The discussion of the specific features of the catalyst carrier above in relation to the first embodiment applies equally in connection to the catalyst carrier for a monolith catalyst of the second embodiment insofar as the relevant features are present.

Whichever type of carrier is used, in one arrangement more than 40 carriers, preferably more than 41 carriers are located within a single tube. More preferably, from about 70 to about 200 carriers may be used. This will enable a reasonable temperature rise of the order of from about 10 °C to about 20 °C to be maintained over each stage.

The radial flow through the, or each, catalyst carrier within the tube means that the gas flow path length is also very low when compared with prior art arrangements. Total catalyst depths of the order of about 2 metres may be achieved within a tube of up to 20 metres of length at catalyst hourly space velocities of about 2400. The low flow path means that the overall pressure drop achieved is an order of magnitude lower than that which would be experienced with the same catalyst in an axial tube not using the process of the present invention.

One advantage of being able to achieve a low overall pressure drop by the process of the present invention is that long tubes with high superficial gas velocities, gases containing high quantities of inerts or a gas recycle may be accommodated without the pressure drop and potential for catalyst crushing disadvantages experienced with high flows through current fixed bed systems. This ability to accommodate recycle will enable overall conversion at lower per pass conversions to be achieved at high catalyst productivity and selectivity.

The catalyst may be repeatedly and reliably loaded into the carrier at a manufacturing facility. The containers may be assembled in connected units which will simplify the loading of the reactor and in particular will mean that the operators do not have to come into contact with the catalyst. The unloading procedure is also simplified since the carriers may be readily discharged before being taken for reprocessing.

In one arrangement of the present invention, a plurality of reactors may be used in parallel.

Liquid product stream separate from the stream exiting the reactor will be recovered. In the process of the present invention, unreacted gas exiting the outlet of the, or each, reactor may be further treated to remove heat. The removed heat may be reused and/or rejected to cooling. Liquid product separated from the stream exiting the reactor will be recovered.

In one arrangement, two or more reactors may be located in series fluid communication with facilities located between each reactor to remove heat. The heat may be reused and/or rejected to cooling. In one arrangement, unreacted feed containing steam exiting the last stage of a series of interconnected reactors may be recycled to any suitable point in the process. In one arrangement it will be recycled to the inlet of the first reactor.

In one alternative arrangement, two or more groups of parallel reactors may be located in series. In this arrangement, groups of parallel reactors are in series communication with facilities located between each group to remove heat. The heat may be reused or rejected to cooling. In one arrangement, liquid product may be removed between each stage with carbon oxides containing steam being passed to a subsequent reaction stage in the series. Carbon oxides containing steam exiting the last stage of a series of interconnected reactors may be recycled to any suitable point in the process. In one arrangement it will be recycled to the inlet of the first reactor.

Where the process includes a plurality of reaction stages, additional feed may be fed to the second and/or one or more of any subsequent stages.

The process of the present invention may be used for the production of anhydrides. In one arrangement it relates to the production of maleic anhydride from a feed stream comprising n-butane or benzene. In an alternative arrangement, it relates to production of phthalic anhydride from a feed stream comprising o-xylene, naphthalene or mixtures thereof.

Any suitable reaction conditions may be used. In one arrangement, the inlet temperature may be in the region of about 100 °C which will give an exit temperature of about 420°C. The reaction pressure may be from about 0.7 bara to about 3.5 bara.

The present invention will now be described, by way of example, by reference to the accompanying drawings in which:

- Figure 1 is a schematic representation of the overall process for the production of anhydrides;
- Figure 2 is a perspective view from above of the catalyst carrier of the present invention;
- Figure 3 is a perspective view of the catalyst carrier from below;
- Figure 4 is a partial cross section viewed from the side;
- Figure 5 is a simplified diagram of the catalyst carrier of the present invention;
- Figure 6 is a schematic illustration of a carrier of the present invention from below when located within a tube;
- Figure 7 is a schematic cross section of three catalyst carriers located within a tube;
- Figure 8 is an enlarged cross-section of Section A of Figure 7;
- Figure 9 is a schematic representation of an alternative embodiment of the present invention, illustrating the flow path;
- Figure 10 is a schematic representation of a third embodiment of the present invention, illustrating the flow path; and

Figure 11 is a schematic representation of the flow path between two stacked carriers of the kind illustrated in Figure 10.

A catalyst carrier 1 of the present invention is illustrated in Figures 2 to 4. The carrier comprises an annular container 2 which has perforated walls 3, 4. The inner perforated wall 3 defines a tube 5. A top surface 6 closes the annular container at the top. It is located at a point towards the top of the walls 3, 4 of the annular container 2 such that a lip 6 is formed. A bottom surface 7 closes the bottom of the annular container 2 and a surface 8 closes the bottom of tube 5. The surface 8 is located in a lower plane than that of the bottom surface 7. Spacer means in the form of a plurality of depressions 9 are located present on the bottom surface 7 of the annular container 2. Drain holes 10, 11 are located on the bottom surface 7 and the surface 8.

A seal 12 extends from the upper surface 6 and an upstanding collar 13 is provided coaxial with the tube 5.

A corrugated upstanding skirt 14 surrounds the container 2. The corrugations are flattened in the region L towards the base of the carrier 1.

A catalyst carrier 1 of the present invention located in a reactor tube 15. The flow of gas is illustrated schematically in Figure 5 by the arrows.

When a plurality of catalyst carriers of the present invention are located within a reactor tube 15 they interlock as illustrated in Figures 7 and 8. The effect on the flow path is illustrated in the enlarged section shown in Figure 8.

A catalyst carrier 101 of a second embodiment is illustrated in Figure 9. A bottom surface 102 closes the bottom of the container 101. Feet 103 extend upwardly from the bottom surface to support a monolith catalyst 104. An upstanding skirt 105 extends from the bottom surface 102. The skirt may be corrugated and may be flattened as in a region towards the bottom surface 103.

A seal 106 is provided to extend from the monolith catalyst 104 and interact with the wall of the reactor tube 107. Baffles 108 extend upwardly for the seal. These serve to direct flow and to separate the carrier from the bottom surface of a carrier located above the carrier. The flow of gas is illustrated schematically by the arrows.

An alternative embodiment of the present invention is illustrated in Figure 10. In this arrangement the monolith catalyst 104 has a longitudinal channel 109 therethrough. In this arrangement, the feet of the first embodiment may be omitted. This carrier is similar in arrangement to the first embodiment. However, additionally a top surface 110 is provided to cover the upper surface of the monolith catalyst. The flow of gas in the arrangement of Figure 10 is illustrated schematically by the arrows.

When a plurality of catalyst carriers of the present invention are located within a reactor tube 107 the effect on the flow path is illustrated in the enlarged section shown in Figure 11.

It will be understood that whilst the catalyst carriers have been described with particular reference to a use in a tube of circular cross-section the tube may be of non-circular cross-section for example, it may be a plate reactor. Where the tube is of non-circular cross-section, the carrier will be of the appropriate shape. In this arrangement, in the embodiment described in which an annular monolith is used it will be understood that the monolith will not be a circular ring and this term should be construed accordingly.

Claims

1. A process for the production of anhydrides by contacting a gaseous feed stream with a particulate catalyst, said process being carried out in a tubular reactor having an inlet and an outlet, said outlet being located downstream of the inlet, said reactor comprising one or more tubes having located therein one or more carriers for said particulate catalyst and cooling medium in contact with said tubes; wherein said catalyst carrier comprises:

an annular container for holding catalyst in use, said container having a perforated inner wall defining a tube, a perforated outer wall, a top surface closing the annular container and a bottom surface closing the annular container;

a surface closing the bottom of said tube formed by the inner wall of the annular container;

a skirt extending upwardly from the perforated outer wall of the annular container from a position at or near the bottom surface of said container to a position below the location of a seal; and

a seal located at or near the top surface and extending from the container by a distance which extends beyond an outer surface of the skirt; said process comprising:

- (a) introducing the gaseous reactants through the inlet;
- (b) passing said reactants downwardly through said at least one tube to the upper surface of the, or the first catalyst carrier where they pass into the passage defined by the inner perforated wall of the container before passing radially through the catalyst bed towards the perforated outer wall;
- (c) allowing reaction to occur as the gas contacts the catalyst;
- (d) passing unreacted reactant and product out of the container through the perforated outer wall and then upwardly between the inner surface of the skirt and the outer wall of the annular container until they reach the seal where they are directed over the end of the skirt and caused to flow downwardly between the outer surface of the skirt and the inner surface of the reactor tube where heat transfer takes place;
- (e) repeating steps (b) to (d) at any subsequent catalyst carrier; and
- (f) removing product from the outlet.

2. A process according to Claim 1 wherein the catalyst has a diameter of from about 100 μm to about 1 mm

3. A process for the production of anhydrides by contacting a gaseous feed stream with a monolith catalyst, said process being carried out in a tubular reactor having an inlet and an outlet, said outlet being located downstream of the inlet, said reactor comprising one or more tubes having located therein one or more carriers for said monolith catalyst and cooling medium in contact with said tubes;

wherein said catalyst carrier comprises:

a container holding a monolith catalyst, said container having a bottom surface closing the container and a skirt extending upwardly from the bottom surface of said container to a position below the location of a seal and spaced therefrom, said skirt being positioned such that there is a space between an outer surface of the monolith catalyst and the skirt; and

a seal located at or near a top surface of the monolith catalyst and extending from the monolith catalyst by a distance which extends beyond an outer surface of the skirt; said process comprising:

- (a) introducing the gaseous reactants through the inlet;
- (b) passing said reactants downwardly through said at least one tube to the upper surface of the, or the first, monolith catalyst where they pass through the monolith catalyst;
- (c) allowing reaction to occur as the gas contacts the catalyst;
- (d) passing unreacted reactant and product out of the catalyst and then upwardly between the inner surface of the skirt and the outer surface of the monolith catalyst until they reach the seal where they are directed over the end of the skirt and caused to flow downwardly between the outer surface of the skirt and the inner surface of the reactor tube where heat transfer takes place;
- (e) repeating steps (b) to (d) at any subsequent catalyst carrier; and
- (f) removing product from the outlet.

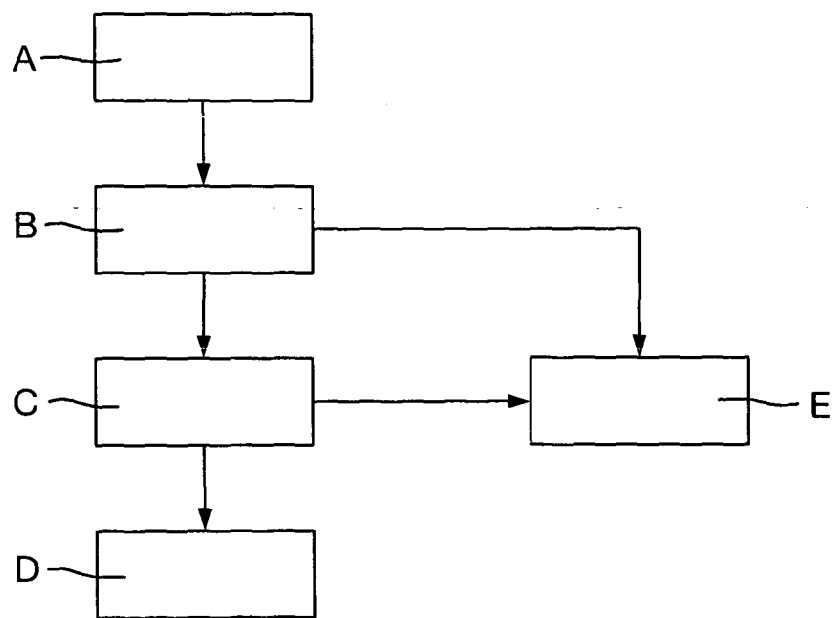
4. A process according to any one of Claims 1 to 3 wherein a plurality of catalyst carriers are stacked within the reactor tube.

5. A process according to any one of Claims 1 to 4 wherein the annular space between the outer surface of the catalyst container and the inner surface of the tube wall is selected to accommodate the gas flow rate required while maintaining high heat transfer and low pressure drop.
6. A process according to any one of Claims 1 to 5 wherein the annular space between the outer surface of the catalyst container and the inner surface of the tube wall is of the order of from about 3 mm to about 10 mm.
7. A process according to any one of Claims 1 to 6 wherein the tubes have a diameter in the region of from about 75 mm to about 130 mm.
8. A process according to any one of Claims 1 to 7 wherein more than 41 carriers are located within a single tube.
9. A process according to any one of Claims 1 to 8 wherein from about 70 to about 200 carriers are located within a single tube.
10. A process according to any one of Claims 1 to 9 wherein a plurality of reactors are used in parallel.
11. A process according to any one of Claims 1 to 10 wherein unreacted gas exiting the outlet of the each or each reactor is treated to remove heat.
12. A process according to Claim 11 wherein the removed unreacted gas is reused.
13. A process according to any one of Claims 1 to 9 wherein two or more reactors are located in series.
14. A process according to Claim 13 wherein the reactors located in series are in fluid communication with facilities located between each reactor to remove heat.
15. A process according to Claim 13 or 14 wherein unreacted feed containing steam exiting the last stage of the series of interconnected reactors is recycled to any suitable point in the process.

16. A process according to Claim 15 wherein unreacted feed containing steam exiting the last stage of the series of interconnected reactors is recycled to the first reactor.
17. A process according to Claim 9 wherein groups of parallel reactors are in series communication with facilities located between each group to remove heat.
18. A process according to Claim 13 or 17 wherein the heat is reused and/or rejected to cooling.
19. A process according to Claim 17, wherein liquid product is removed between each group of parallel reactors with unreacted feed containing steam being passed to a subsequent reaction reaction group in the series.
20. A process according to Claim 20 wherein unreacted feed containing steam exiting the last stage of a series of interconnected reactors is recycled to any suitable point in the process.
21. A process according to Claim 20 wherein the stream is recycled to the inlet of the first reactor.
22. A process according to any one of Claims 1 to 21 wherein the process is for the production of maleic anhydride from a feed stream comprising n-butane or benzene or is for the production of phthalic anhydride from a feed stream comprising o-xylene, naphthalene or mixtures thereof.
23. A process according to any one of Claims 1 to 22 wherein the inlet temperature is about 100 °C.
24. A process according to any one of Claims 1 to 23 wherein the reaction pressure is from about 0.7 bara to about 3.5 bara.

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Fig. 1



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Fig. 2

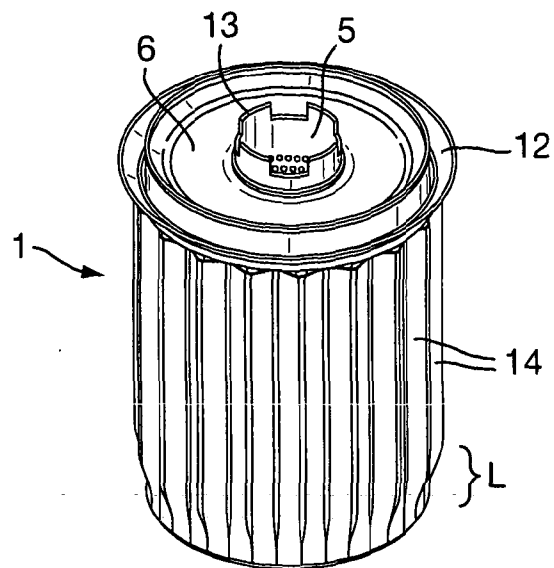


Fig. 3

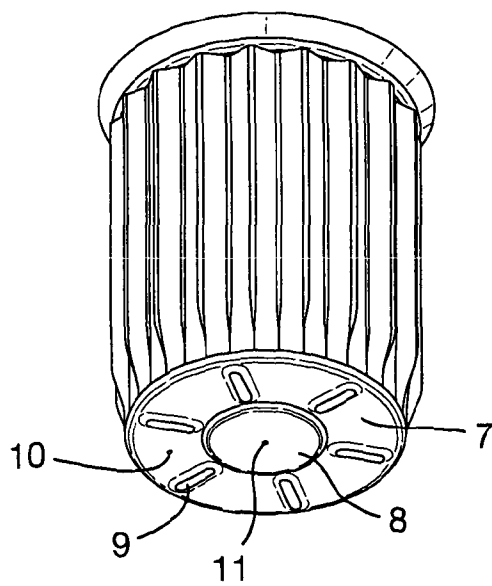


Fig. 4

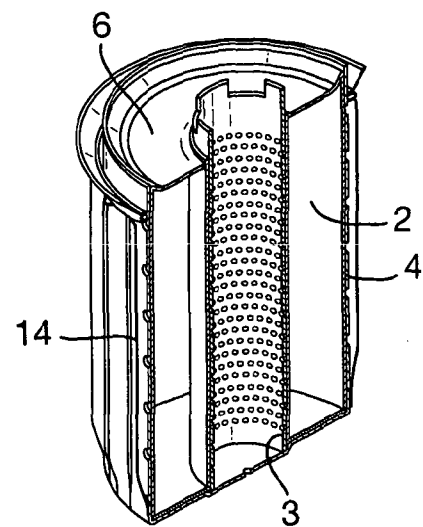


Fig. 5

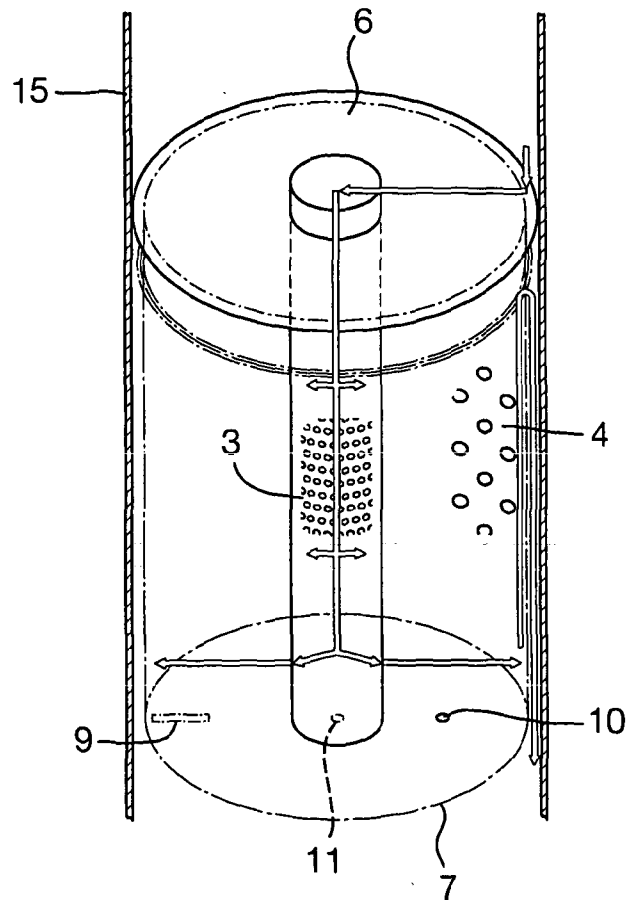
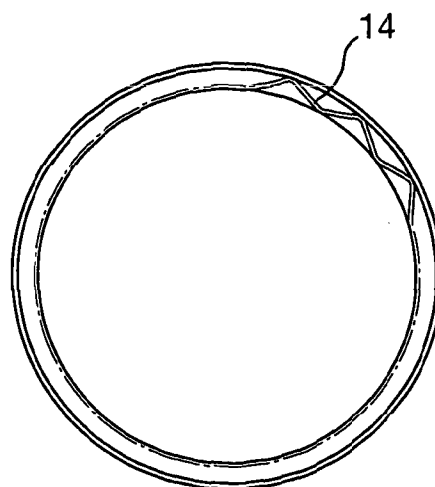


Fig. 6



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Fig. 7

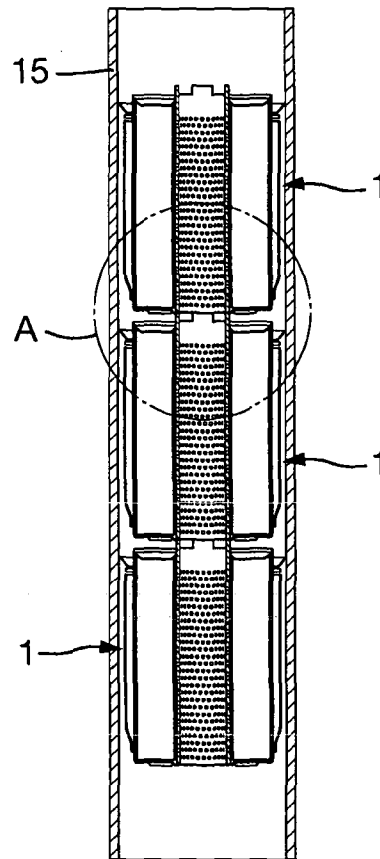
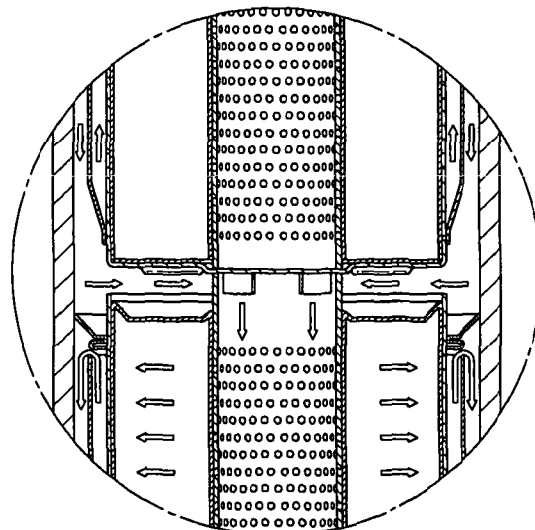


Fig. 8



Detail A

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Fig. 9

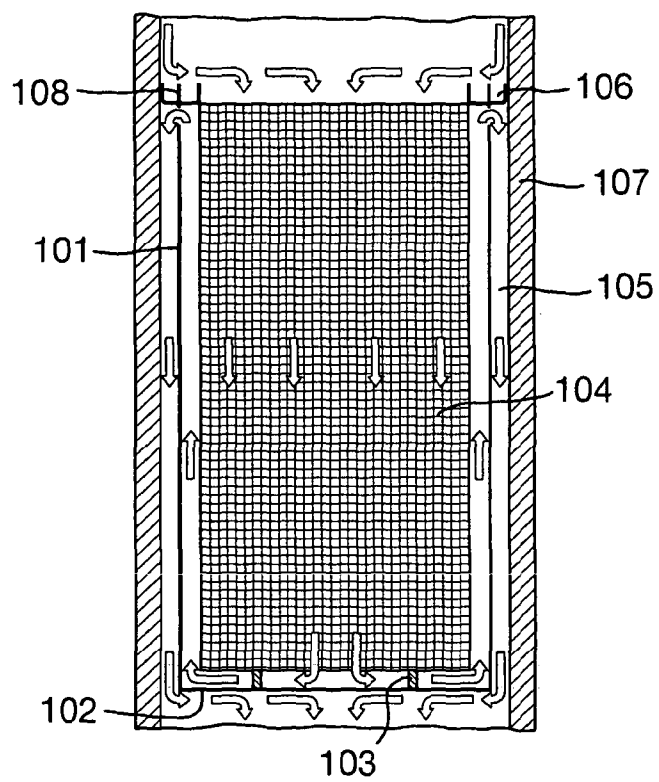
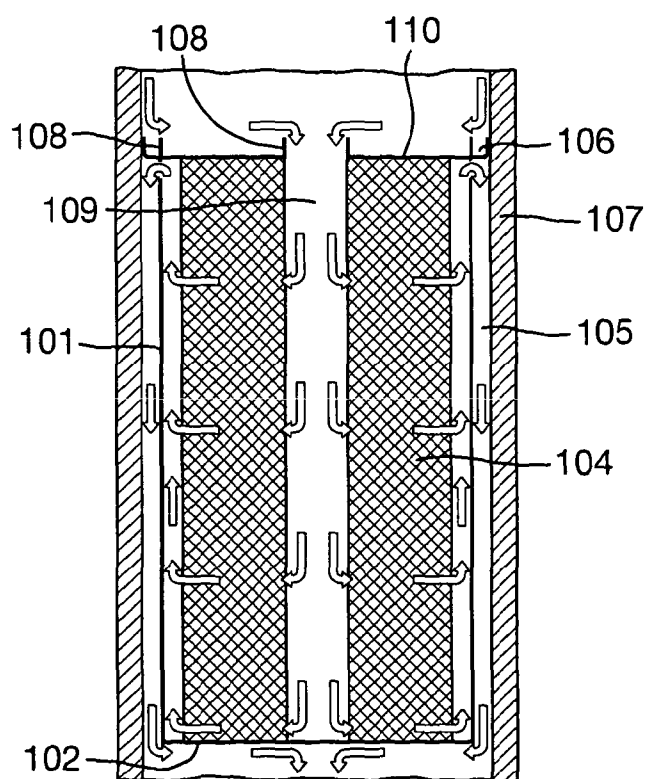
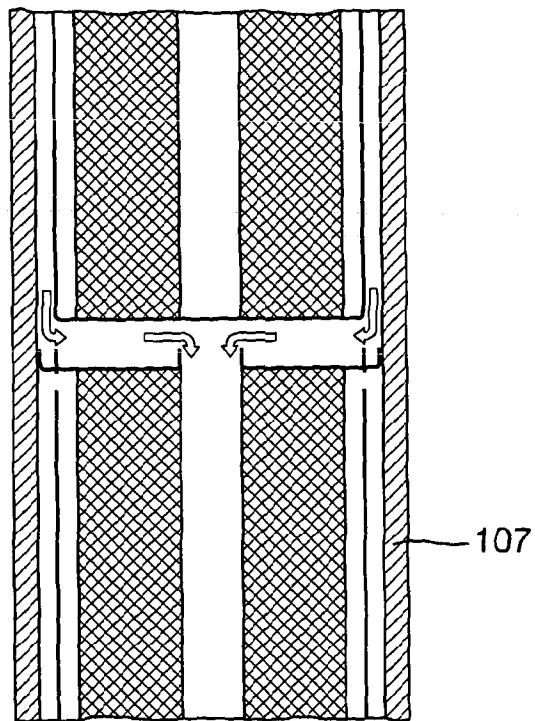


Fig. 10



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Fig. 11



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/050233

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J8/06 B01J19/24 C07C51/31
ADD.

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 C07C

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

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

☒ See patent family annex.

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Date of the actual completion of the international search

20 April 2012

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02/05/2012

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/050233

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International application No

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