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COMPLETE SPECIFICATION

## Apparatus for the Catalytic Gas Reactions in Liquid Media

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, a German Company, of Homberg/Niederrhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to apparatus for carrying out gas reactions in the presence of liquid or solid catalysts which are dissolved or maintained in finely divided suspension in a liquid medium, and particularly to such apparatus for carrying out the hydrogenation of the oxides of carbon under elevated gas pressure to form hydrocarbons or organic compounds which contain oxygen.

The invention relates specifically to reaction apparatus in which the liquid medium is maintained stationary during the gas reaction, that is to say in which it is not subjected to any circulation or recycling inside or outside the reaction space.

It is known that in gas reactions which are carried out in the presence of catalysts in a liquid medium, and in which the gaseous phase does not disappear completely when passing through the liquid medium, being rather preserved as a separate phase on the whole of its path through the liquid medium due to the incomplete solubility of the gaseous starting materials and end products, the degree of gas conversion is proportional to the area of the boundary surface between the gas and the liquid. In such a system of distribution of gas in liquid, the area of the boundary surface is determined by the size of the gas bubbles.

For certain reactions, including the Fischer-Tropsch synthesis, it has been found to be adequate to carry out the reactions without using any special method of introducing or distributing the gas in the liquid medium, as the gas bubbles which form in the liquid medium are of a size which is almost independent on the manner in which the gas in introduced into the liquid medium. This is due to the fact that the size of the gas bubbles is largely determined by the surface tension and viscosity of the liquid medium under the reaction conditions. However, in order to obtain a substantially complete conversion of the gas, it is necessary for the gas to have a determined residence time in the liquid medium, and this time of residence should, as nearly as possible, be the same for each of the gas bubbles.

These requirements are met by passing the synthesis gas upwardly into a narrow and relatively tall column of liquid at elevated pressure and at elevated temperature without using special means for distributing the gas, the quantity of gas being such that the space load, measured at the pressure and temperature of the synthesis, is between about 5 and 100 litres of gas per litre of liquid medium per hour. At a certain distance above the position at which the gas is introduced into the liquid medium, there develops a state in which the mixture of gas and liquid is such that the gas bubbles are almost uniform in size, are distributed substantially uniformly over the whole horizontal cross-section of the column, and ascend at an almost uniform speed. The total volume of the liquid/gas system is directly proportional to the gas throughput, whereas the total contact time of the gas bubbles is almost independent of the gas throughput. As the gas throughput increases, the distance between the gas bubbles is reduced without coalescence of the gas bubbles taking place. The nature of this system, which may be termed a "liquid/gas suspension system", has not yet been fully explained. It has, however, been found that in this system the liquid is in a state of very fine turbulence in which the eddies are approximately only of the order of magnitude of the gas bubbles,

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that the bulk of the liquid remains stationary, that is to say, only a small fraction thereof travels upwards with the gas bubbles, and that, due to the friction between the gas bubbles and the liquid, a continual and rapid renewal or change of the intersurface occurs. It appears that through these factors, together with the fine turbulence of the liquid phase, the exchange of substances between the gaseous phase, the liquid phase, and the surface of the catalyst is facilitated and improved to such a degree that the hydrogenation of carbon monoxide is no longer impeded by the liquid medium, but proceeds at much the same rate as in the known process using a dry catalyst whirled up to simulate a fluid, that is to say, the so-called fluidized catalyst process. Thus, in the process carried out in the liquid phase with a stationary column of liquid, up to 15 litres (760 mm. Hg., 0° C.) of $CO+H_2$ may be converted per gram of catalyst per hour. This conversion may be obtained with a single pass of the gas through the liquid medium and at temperatures below 300° C.

By virtue of the high load capacity of the catalyst achieved in accordance with this process, combined with a high maximum content of catalyst in the suspension which may be up to 500 grams of the main or base catalyst metal per litre of non-inflated or gas-free suspension, without the suspension losing its property of ready fluidity or mobility, it is possible to obtain space-time yields of reaction products which are higher than those obtained by other known liquid phase processes.

In the Fischer-Tropsch synthesis carried out with a suspended iron catalyst, the particle size of which is advantageously maintained between 0.005 mm. and 1 mm. with a yield of 170 grams per normal cubic metre of $CO—H_2$ used and with a single pass of the gas at a temperature of approximately 275° C. a gas pressure of 25 atmospheres and an hourly throughput of up to 1250 litres of $CO+H_2$ (measured at 0° C. and at a pressure of 760 mm. Hg.), approximately 5 kilograms of synthesis products containing more than 3 carbon atoms in the molecule may be produced within 24 hours per litre of reaction space. In accordance with the known process, this synthesis may be carried out smoothly in reaction spaces having a diameter of 20 centimetres. However, as the horizontal diameter of the reaction space increases, the degree of gas conversion decreases, and it becomes increasingly difficult to maintain a constant gas conversion. The greater the horizontal diameter of the reaction space, the more the body of liquid will tend to pass from the stationary state into a state of vertical rotation or circulation. The liquid then flows downwardly along the walls forming the boundary of the reaction space, and at the bottom flows towards the centre of the reaction space while entraining all the gas bubbles introduced into the centre of the base. The compressed, central gas stream drags the liquid upwardly, while the compressed gas bubbles coalesce to form giant and elongated gas bubbles. It is only at the upper position of reversal of the flow of the liquid, adjacent to the surface of the column of liquid, that the gas spreads out horizontally over the cross-section of the column and the large gas bubbles partially disintegrate. This movement of the gas and liquid is diagrammatically illustrated in Figure 1 of the accompanying drawings. The synthesis gas is passed through a line 2 upwardly into a reactor 1 within which the catalyst suspension 3 is contained, the gas stream being distributed by the nozzles or perforations 6 of the gas distributing plate 4. The movement and circulation of the liquid in the reaction space is shown by the arrows 5. It will be understood in this respect that the hydrodynamic pressure exerted on the gas distributing plate 4 at positions close to the wall of the reactor 1 may be higher than in the centre of the plate 4, whereby the passage of gas through the outer nozzles or perforations 6 is completely suppressed, so that the bulk of the gas enters the reaction space solely through the central nozzles of the plate 4. In addition, the rate of flow of the eddying or circulating liquid increases with the absolute height of the column of liquid. There is no purpose in trying to overcome this disadvantage by allowing the gases to pass into the catalyst suspension only at positions adjacent to the periphery of the distributing plate 4, as diagrammatically illustrated in Figure 2 of the accompanying drawings. In this case, a similar state of affairs will develop, but with the difference that in addition to the tall eddy of liquid, a small eddy also develops in the liquid at 7 below the funnel formed by the gas stream.

In a distributing system of this kind, the time of contact of the individual batches of gas is extremely irregular due to the irregular size of the gas bubbles and because part of the gas bubbles is incorporated in the circulating liquid. Thus, while on the one hand some of the gas does not contact the catalyst at all, that is to say, it slips through the suspension without contacting the suspended catalyst, on the other hand some of the gas, together with the reaction products contained therein, is repeatedly brought into contact with the catalyst for a longer time than is desirable. Moreover, the fresh gas is diluted by the tail gas entrained by the vertical cycle of liquid.

Thus these eddies in the liquid not only result in a lower gas conversion, but also cause undesirable secondary reactions. Over and beyond this, in the Fischer-Tropsch synthesis the catalyst which then circulates rapidly together with the liquid is substantially damaged by the rapid change in the surrounding conditions, so that its efficiency is reduced, its activity decreasing more rapidly than in the synthesis with a stationary column of liquid, in which the individual catalyst particles reside for a comparatively long time in a determined zone in which the composition of the gas is substantially constant.

Various proposals for improving the distribution of the gas in liquids in large reaction spaces have been made. These include the use of rotating bodies, the so-called turbo-mixers, or the introduction of gas by means of the Segner wheel. One form of Segner wheel is described in United States Patent Specification No. 1,157,993, the wheel comprising four arms disposed symmetrically about a collar or hub which is mounted for rotation about its axis, the arms being provided with orifices through which the gas is fed into the reactor. The wheel is mounted adjacent to the bottom of the reactor, and the orifices in the arms are so provided that the passage of the gas through the orifices into the liquid medium in the reactor causes the wheel to rotate and sweep the bottom of the reactor and so whirl up any catalyst that may have settled out of the liquid medium. It has also been proposed to fix or determine the direction of the swarms of gas bubbles, which enter at the bottom of the reaction space through porous plates or individual nozzles, by means of guide members, such as tubes or plates. These guide members are, however, only provided at or close to the bottom or base of the reaction space and are shorter in height than the column of liquid.

The individual installations or members so provided in the reactor act in the manner of air-lift pumps, so that in reaction apparatus thus equipped, the circulation of the liquid, while being controlled, is nevertheless intensified.

By these known proposals, the disadvantageous consequences with respect to the gas conversion, the properties of the product and the efficiency of the catalyst caused by the circulation of the liquid, are not removed. Apparatus of this kind may be sufficient and adequate for gas reactions in which the tail gas is chemically identical with the primary or initial gas, such as is the case, for example, in the hardening of fat. None of these known proposals is sufficient or adequate with gas reactions in which the composition of the gas changes, in which reaction products have to be discharged together with the tail gas, and in which the gas conversion should be as complete as possible with a single pass of the gas.

In none of the known apparatus is the object particularly essential for the Fischer-Tropsch synthesis realised, namely that of maintaining the liquid medium and the suspended catalyst substantially stationary, whilst nevertheless allowing the gas bubbles to be of substantially uniform size, to be substantially uniformly distributed and to travel at a substantially uniform rate through the liquid medium.

It is an object of the invention to provide a reactor whereby the disadvantages hereinbefore described may be removed or substantially avoided.

According to the invention, a reaction apparatus for carrying out reactions between gaseous reactants in the presence of a catalyst dissolved or suspended in a liquid medium through which a mixture of the gaseous reactants is passed upwardly in the form of bubbles, comprises a vertical reactor having a diameter or width of not less than 30 centimetres and a length of not less than 1.5 metres, a number of substantially uniform and vertical members within the reactor dividing the major part of the cross-section of the reactor into a number of vertical shafts which are open at both ends and which have a diameter or width of at least 5 centimetres and a length which is from 10 to 200 times the average diameter or width of the shafts, the shaft walls being substantially liquid-tight with their lower ends disposed at a distance above the inlet or inlets for the gaseous reactants which is not substantially less than the diameter or width of the reactor, and with their upper ends terminating in the upper part of the reactor at one or more levels such that the surface of the liquid medium in each shaft is disposed within the shaft when the reactor is in operation and the liquid medium is inflated by the bubbles of the gaseous reactants.

When the apparatus according to the invention is used, for example, in the Fischer-Tropsch synthesis, it is somewhat surprising that the gas is distributed in the liquid in the manner which is diagrammatically illustrated in Figure 3 of the accompanying drawings. In the sump 15 disposed below the shafts 14 of the reactor 11, the distribution of the gas, which is introduced into the reactor through the inlet 12, is coarse and irregular. Here also in the sump 15, eddies, though of a small vertical dimension, develop in the liquid. The lower edge of the bundle of shafts 14 effects the movement of gas and liquid in the sump 15 in the manner of the surface of a liquid, in that the eddies in the liquid have their upper point of reversal at a substantial distance therefrom, thus drawing the generally somewhat compressed stream of gas bubbles apart in the direction of the periphery. The shafts 14 disposed further away from the axis are thereby supplied with substantially the same amount of gas as the central shafts. In contrast with the sump 15, the columns of liquid, the degree of inflation of which is determined by the quantity of the gas in the shafts 14, are substantially stationary. The tail gas leaves the reactor 11 through the outlet 13.

As the surface of the column of liquid in each shaft is disposed within the shaft and the upper ends of the shafts are all open and terminate in the common upper gas space 16, the supply of gas to the shafts is equalized to such a degree that the reaction apparatus according to the invention shows substantially the same results in operation as a reaction apparatus the dimensions of which correspond to those of a single shaft having a diameter of less than 20 centimetres, and which, moreover, is provided with its own gas supply. Furthermore, the hydrostatic pressure of the columns of liquid at the base of the shafts is practically the same for all the shafts, independently of small or periodical differences in the passage of the gas.

The surprising effects resulting from the division of the reaction apparatus into shafts in accordance with the invention, may be summed up as follows:—

(1) The equalizing or balancing effect produced by the shafts on the supply of gas to the individual shafts, is almost independent of the processes taking place in the sump.

(2) The formation of a stable liquid/gas suspension system in each shaft with a substantially stationary column of liquid and substantially uniform size and substantially uniform velocity of ascent of the gas bubbles.

(3) The automatic supply to each individual shaft of an amount of suspended catalyst proportional to the quantity of gas entering the shaft. When for example, gas is prevented from entering a shaft by a baffle plate, the liquid in that shaft is substantially free from suspended catalyst.

(4) The gas reaction in the shafts proceeds absolutely identically with the results obtained in the laboratory under similar operating conditions and with the same efficiency. The reaction is substantially independent of the manner in which the gas is introduced or distributed at the bottom of the sump below the shafts.

A selection of specific constructions of reaction apparatus according to the invention is hereinafter described with reference to Figures 4 to 16 of the accompanying drawings.

The diameter or width of the shafts is at least 5 centimetres and may be up to 30 centimetres or even more; preferably, however, it is not greater than 30 centimetres. The diameter or width of the shafts is determined by the height of the apparatus or shafts and by the cross-section of heat-exchange tubes which may be provided in the shafts.

The height or length of the shafts is determined by the time provided for contact of the gas bubbles with the catalyst suspension; this is advantageously determined experimentally by means of tests on a small or pilot scale.

The construction of the reaction apparatus provided according to the invention may be substantially facilitated by forming each individual shaft as a separate casing. This casing must be impervious to liquid; its walls may be as thin as the technique of manufacture permits. If desired, plates or sheets having a thickness of up to 0.5 mm. may be used for the walls, more particularly when it is thereby possible to prevent corrosion.

Shafts of circular cross-section, that is to say, ordinary tubes the walls of which are as thin as possible, may be used, these tubes being mounted so as to be packed together as closely as possible (triangular or delta formation), or mounted so that the axes of four adjacent tubes are disposed at the corners of a square. In Figures 4, 5 and 6, the different arrangements of circular shafts *a* are shown, with heat-exchange tubes *b* mounted within and/or externally of the shafts *a*.

A particularly efficient utilization of the reaction space is obtained by using shafts formed as the casings of regular hexagonal prisms, because in this case clearances or dead spaces between the shafts may be avoided. Such an arrangement is illustrated in Figures 9 and 10, the shafts *d* being of hexagonal cross-section and having heat-exchange tubes *e* mounted within them.

To prevent the gas bubbles from entering the dead spaces between the circular shafts or the spaces, hereinafter referred to as segmental spaces, between the bundle of shafts and the inner wall of the reactor, baffle plates are preferably provided directly below the bottom edge of the bundle of shafts. The baffle plates are disposed at an angle to the vertical with their lower surfaces inclined upwardly in the direction of the shafts, and the baffle plates are so provided as to leave sufficient space to permit the liquid in the dead spaces and in the segmental spaces to communicate with the liquid in the sump.

One construction of apparatus according to the invention is diagrammatically illustrated by way of example in Figures 7 and 8, Figure 7 being a longitudinal section of the apparatus along the line X—X of Figure 8, and Figure 8 being a transverse section along the line Y—Y of Figure 7. The cylindrical reactor 21, the lower end of which is tapered to form a cone, is provided at the bottom with a central gas inlet pipe 22, the inlet being provided with a construction or nozzle 23. The gas inlet pipe 22 is provided with a check valve 24, and a valved conduit 25 through which a liquid may be passed for rinsing or clearing the nozzle 23. An outlet 26 for the tail gas is provided at the top of the reactor. A bundle of shafts 27 is disposed within and longitudinally of the reactor 21. A governor or regulator 28 for the charge or liquid contents of the reactor 21 is provided in one of the segmental spaces 38 disposed between the bundle of shafts 27 and the inner wall of the reactor 21 and serves to control the respective valves for the supply and discharge pipes, according to whether the liquid contents of the reactor 21 decrease or increase during the reaction. Baffle plates 29 are provided to prevent the admission of gas into the segmental spaces. A system of tubes

30 which pass longitudinally through the shafts 27, comprises a heat exchange system which is supported on members 31 within the reactor 21. In operation, a heat transfer medium is passed into the tubes 30 through a line 32 and headers 33 disposed in the sump 39 of the reactor 21, and is withdrawn from the tubes 30 through headers 34 and line 35, the line 35 passing out of the reactor 21 through a gland 36 provided in the reactor wall. If necessary, liquid medium substantially free of catalyst may be withdrawn continuously or intermittently through valved conduits 37, for example, when it is desired to withdraw reaction products of high molecular weight which are not gaseous under the reaction conditions and which are not, therefore, discharged with the tail gas through the outlet 26. The exchange of liquid between the shafts 27, the sump 39, and the segmental space 38 is generally sufficient for this purpose in spite of the almost stationary condition of the liquid in the shafts 27. A valved tube 40 is advantageously provided for charging the reactor with catalyst suspension and for removing catalyst suspension from the reactor.

The tubes 30 of the heat exchange system must extend as low as possible into the sump 39, the position of the inlet headers 33 being advantageously approximately 100 centimetres or more below the lower edge of the bundle of shafts 27.

The heat exchange tubes 30 are passed vertically through the reactor. In the construction illustrated in Figures 7 and 8, one heat exchange tube is provided within each of the shafts; a similar arrangement is also illustrated in Figure 4. More than one heat exchange tube may, however, be provided within each shaft, as illustrated in Figures 9 and 10. Some of the heat exchange tubes may also be provided externally of the shafts as shown in Figure 6, or all of them may be passed through the spaces between the shafts, for example, as illustrated in Figure 5.

With the heat exchange tubes extending through the interior of the shafts, the smallest horizontal distance between them and from the inner wall of the shaft should exceed 3 centimetres.

The distribution of gas at the bottom of the sump may also be effected over the whole cross-section, and in cases where a suspended, solid catalyst is being used, the openings or mouths of the gas inlets or nozzles may advantageously be directed downwardly towards the bottom of the reactor. Furthermore, it is advantageous to wet or moisten the gas inlet nozzles continuously from the gas side by means of a liquid medium.

Suitable means for carrying out one or more of these methods of feeding the gas into the reactor, are diagrammatically illustrated by way of example in Figures 11, 12 and 13. Figure 11 is a longitudinal section of the sump of a reactor into which the gas is fed through a series of nozzles or jets 41 provided in lines 42, the nozzles or jets 41 being directed downwardly towards the bottom of the reactor. Scavenging or cleaning oil for the nozzles or jets 41 is fed into the lines 42 through one or more lines 43. Figures 12 and 13 are plan views of two different means of feeding and distributing the gas. In the means illustrated in Figure 12, the gas is fed into the reactor through four pipes 44 disposed 90° apart, the gas passing from the pipes 44 into a series of concentrically disposed pipes 45 provided with perforations, nozzles or jets through which the gas passes directly into the reaction space. The means illustrated in Figure 13 comprises a series of gas inlet tube 46 disposed in parallel relationship, the tubes being provided with nozzles, jets or the like through which the gas passes directly into the reaction space.

The division of the gas feed into determined zones over the cross-section of the lower part of the reactor, as illustrated in Figures 11, 12 and 13, renders possible the control of the quantity of gas admitted to each zone. In the reaction apparatus according to the invention, such control or regulation is only necessary in special circumstances, for example for whirling up settled catalyst after a stoppage or interruption of operation, or when it is necessary occasionally to operate with quantities of gas which are so low that the cross-sectional load is substantially below approximately 10—15 litres (at the pressure and temperature of operation) per square centimetre of free reactor cross-section per hour.

Four possible constructions 47, 48, 49 and 50 of nozzles suitable for introducing the gas centrally at the tapered bottom part of the reactor, are diagrammatically illustrated by way of example in Figure 14.

It has been found that, when gas reactions are carried out in the reaction apparatus according to the invention, cross-sectional loads in the range of approximately from 3 to 200 working litres of gas (at the pressure and temperature of operation) per square centimetre of free reactor cross-section per hour, are suitable for the liquid-gas suspension system.

The mobility of the liquid medium in the operating condition is of extreme importance for the liquid-gas suspension system, and the viscosity of the liquid medium containing the suspended catalyst should preferably be below 3° Engler approximately, which corresponds approximately to 21 centistokes. In the Fischer-Tropsch synthesis, the reaction proceeds particularly rapidly when the viscosity of the suspension lies below approximately 1.4° Engler or 5.2 centistokes.

The heat of condensation of steam may be used in known manner for heating the reaction apparatus and for supplying the heat of reaction in endothermic reactions. Similarly, for indirect heat exchange in exothermic reactions, water may be vapourised in the same tube system to dissipate heat of reaction.

Due to the intense, fine turbulence of the liquid in the liquid-gas suspension system in the shafts, the transmission of heat to the cooling surfaces is accelerated to such a degree that, even when hydrocarbons are used as the liquid medium, the transmission of heat using vertical, smooth steel tubes through which cooling water flows, is generally at least 300 kilocalories per sq. metre of cooling surface per degree centigrade per hour.

With certain gas reactions, for example, with the Fischer-Tropsch synthesis, it may be advantageous, in view of the gradual decrease in the content of the effective or reactive constituents of the gas as it flows upwardly through the liquid, to allow the temperature to increase in the upward direction, that is to say, to provide a positive temperature gradient in the direction of flow of the gas through the liquid medium. This may, for example, be attained either by lining some or all of the cooling surfaces, or by creating or providing a vapour or gas cushion between some or all of the tubes, through which the coolant flows, and the reaction medium.

Alternatively or additionally, the cooling surface may be made smaller in known manner by reducing the diameter of the cooling tubes, or the number of cooling tubes may, in the vertical direction, be reduced relatively to the horizontal cross-section by introducing from below more than one cooling tube into each shaft and merging two or more cooling tubes into one another at one or more levels in such a manner that, for example, only a single cooling tube issues from the top end of the shaft.

It has also been found to be advantageous to provide means to permit a steam or vapour cushion of variable depth to develop in the upper part of each of the cooling tubes or of a majority of the cooling tubes. Means to provide such a cushion of steam, or a cushion of the vapour of another liquid coolant, is diagrammatically illustrated by way of example in Figure 15. For the sake of clarity, the shafts have been omitted from the figure. Immersion tubes 60 are provided in the cooling tubes 61. The cooling water which circulates through the steam drum 62 and the pump 63 may be passed wholly through the header 64, or, depending upon the extent to which the temperature in the upper part of the reaction space is to be increased, the cooling water may be passed more or less completely through the header 65; this may be controlled by adjusting the valves 66 and 67 accordingly.

When both valves 66 and 67 are open, the cooling water together with the steam generated in the tubes 61 by absorption of the heat of reaction, passes into the steam drum 62 through the header 64 and also through the immersion tubes 60 and the header 65. There is a strong transmission of heat to the cooling water in the tubes 60 up to the uppermost level of the liquid reaction medium, so that the temperature in the upper layers of the liquid reaction medium is practically the same as in the liquid reaction medium in the lower parts of the vertical shafts and no increase in the temperature of the liquid reaction medium occurs in the direction of flow of the gas.

When the valve 66 is closed, the cooling water and the steam can pass into the drum 62 only through the immersion tubes 60, header 65 and valve 67. The steam is mainly generated on the inner surfaces of the tubes 61, and a part thereof passes through the annular spaces 68 and is trapped in the header 64. The level of the cooling water in the annular spaces 68 is depressed as the amount of trapped steam increases until the level of the water in the annular spaces 68 is depressed to the lower ends of the immersion tubes 60. The cushion of steam so formed in the annular spaces 68 substantially reduces the transmission of heat from the liquid reaction medium to the water in the immersion tubes 60, with the result that an increase in temperature occurs in the corresponding layers of the liquid reaction medium so providing a positive temperature gradient in the direction of flow of the gaseous reactants through the reaction medium. The length of the steam cushions in the annular space 68 can be varied by adjusting the valve 66.

A cushion of steam may thus be maintained in each of the annular spaces 68, the length of the cushion being adjustable.

Alternative means for the adjustable reduction or regulation of the transmission of heat from the liquid reaction medium in the direction of flow of the gaseous reactants, is diagrammatically illustrated by way of example in Figure 16. The vertical shafts are omitted from the figure for the sake of clarity. The cooling tubes 71 are in their upper parts surrounded by tubes 72 which are open at their lower ends, each tube 72 being substantially concentric with the cooling tube 71 on which it is mounted. The tubes 72 are connected through a header 73 and a valve 74 to the gas space above the upper ends of the shafts (not shown). The gaseous reactants can enter and flow through the annular spaces 75 disposed between the cooling tubes 71 and the tubes 72.

When the valve 74 is fully open, the level of the liquid reaction medium in the annular spaces 75 is at its highest and the tubes 72 do not hinder the transmission of heat from the liquid reaction medium to the cooling water in the tubes 71. There is then practically no increase in temperature in the vertical direction in the liquid reaction medium.

Upon closure of the valve 74, the gas bubbles passing upwardly through the annular spaces 75 are trapped in the header 73 and the level of the liquid reaction medium in the spaces 75 is gradually depressed until it reaches the lower end of the tubes 72. A gas cushion is thus formed between the cooling water in the tubes 71 and the liquid reaction medium around the tubes 72, and the rate of transmission of heat from the liquid reaction medium to the cooling water is considerably reduced in the zone of the gas cushions and the temperature of the liquid reaction medium in this zone increases. The length of the cushions of gas in the annular spaces 75 is controlled by opening the valve 74 to a greater or lesser extent.

In the reaction apparatus according to the invention, instead of using a heat-transfer system with a volatile, liquid coolant, it is also possible to use a non-volatile coolant, that is, a liquid which does not vaporise under the reaction conditions. In this case the coolant is recycled upwardly through the cooling system of the reactor and through an external heat exchanger, in which, for example, the reaction heat withdrawn from the reactor is utilized for the generation of steam. The vertical temperature gradient in the shafts is then obtained by controlling the rate at which the coolant is circulated by a pump or other means.

An additional advantage of operation with the reaction apparatus according to the invention lies in the fact that, in contrast with reaction apparatus in which the catalyst suspension circulates, deposits of catalyst on the walls are avoided. This advantage appears to be due to the fine, intense turbulence of the liquid medium in the stationary distributing system.

In our co-pending Application No. 13793/54 there is described and claimed a reaction apparatus for the hydrogenation of carbon monoxide in the presence of a catalyst suspended in a liquid medium, comprising a cylindrical vessel relatively tall compared to its diameter and forming the reaction chamber, one or more bundles of tubes disposed in the vessel and through which a cooling medium may be passed, a series of heat-conducting plates connected to the tubes and forming a series of liquid-tight vertical shafts which extend substantially over the whole of the cross-section of the vessel, each vertical shaft being of relatively small cross-sectional area, being open at both ends and extending over the greater part of the length of the vessel, the lower edges of the series of vertical shafts ending short of the base of the vessel in a common space for the liquid medium, a common gas space for the tail gas above the upper edges of the series of vertical shafts, and a single, axially-provided gas inlet at the bottom of the vessel, the cross-section of the vessel being decreased below the lower edges of the vertical shafts to converge on to the gas inlet, the distance between the lower edge of the series of vertical shafts and the gas inlet being at least as great as the diameter of the cylindrical part of the vessel.

What we claim is:—

1. A reaction apparatus for carrying out reactions between gaseous reactants in the presence of a catalyst dissolved or suspended in a liquid medium through which a mixture of the gaseous reactants is passed upwardly in the form of bubbles comprising a vertical reactor having a diameter or width of not less than 30 centimeters and a length of not less than 1.5 metres, a number of substantially uniform and vertical members within the reactor dividing the major part of the cross-section of the reactor into a number of vertical shafts which are open at both ends and which have a diameter or width of at least 5 centimetres and a length which is from 10 to 200 times the average diameter or width of the shafts, the shaft walls being substantially liquid-tight with their lower ends disposed at a distance above the inlet or inlets for the gaseous reactants which is not substantially less than the diameter or width of the reactor and with their upper ends terminating in the upper part of the reactor at one or more levels such that the surface of the liquid medium in each shaft is disposed within the shaft when the reactor is in operation and the liquid medium is inflated by the bubbles of the gaseous reactants.

2. A reaction apparatus according to Claim 1, in which the length of the shafts is from 20 to 100 times the average diameter or width of the shafts.

3. A reaction apparatus according to either of the preceding claims, in which each individual shaft is formed by its own separate casing.

4. A reaction apparatus according to any one of the preceding claims, in which tubes of circular cross-section are used to form the shafts.

5. A reaction apparatus according to any one of Claims 1 to 3, in which the shafts are formed by regular hexagonal hollow prisms which are open at both ends.

6. A reaction apparatus according to any one of the preceding claims, in which the lower ends of the shafts are disposed in the same horizontal plane.

7. A reaction apparatus according to any one of the preceding claims, including baffle plates which are provided at a small distance below the lower edge of the bundle of shafts to prevent substantial amounts of gas from entering the space between the shafts and/or the space between the bundle of shafts and the inner wall of the reactor.

8. A reaction apparatus according to any one of the preceding claims, including a member for controlling the liquid contents of the reactor, the said member being provided in the space disposed between the bundle of shafts and the inner wall of the reactor, said space

being substantially unaffected by the passage of gas.

9. A reaction apparatus according to any one of the preceding claims, including one or more means for the continuous or intermittent withdrawal from the space between the bundle of shafts and the inner wall of the reactor of reaction products of high molecular weight which are liquid under the reaction conditions.

10. A reaction apparatus according to any one of the preceding claims, including heat-exchange tubes for the indirect supply or removal of heat, the heat-exchange tubes being provided coaxially or otherwise parallel with the shafts and being of a length greater than the length of the shafts so that the position at which the heat-exchange tubes enter their headers is disposed outside the bundle of shafts.

11. A reaction apparatus according to Claim 10, in which the lower header or headers of the heat-exchange tubes is or are at a vertical distance of at least 100 centimetres from the lower edge of the bundle of shafts.

12. A reaction apparatus according to Claim 10, or Claim 11, in which the vertical heat-exchange tubes are passed through the interior of the shafts, their minimum distance from each other or from the inner wall of the shaft being more than 3 centimetres.

13. A reaction apparatus according to any one of Claims 1 to 4 and 6 to 9, including heat-exchange tubes for the indirect supply or removal of heat, the heat-exchanger tubes being provided parallel to the shafts and of a length greater than that of the shafts with some at least of the heat-exchange tubes being disposed outside the shafts.

14. A reaction apparatus according to any one of Claims 1 to 4 and 6 to 9, including heat-exchange tubes for the indirect supply or removal of heat, the heat-exchange tubes being provided outside the shafts and in direct contact with the outer surfaces of the shafts.

15. A reaction apparatus according to any one of Claims 1 to 14, including gas inlet means through which the gas is introduced in such manner as to be substantially uniformly distributed over the total cross-section of the reaction space.

16. A reaction apparatus according to Claim 15, in which the nozzles, jets, perforations or like members or openings through which the gas passes into the reactor are so provided as to direct the entrant gas downwardly towards the bottom of the reactor.

17. A reaction apparatus according to any one of Claims 1 to 14, in which the reaction space is tapered at a position below the lower edge of the bundle of shafts, to form or to locate a single, axial gas inlet.

18. A reaction apparatus according to any one of Claims 1 to 17, including means for supplying the gas inlet line, preferably at a position directly before entry into the reactor, with a medium which is liquid under the reaction conditions and by which the gas inlet openngs are substantially continuously wetted.

19. A reaction apparatus according to any one of Claims 1 to 18, including means for the utilization of the latent heat of steam for heating the reaction space and/or for supplying the reaction heat in endothermic reactions, and for dissipating the heat of reaction in exothermic reactions.

20. A reaction apparatus according to any one of Claims 1 to 19, including means for providing a positive temperature gradient in the liquid medium along at least a part of the path of the gaseous reactants through the liquid medium.

21. A reaction apparatus according to any one of Claims 1 to 19, in which means are provided to vary the rate of heat transmission between the liquid medium and the coolant in a system of heat-exchange tubes provided longitudinally within the reactor, said means comprising a casing provided about or within each of the majority of the heat-exchange tubes or of each of the heat-exchange tubes, and means for maintaining a cushion of gas or vapour about or within at least a part of each casing and between the coolant and the liquid medium.

22. A reaction apparatus according to Claim 21, including means for varying the length of the cushion of gas or vapour.

23. A reaction apparatus according to any one of Claims 1 to 19, in which, for use in exothermic reactions, the area of the cooling surface of the cooling system is reduced in stages in the upward direction by reducing the diameter of the cooling tubes in the upward direction and/or by reducing the number of cooling tubes in the upward direction.

24. A reaction apparatus according to any one of Claims 1 to 19, including a heat-transfer system in the reactor and a heat-exchanger provided outside the reaction space in series with the heat-transfer system, through which system and heat-exchanger a liquid which does not vaporise under the reaction conditions can be circulated.

25. A reaction apparatus according to Claim 24, including positive means for controlling the rate of circulation of the liquid through the heat-transfer system and the heat exchanger, whereby a vertical temperature gradient in the reaction space may be maintained and varied.

26. A reaction apparatus according to any one of the preceding claims, in which the diameter or width of the shafts is not greater than 30 centimetres.

27. A reactor substantially as hereinbefore described with reference to Figure 3.

28. A reactor substantially as hereinbefore described with reference to Figures 7 and 8.

29. A reaction apparatus according to any one of Claims 1 to 19, including means for

maintaining a positive temperature gradient substantially as hereinbefore described with reference to Figure 15 or Figure 16.

30. A reaction apparatus according to any one of the Claims 1 to 16, including gas inlet means substantially as hereinbefore described with reference to and as illustrated in any one of the Figures 11 to 13.

31. A reaction apparatus according to any one of the preceding claims, including gas inlet means substantially as hereinbefore described with reference to and as illustrated in any one of the examples shown in Figure 14.

32. A process for the catalytic hydrogenation of an oxide of carbon, whenever carried out in the reaction apparatus claimed in any one of the preceding claims.

EDWARD EVANS & CO.,
53—64, Chancery Lane, London, W.C.2,
Agents for the Applicants.

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787123 COMPLETE SPECIFICATION
7 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1

FIG. 1

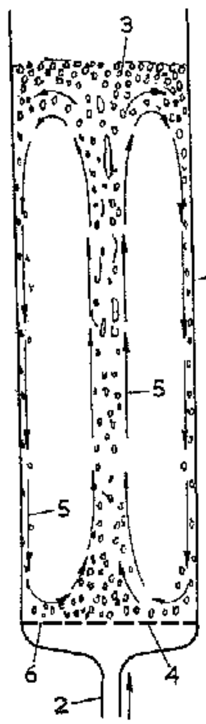



FIG. 2

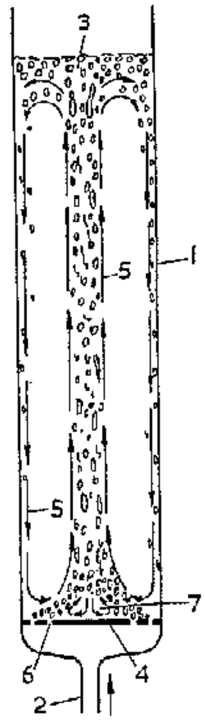
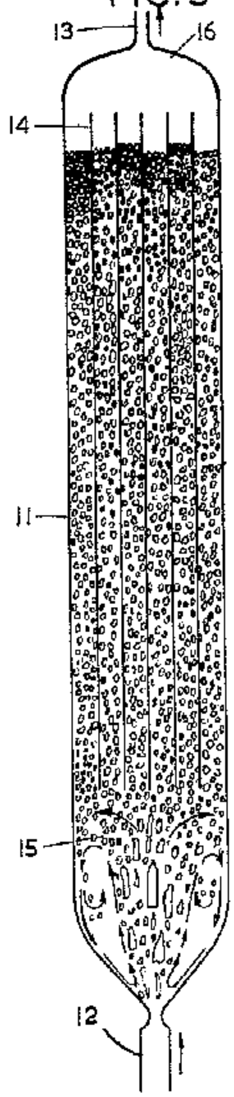



FIG. 3



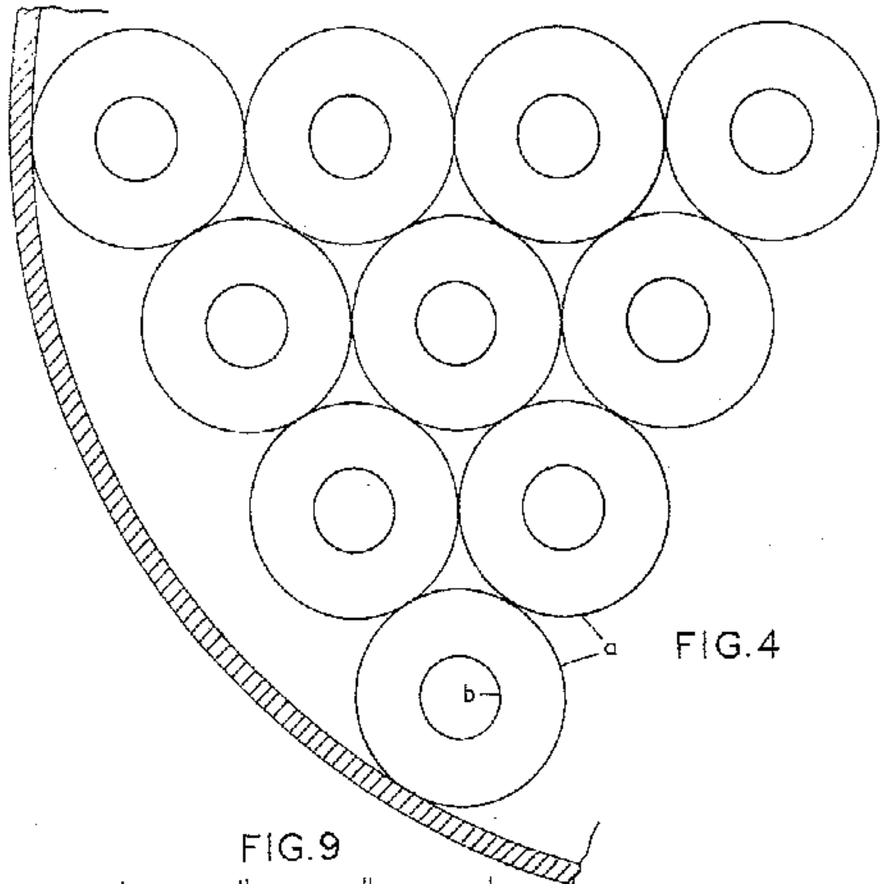



FIG.4

FIG.9

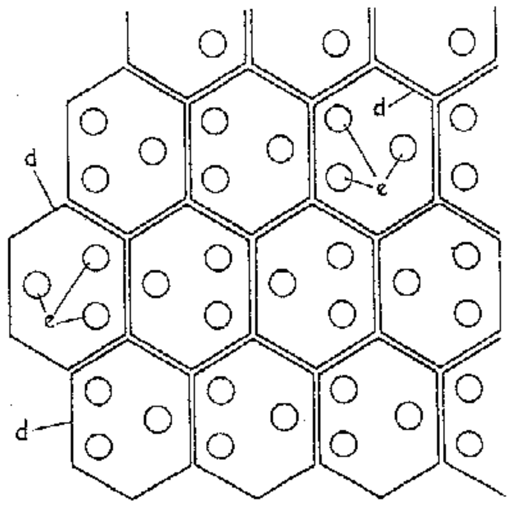
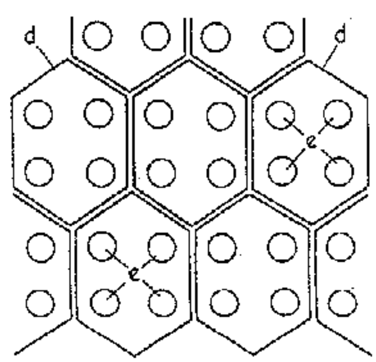
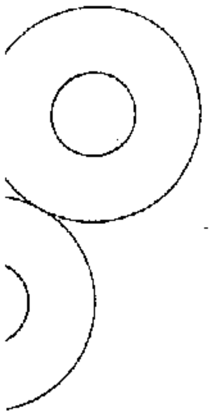



FIG 10





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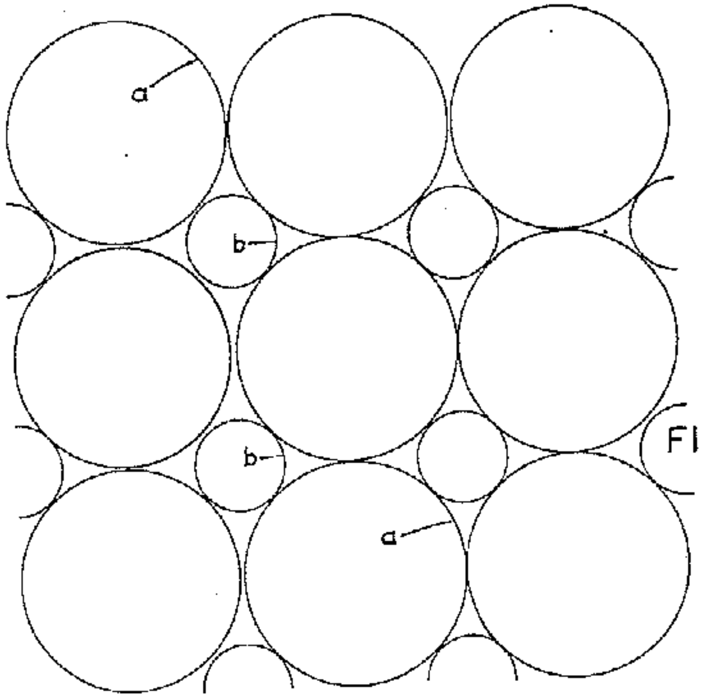


FIG.5

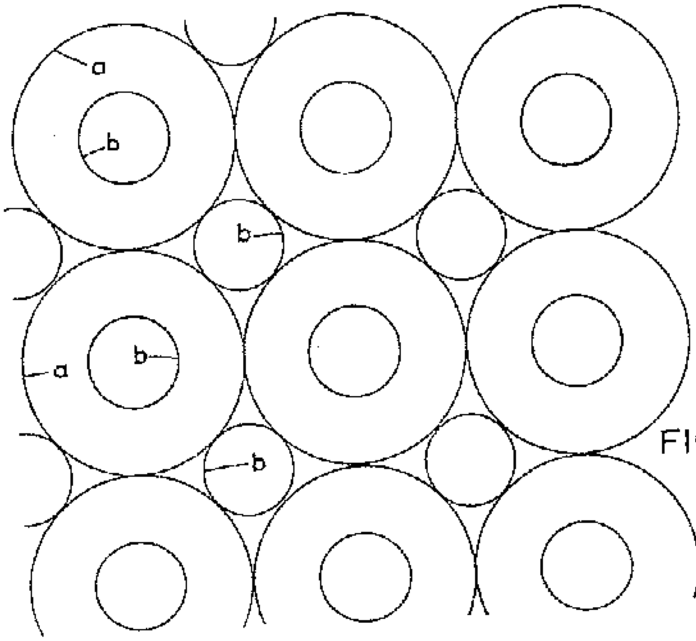


FIG.6

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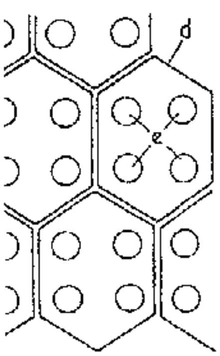

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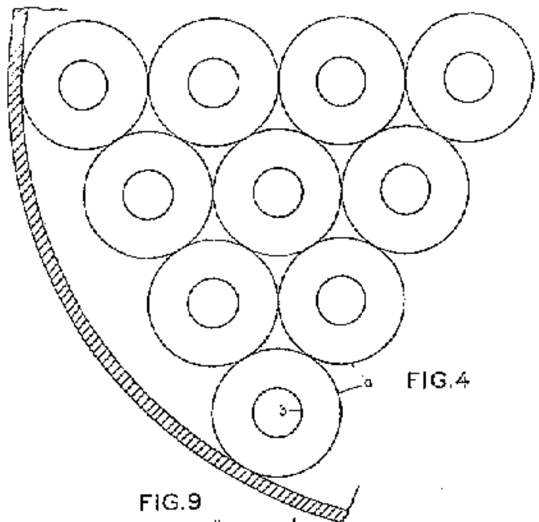



FIG.4

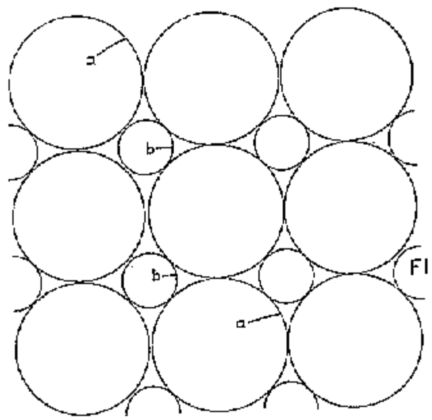



FIG.5

FIG.9

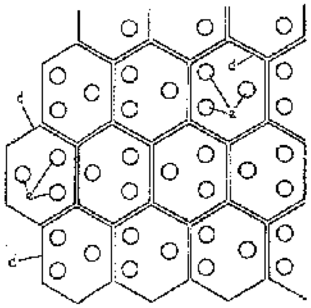
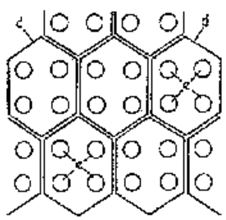



FIG 10



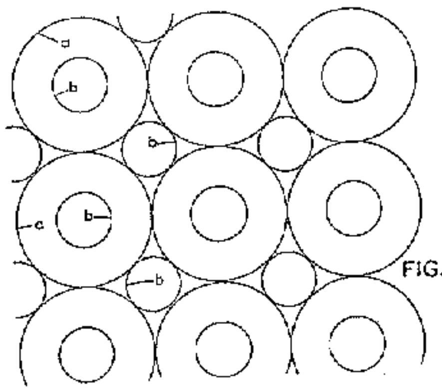




FIG.6

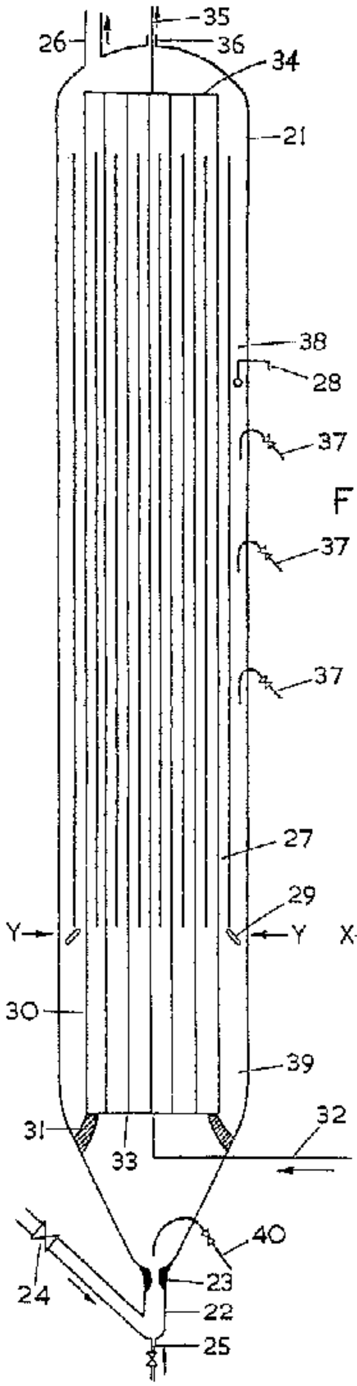

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FIG. 7

FIG. 8

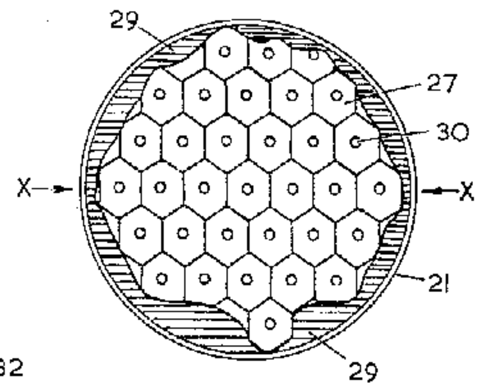
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FIG. 11

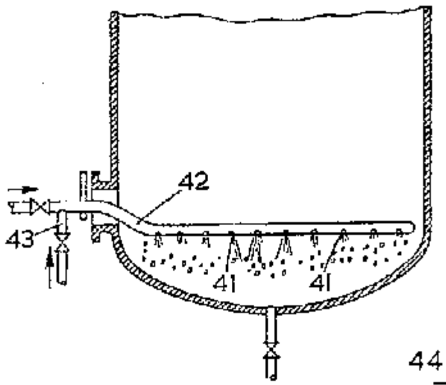



FIG. 13

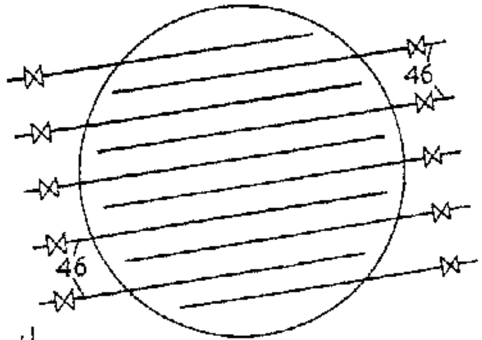



FIG. 12

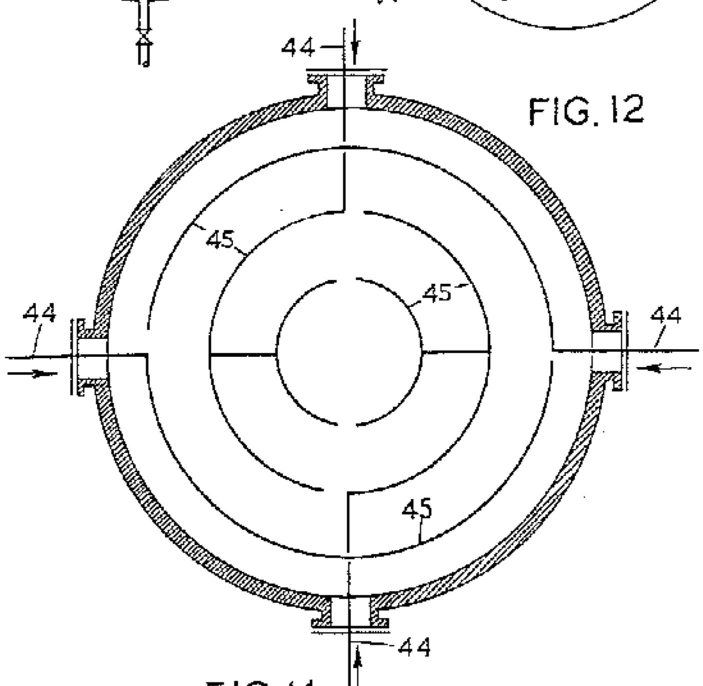
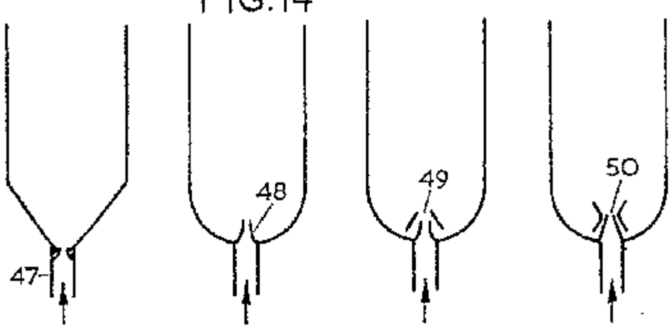



FIG. 14



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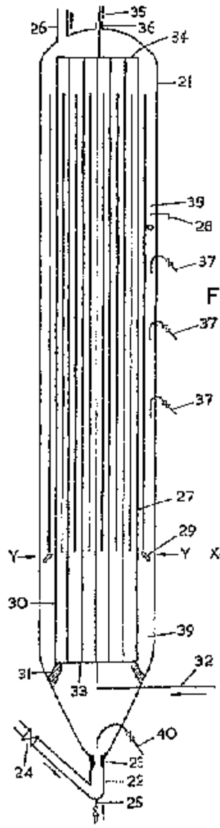



FIG. 7

FIG. 8

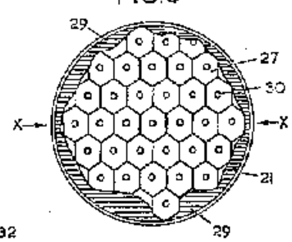



FIG. 11

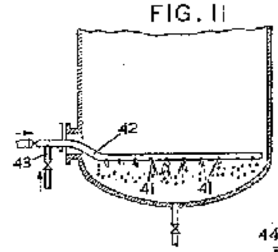



FIG. 13

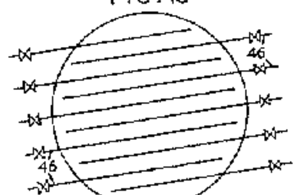



FIG. 12

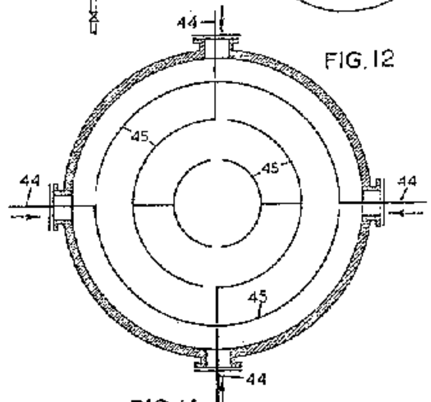
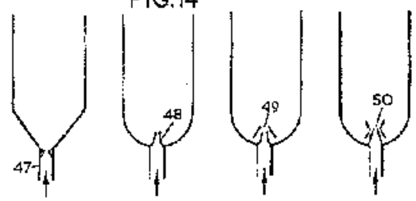



FIG. 14



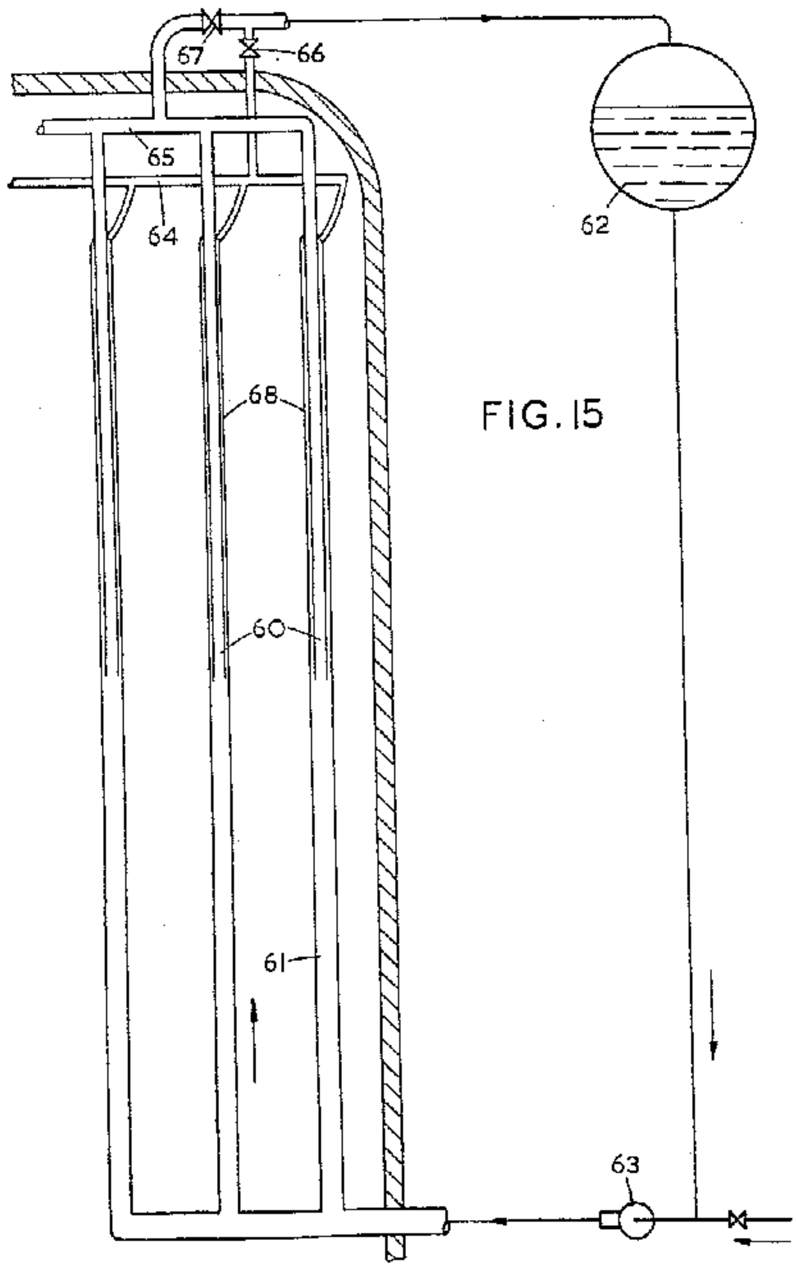



FIG.15

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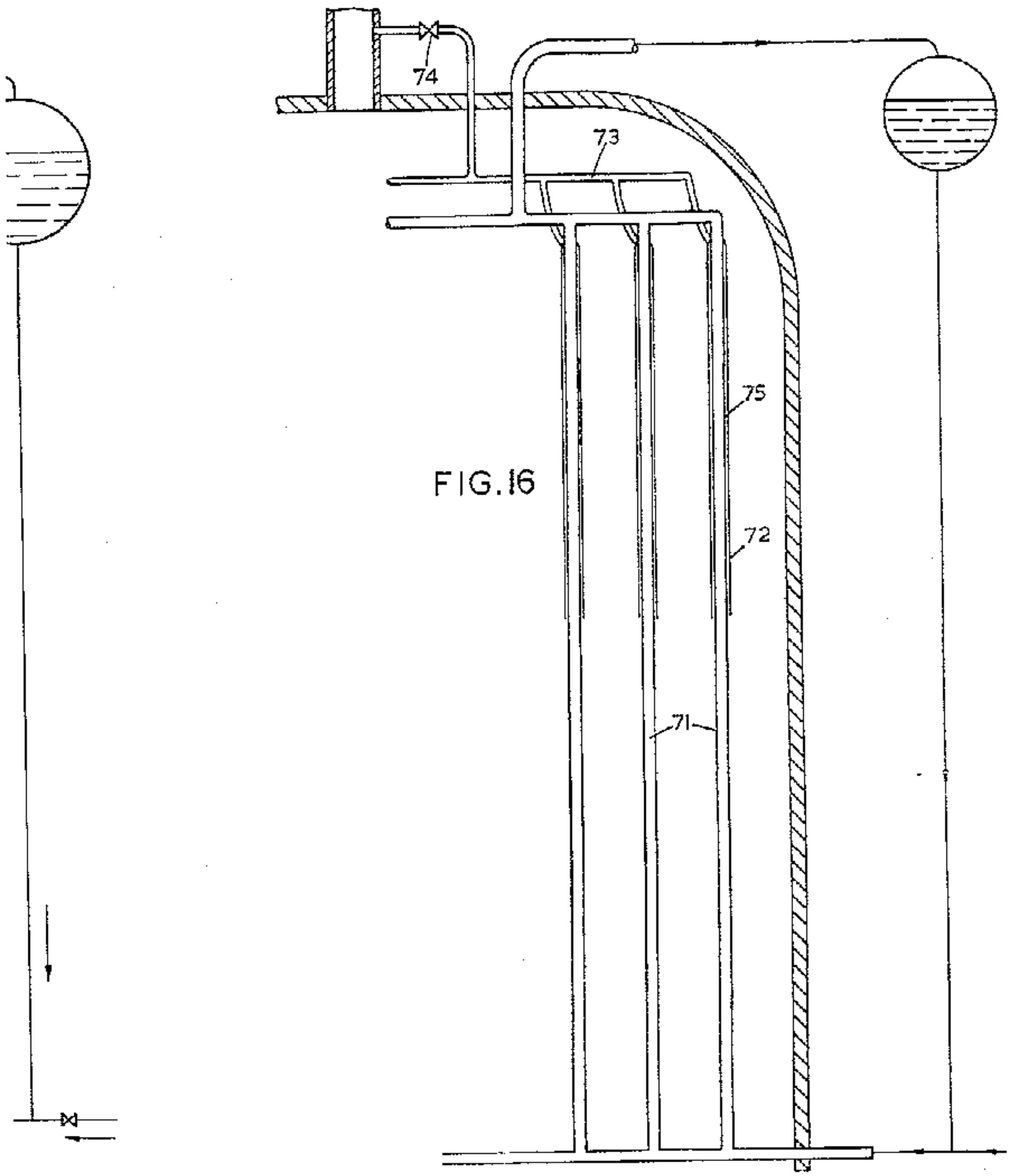


FIG. 16

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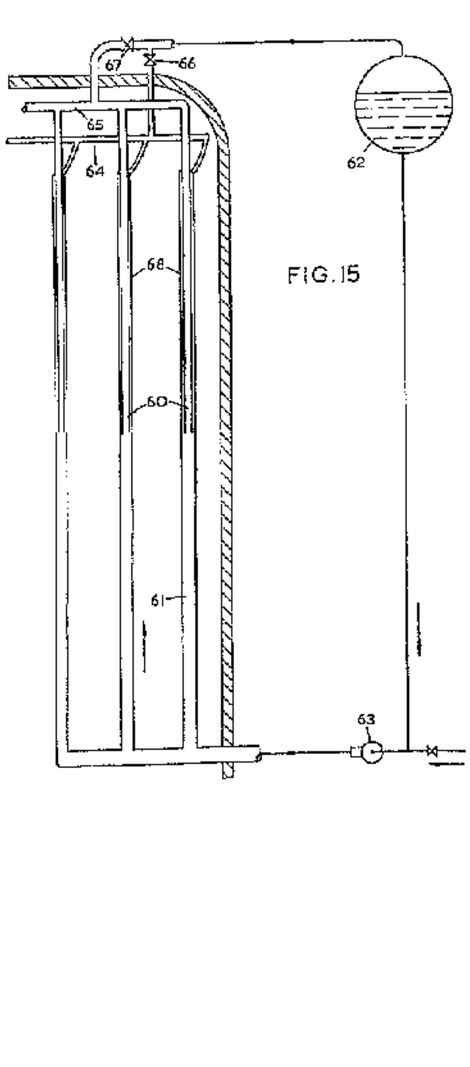


FIG. 15

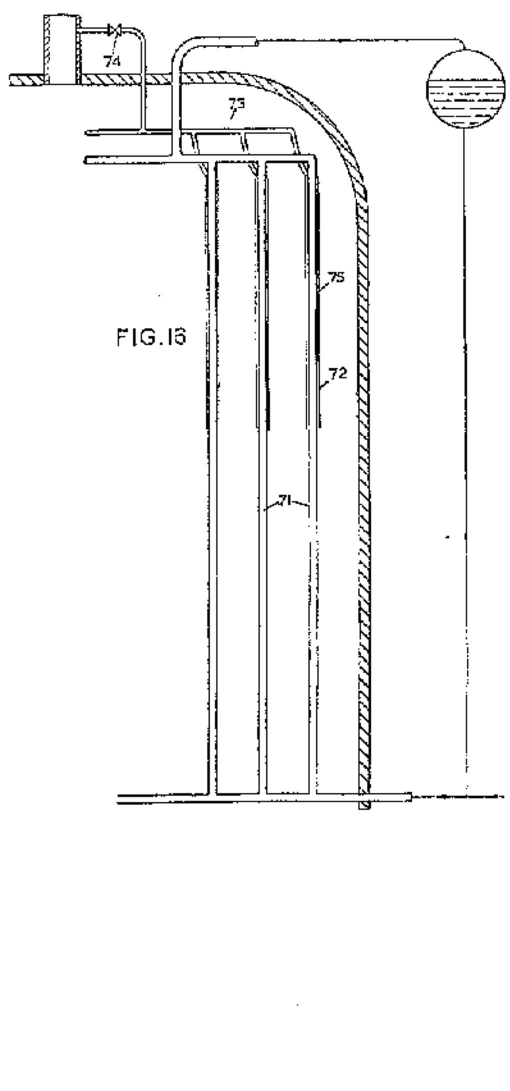


FIG. 16

# PATENT SPECIFICATION

**787,123**

*Date of Application and filing Complete Specification Jan. 20, 1955.*

*No. 1828/55.*

*Application made in Germany on March 18, 1954.*

*Complete Specification Published Dec. 4, 1957.*

Index at Acceptance:—**Class 1(1), A3A2.**

International Classification: —**B01j.**

COMPLETE SPECIFICATION

## ERRATA

SPECIFICATION No. 787,123

Page 3, line 112, *for* " effects " *read* " affects "
Page 4, line 113, *for* " construction " *read* " constriction "

THE PATENT OFFICE,
21*st April,* 1958.

circulation or recycling inside or outside the reaction space.

It is known that in gas reactions which are carried out in the presence of catalysts in a liquid medium, and in which the gaseous phase does not disappear completely when passing through the liquid medium, being rather preserved as a separate phase on the whole of its path through the liquid medium due to the incomplete solubility of the gaseous starting materials and end products, the degree of gas conversion is proportional to the area of the boundary surface between the gas and the liquid. In such a system of distribution of gas in liquid, the area of the boundary surface is determined by the size of the gas bubbles.

For certain reactions, including the Fischer-Tropsch synthesis, it has been found to be adequate to carry out the reactions without using any special method of introducing or distributing the gas in the liquid medium, as the gas bubbles which form in the liquid litres of gas per litre of liquid medium per hour. At a certain distance above the position at which the gas is introduced into the liquid medium, there develops a state in which the mixture of gas and liquid is such that the gas bubbles are almost uniform in size, are distributed substantially uniformly over the whole horizontal cross-section of the column, and ascend at an almost uniform speed. The total volume of the liquid/gas system is directly proportional to the gas throughput, whereas the total contact time of the gas bubbles is almost independent of the gas throughput. As the gas throughput increases, the distance between the gas bubbles is reduced without coalescence of the gas bubbles taking place. The nature of this system, which may be termed a " liquid/gas suspension system ", has not yet been fully explained. It has, however, been found that in this system the liquid is in a state of very fine turbulence in which the eddies are approximately only of the order of magnitude of the gas bubbles,