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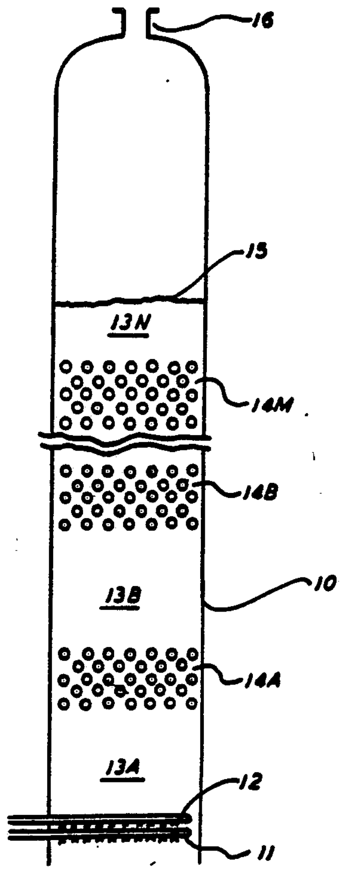
(54) Title: FLUIDIZED BED

(57) Abstract

A fluidized bed vessel (10) including horizontal heat exchanger tube banks (14A, 14B, 14M) having tubes spaced from each other to provide for essentially plug flow of gas through the vessel and breaking of rising bubbles while also obtaining adequate heat transfer and solids exchange. The vessel is particularly useful for producing maleic anhydride.



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FLUIDIZED BED

This invention relates to a fluidized bed, and the use thereof for contacting a gas phase with solid particles.

This invention further relates to a new and improved process for effecting a reaction in a fluidized bed.

This invention additionally relates to the production of maleic anhydride in a fluidized bed.

Fluidized beds are generally known in the art as being suitable for effecting contact between a gas and solids. In particular, such fluidized beds are known to be suitable for effecting catalytic reactions wherein one or more gas reagents are contacted with a particulate solid catalyst.

Although a fluidized bed reactor offers advantages with respect to fixed bed catalytic reactors, a fluidized bed system suffers from a few fundamental drawbacks, such as (a) poor catalyst-to-gas contact, (b) bulk bypass of gas bubbles, and (c) back-mixing of the gas. All these potential drawbacks can lead to a reduction in conversion and/or selectivity.

In accordance with one aspect of the present invention, there is provided an improved fluidized bed vessel wherein the vessel is provided with a plurality of horizontal heat exchanger tubes positioned within the vessel in at least one horizontal row with the horizontal tubes having spaces therebetween to provide a free flow area between the tubes so that there is fluid flow communication between the portions of the vessel above and below the tubes. The spacing and arrangement of the tubes are selected in a manner such that the ratio of free area between the tubes to the free area of the vessel in the absence of tubes provides for breaking of rising bubbles. In addition, the free area between the tubes provides flow parameters whereby the gas flows through the bed in essentially plug flow, i.e., with gas backmix largely eliminated. Moreover, the spacing is such that there is an exchange of solids between the portions above and below the tubes so as to enable adequate temperature control and to avoid particle size segregation.

The heat exchanger tubes in the vessel have a total surface area such as to provide the heating or cooling requirements for the vessel; for example, if the vessel is employed for an endothermic reaction, then the heat exchanger tubes will have a surface area so as to provide for appropriate heating. Similarly, if the fluidized vessel is employed for an exothermic reaction, then the total surface area of the heat exchange tubes is sufficient to meet the cooling requirements for the reaction. In accordance with the preferred embodiment, the heat exchanger tubes will be placed in several vertically spaced horizontal banks, with each horizontal bank having at least one row of horizontal tubes and preferably each bank having several horizontal rows of tubes. The open spaces between vertically spaced tube banks and between a tube bank and either the feed inlet or the reactor outlet define compartments of chambers of fluidized solids. The open spaces or compartments assure that the fluidized bed is rehomogenized in the event that there is a tendency toward localized channeling or inhomogenity due to the presence of horizontal or vertical obstructions, and that lateral mixing is not impaired, thereby minimizing the possibilities of unwarranted lateral temperature and concentration gradients. Accordingly, in each of the superimposed compartments or chambers, there is continuous mixing of the solid phase.

The horizontal and vertical spacing between tubes within a horizontal bank, and the vertical spacing between horizontal tube banks over the vertical length of the reactor are selected so as to effectively break rising bubbles, minimize gas backmix, and increase conversion and/or selectivity without causing a significant pressure drop or attrition or segregation of solid particles. In addition, the tube spacing and arrangements are optimized for the maximum possible bed-to-tube heat transfer coefficient, with minimum sacrifice of the bubble control and backmix prevention capability of tube banks.

In accordance with the present invention, the horizontal tubes in at least one tube bank (the at least one tube bank may contain one or more rows of horizontal tubes) are arranged in a manner such that the free cross-sectional area of spaces between the tubes in the bank, as projected in a plan view of the at least one tube bank (the "Projected Free Area") is less than 60% and preferably less than 50% of the cross-sectional area of the vessel without tubes. The total open space or free area between tubes in a horizontal plane through the tube bank (cross-sectional area of the total space between tubes in each horizontal row of tubes) is generally at least 10% and preferably at least 20% of the cross-sectional area of the vessel without tubes. As should be apparent, the "Projected Free Area" for a tube bank can be 0%, even though the free area in each horizontal plane through the tube bank is at least 10%. Thus, for example, by staggering tubes in successive rows in the tube bank it is possible to obtain a "Projected Free Area" for the tube bank which is less than the free area between the tubes in each horizontal plane through the tube bank.

The at least one tube bank preferably contains at least two rows of horizontal tubes, and the reactor preferably includes at least two vertically spaced banks of horizontal tubes.

The size and number of tubes, and the spacings between the tubes, as well as the possible staggering of the tube arrangement in each bank (i.e., whereby tubes in one row are aligned with the inter-tube spaces of an adjacent row) will be such as to provide for essentially plug flow of the gas through the vessel, while maintaining a good exchange rate of solids between compartments. In addition, such arrangement will cause effective redistribution and breaking of the rising bubbles, without causing a significant pressure drop, or attrition or segregation of solid particles. Furthermore, the tube spacings and arrangements are optimized for the maximum sacrifice of the bubble control and backmix prevention capability of the tube banks.

The vertical spacing between the tube banks is selected so as to maximize conversion and/or selectivity by providing for effective breaking of rising bubbles and an essentially plug flow of gas through the vessel.

In some cases, the conditions are such that the number of heat exchanger tubes required for breaking of rising bubbles is greater than the heat exchange requirements. In such a case it is possible to use "dummy" tubes or appropriate baffling to provide for breaking of rising bubbles and essentially plug flow of gas through the vessel.

The breaking of rising bubbles also reduces back-mixing of solids between compartments defined by the horizontal tube wall. In general, some back-mixing of solids is desirable in that such back-mixing improves heat transfer and prevents segregation of the solid particles. In some cases, it can be advantageous to restrict the solids backmixing to some extent in order to establish temperature differences between compartments. In any case, the use of spaced banks of heat exchanger tubes allows for optimum temperature control in that each bank may be separately controlled.

The tubes in each bank can have the same or different diameters. The tubes may be circular, elliptical, etc., and may be employed with or without fins. The tubes are preferably arranged in a heat exchanger coil having a hairpin shape which adjusts to large changes in temperature without creating mechanical stresses. Similarly, the axis of tubes in a tube bank need not be aligned with each other; i.e., criss-crossing of tube rows in a bank. The selection of a particular type of tube and arrangement is deemed to be within the scope of those skilled in the art from the teachings herein.

In accordance with a preferred embodiment, the horizontal tubes are placed in the vessel in a manner so as to form banks which are located at predetermined heights of the bed. Such tube banks, in effect, form a wall having a plurality of passages therethrough defined by the free area between the tubes. The relative position of the tubes within each bank, as well as the diameter of the tubes, determines the fraction of the cross section of the reactor which is left free for circulation between the compartments formed by the horizontal tube wall. The diameter and relative placement of the tubes within the bank control the degree to which the gas bubbles arriving from the compartment below the bank will be redisbursed into small bubbles while passing through the bank.

The horizontal tubes are spaced in the tube bank so as to provide a tube bank having a reduced flow area, as hereinabove described, to redistribute and break rising bubbles, while minimizing pressure drop, as well as attrition and segregation of solid particles. The selection of a specific arrangement should be apparent to those skilled in the art from the teachings herein.

In accordance with a preferred embodiment, the fluidized bed is employed as a reactor, and at least a portion of the fluidized bed of solids within the reactor is comprised of solid catalyst particles. It is to be understood, however, that the fluidized bed may be employed for other purposes.

The gas which is passed through the bed may be comprised of one, two or more components.

As hereinafter indicated, the fluidized bed reactor is particularly suitable for use in an exothermic reaction; however, the fluid bed may also be employed for an endothermic reaction. The fluidized bed has particular applicability to the production of maleic anhydride.

In most cases, the reactor is divided into three or more compartments by the horizontal tube banks. In such a case, the bottommost tube bank is preferably placed as close to the inlet means, such as a gas sparger or grid, as is physically possible to remove the heat generated in an intense reaction zone close to the inlet means. The uppermost tube bank is preferably placed within the fluidized bed of solids but below the top surface thereof so that there is some entrainment of solids into the free space immediately above the bed. Such an arrangement creates a free board (splash) zone in which the solids and gas more intimately contact each other. In the case where the vessel is used as a reactor, conversion and/or yield can be increased. However, if it is desired to minimize additional gas-solid contact, then the uppermost tube bank is placed at, and even extending above, the top surface of the bed.

The invention will be further described with respect to the following drawing, wherein:

The drawing is a simplified schematic diagram of a fluidized bed vessel in accordance with the invention.

It is to be understood, however, that the scope of the invention is not to be limited to the specifically disclosed embodiment.

Referring now to the drawing, there is shown a vessel 10, which includes a first gas inlet, in the form of a sparger 11, and a second gas inlet, in the form of a sparger 12. It is to be understood that other gas inlets could be used. The reactor is described with respect to the production of maleic anhydride, wherein a hydrocarbon such as n-butane would be introduced into one of the spargers 11 and 12, and air would be introduced into the other of the spargers 11 and 12.

The vessel 10 is divided into a plurality of compartments, 13B through 13N, each of which contains a fluidized bed of catalyst suitable for producing maleic anhydride by oxidation of a hydrocarbon. The compartments are limited above and below by partitions comprised of banks of horizontal heat exchanger tubes, generally designated as 14A through 14M. The heat exchanger banks 14A through 14M are formed from a plurality of horizontally disposed tubes, which are sized and spaced from each other, as hereinabove described, so as to break rising bubbles and provide for essentially plug flow of the gas through the vessel 10 while maintaining a good exchange rate of solids between compartments above and below the banks. Across each of the horizontal tube banks, 14A through 14M, there is a backmixing of catalyst; however, the fluid phase flows across said tube banks in essentially plug flow; i.e., without backmixing between compartments.

The vertical spacing between successive banks 14A - 14M is set based on the desired conversion, with conversion being increased provided the total bed height is maintained constant (thus, there is an increase in the number of compartments). In general, the vertical space between successive tube banks is in the order of from 0.2 to 4.0 meters, preferably less than 2.0 meters. It is to be understood that the space between any two successive banks can vary or be the same over the length of the vessel. Bubbles grow more rapidly in beds of high density and large particle size, and in such beds a closer spacing between successive tube banks may be required to achieve a desired conversion. For beds of smaller particle size, a desired conversion may be achieved with a larger spacing between successive tube banks.

As hereinabove described, the tubes are arranged in each tube bank so as to provide a "Projected Free Area" in each bank of less than 60% of the cross-sectional area of the vessel, with the total free area between tubes in each individual horizontal row of tubes in each tube bank being at least 10% of the cross-sectional area of the vessel so as to insure adequate flow between the tubes. The specific "Projected Free Area" for a tube bank is selected within the hereinabove described range so as to cause significant bubble breaking while large enough for a good exchange rate of solids between adjoining compartments. A closer spacing of tubes in a bank results in smaller bubbles, higher pressure drops and more difficult exchange of solids between compartments. A decreased bubble size increases conversion. The spacing of tubes in each bank is selected to provide desired conversion consistent with pressure drop, heat transfer and solid exchange.

The lowermost bank 14A is spaced from the uppermost sparger 11 as hereinabove described. The uppermost bank 14M is positioned near the top of the bed but below the top surface of the bed, whereby there is some entrainment of the catalyst particles in the splash zone 15 above the top of the expanded bed.

The reaction product, as well as any unreacted starting material, is withdrawn from the top of reactor 10 through an outlet conduit 16. The outlet portion of the vessel 10 may be provided with a conventional cyclone separator system, either external or internal, so as to return any catalyst fines which are entrained in the outlet gas. Other catalyst recovery systems (e.g., sintered metal mesh, ceramic, fabric filter systems) may be used instead of, or in addition to, the cyclone separation system.

The fluidized bed vessel of the present invention may be employed for effecting contact between a wide variety of solids and gases; however, such vessel has particular use as a fluidized bed reactor wherein one or more reactants are contacted with a solid catalyst. The fluidized bed reactor has particular applicability to exothermic reactions, such as the production of maleic anhydride.

The present invention will be further described with respect to the production of maleic anhydride from n-butane; however, as know in the art, saturated or unsaturated C4 to C10 hydrocarbons or mixtures thereof, in addition to n-butane, may be employed as a feed for producing maleic anhydride; for example, 1,3-butadiene or a C4 cut from a refinery.

Conditions under which maleic anhydride may be produced using the reactor of the present invention are temperatures of from 330°C-490°C, particularly 370-450°C. Although a uniform temperature profile along the length of the reactor is ordinarily desired; in some situations, a profile may be desired and is achievable by the present invention.

A concentration of hydrocarbon (butane) in air generally is 1-20 volume percent, or higher, particularly 2-8 volume percent. Superficial gas velocities of from 0.5 to 5 feet/second may be used.

The catalyst used may be any catalyst effective for oxidizing a hydrocarbon to maleic anhydride, particularly one containing vanadium and phosphorus, as known in the art. The catalyst particle size distribution will by typical of those used in a fluidized bed process, with an average particle size being from 20-500 microns, preferably less than 150 microns.

The present invention is particularly advantageous in that it is possible to use a fluidized bed at higher conversions at acceptable selectivities. Thus, for example, by use of the present invention for the production of maleic anhydride, it is possible to achieve conversions in excess of 70% and as high as 90% or more, while maintaining selectivity of at least 50% and in some cases at least 70%.

Although the fluidized bed vessel has particular applicability to the production of maleic anhydride, it is to be understood that the scope of the invention is not limited to such production in that the fluidized bed vessel may be used for other purposes.

Numerous modifications and variations of the present invention are possible in light of the above teachings and, therefore, within the scope of the appended claims, the invention may be practiced otherwise than as particularly described.

WHAT IS CLAIMED IS:

1. An apparatus, comprising:

A fluidized bed vessel; inlet means for introducing a gas into a lower portion of the vessel; and outlet means for withdrawing a gas from an upper portion of the vessel; and at least one horizontal heat exchanger tube bank positioned in said vessel, said heat exchanger tube bank containing at least one row of a plurality of horizontally disposed tubes, said horizontal tubes having spaces therebetween to provide a free flow area between the tubes for fluid flow communication between the vessel interior above and below the tube bank; the percentage of cross-sectional area defined by spaces between the tubes as projected in a plan view of the at least one tube bank relative to the free cross-sectional area of the vessel without a tube bank being less than 60% to provide for essentially plug flow of the gas through the reactor vessel and breaking of rising bubbles.

2. The apparatus of Claim 1 wherein the vessel includes at least two vertically spaced tube banks, each of said at least two tube banks having at least two rows of horizontal tubes having spaces therebetween to provide a free flow area between the tubes.

3. The apparatus of Claim 2 wherein the open cross-sectional area between the tubes of each horizontal row is at least 10% of the cross-sectional area of the vessel without tubes.

4. The apparatus of Claim 3 wherein the vessel includes a bed of solid particles and at least two tube banks are within the bed of solid particles.

5. The apparatus of Claim 4 wherein successive tube banks are vertically spaced from each other at a distance of from 0.2 to 4.0 meters

6. The apparatus of Claim 5 wherein said percentage is less than 50%.

7. The apparatus of Claim 6 wherein successive tube banks are spaced from each other at a distance of from 0.2 to 2.0 meters.

8. A process for producing maleic anhydride, comprising:

reacting a gas containing a hydrocarbon and oxygen in a fluidized bed of oxidation catalyst in the apparatus of Claim 1 whereby the gas flows through the fluidized bed in essentially plug flow with breaking of rising bubbles; and withdrawing an effluent including maleic anhydride from the outlet means;

9. The process of Claim 8 wherein the oxidation catalyst has a particle size of 20-500 microns.

10. The process of Claim 9 wherein said reacting is effected at a temperature of from 330°C to 490°C.

11. The process of Claim 10 wherein the hydrocarbon is n-butane.

12. The process of Claim 9 wherein the particle size is from 20 to 150 microns.

13. The process of Claim 12 wherein the temperature is from 370°C to 450°C.

14. A process for producing maleic anhydride, comprising:

reacting a gas containing a hydrocarbon and oxygen in a fluidized bed of oxidation catalyst in the apparatus of Claim 7 whereby the gas flows through the fluidized bed in essentially plug flow with breaking of rising bubbles; and withdrawing an effluent including maleic anhydride fro the outlet means.

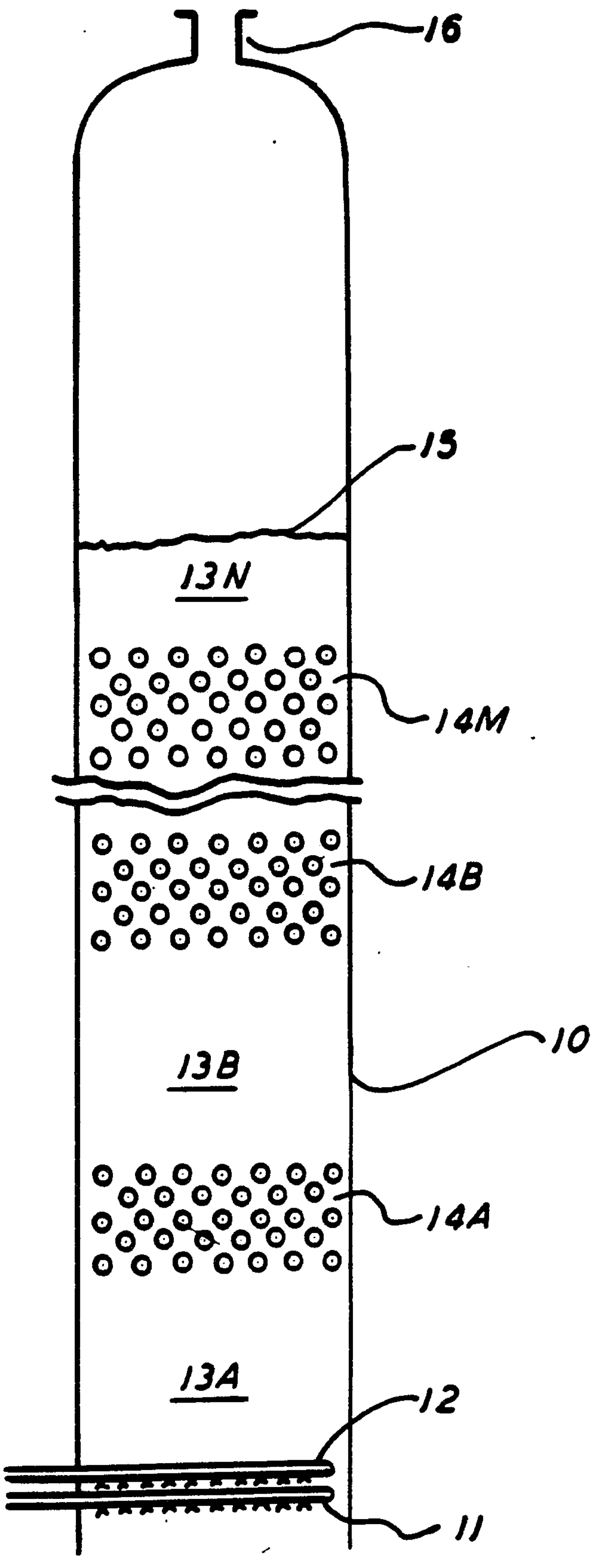
15. The process of Claim 14 wherein the oxidation catalyst has a particle size of 20-500 microns.

16. The process of Claim 15 wherein said reacting is effected at a temperature of from 330°C to 490°C.

17. The process of Claim 16 wherein the hydrocarbon is n-butane.

18. The process of Claim 15 wherein the particle size is from 20 to 150 microns.

19. The process of Claim 18 wherein the temperature is from 370°C to 450°C.


16
15
13N
14M
14B
13B
10
14A
13A
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11

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/03194

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: B 01 J 8/24; C 07 C 51/215; C 07 C 57/145

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	B 01 J; C 07 C; F 22 B; F 23 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 2983259 (E.C. WITTKE) 9 May 1961 see column 1, lines 15-19; column 2, lines 21-53; column 4, line 7 - column 5, line 59; figures 1,2	1,2
Y		8,10-14, 16-19
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Y	US, A, 4351773 (E.C. MILBERGER et al.) 28 September 1982 see abstract; claims 1,7,8,11	8,10-14, 16-19
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* Special categories of cited documents: [10]

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

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
22nd February 1988	06 APR 1988
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 8703194
SA 20038

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 12/03/88
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 2983259	-	None	
US-A- 4351773	28-09-82	EP-A,B 0056902	04-08-82
		JP-A- 57122944	31-07-82
		CA-A- 1172235	07-08-84

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