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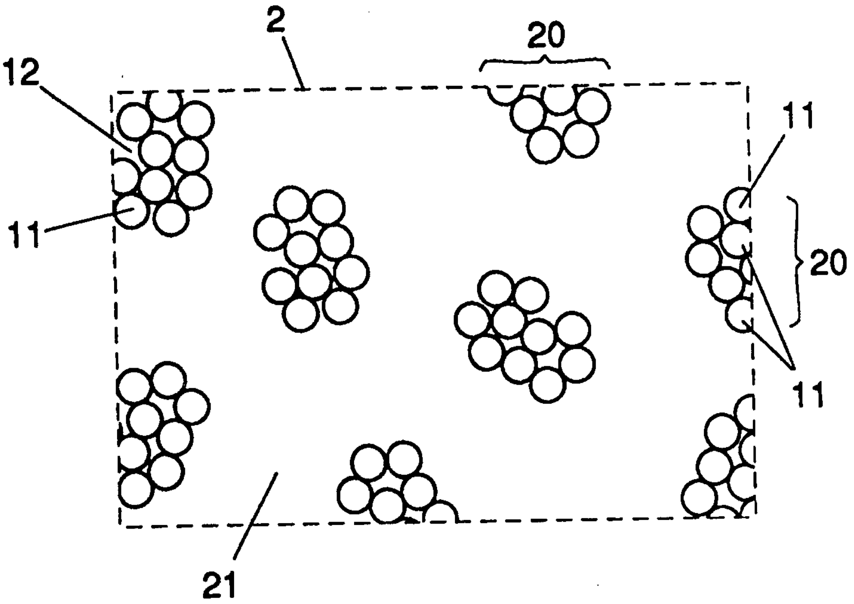

(57) Abstract

Described is a reactor (1) at least partially filled with catalyst granules (11), which is intended for catalytically reacting at least one gas and at least one liquid with each other. According to the invention the catalyst granules (11) are collected in agglomerates (20) with relatively small relative distances between the granules and relatively large distances between the agglomerates.

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Title: Reactor filled with catalyst material, and
catalyst therefor

The present invention relates to a reactor at least partially filled with catalyst granules, which is intended for catalytically reacting at least one gas and at least one liquid with each other.

In particular, the invention relates to such a reactor for the treatment of oil products, such as the desulfurization of heavy oil by means of hydrogen gas, for which reason the invention will be explained below with reference to this example of an application, but it is emphasized that the invention is not limited to this application.

In practice, the desulfurization of heavy oil by means of hydrogen gas takes place in a reactor filled with granular catalyst material. Each individual catalyst means therefore has the form of a granule, and may have the form of, e.g., a sphere, an elongated cylinder or a flat cylinder (pill), the dimensions of each granule being in the order of 1 mm. The catalyst granules have been poured in a random manner, and these catalyst granules supporting each other define therebetween a capricious pattern of passageways, the dimensions of which are typically in the millimeter range. The heavy oil and the hydrogen gas are pressed through these passageways while reacting with each other, the material of the granules fulfilling a catalyzing role. More in particular, the granules are generally porous, and the gas/liquid reaction takes place in the pores of the granules, the dimensions of which pores are typically in the nanometer range.

This is connected with different problems.

A first problem is concerned with the size of the individual catalyst granules. The larger the granules are chosen, the smaller the available exterior catalyst surface is in proportion to the catalyst volume or catalyst weight. In case the catalyst material consists of a porous support containing the active catalyst, this means that with larger granules it becomes increasingly difficult to cause the active catalyst present in the interior of the catalyst granules to efficiently contribute to the reaction to be catalyzed (diffusion limitation). A larger dimension of the catalyst granules is therefore connected with a diminished efficiency.

However, the smaller the granules are chosen, the more the flow resistance of the catalyst bed increases. At a constant yield this means a greater pressure drop over the catalyst, which is synonymous with a greater loss of energy, and for pushing the materials to be reacted more power is required.

A second problem is concerned with the manner in which the materials to be reacted can flow through. The reactor can be operated in two principally different ways, namely in a concurrent mode or in a countercurrent mode. A concurrent mode is characterized in that the gas and the liquid flow through the reactor in the same direction, i.e. in general vertically upwards ("upflow" reactor) or downwards ("trickle-flow" reactor). In particular the lastmentioned reactor is frequently used in oil refining. Operating in such a concurrent mode has some important drawbacks, especially when in the reaction to be catalyzed a gaseous reaction product is formed, as is the case in the desulfurization of heavy oil by means of hydrogen gas, in which H_2S is formed. The more the liquid advances in the reactor, the more it is contaminated with this gaseous reaction product, which counteracts the reaction to be catalyzed. Furthermore, as the liquid advances in the catalyst bed, the temperature of the liquid will increasingly rise or fall, depending on whether the reaction to be catalyzed is exothermic or endothermic, so that in a commercial reactor arrangements are to be made to keep the temperature within specific limits.

Since both the gas and the liquid must move via the same twisting paths between the catalyst granules, which paths repeatedly have constrictions and repeatedly communicate with each other, a high degree of mixing is obtained on a microscale. As a result, a good mass transfer from the liquid to the liquid/solid interphase is achieved, and a good mass transfer from gas to liquid too. Because of the good mass transfer between the two phases and the simultaneous presence of the two phases in each volume element of the catalyst bed it is ensured that in each part of the catalyst bed the gas and the liquid come very near to the condition of equilibrium. It is true that such a good mass transfer is desirable from the reaction viewpoint, but this is connected with an equally good transfer of impulse (from flowing liquid to still solid matter), which causes a releatively great pressure drop.

A countercurrent mode is characterized in that the gas and the liquid flow through the reactor in opposite directions. This does not involve the drawbacks of contamination with gaseous reaction product and temperature problems, as described above with respect to a concurrent mode.

However, another drawback is involved. It will be clear that such a mode cannot be accomplished by driving both the gas and the liquid on the basis of pressure gradients, since the pressure gradients required therefor must be opposite to each other for the gas and the liquid. On the other hand, it is possible to push the liquid by gravity, and in fact, a method is known by which the oil is caused to trickle through the catalyst bed from the top downwards and the hydrogen gas is blown from the bottom upwards, but such a method only proceeds at a low maximally applicable velocity and is therefore of little commercial use. One aspect that plays a role is the fact that it is desirable for an effective use of the catalyst material to choose the granular size relatively small, in general less than 3 mm, so as to prevent a strong pore diffusion limitation. Under such conditions, and at the velocities occurring in a commercial scale reactor, the downward flow of the oil is too much hindered by the upward gas flow. Exactly as stated above with respect to the concurrent mode, there is a good impulse transfer from gas to liquid, and in the case of a countercurrent mode the gas tends to push the liquid up and to counteract the driving force of gravity. When the above impulse transfer increases too much, the liquid can no longer flow away through the catalyst bed (overflowing of the catalyst bed).

It is an object of the invention to remove the above drawbacks.

A general object of the invention is to provide a reactor and a catalyst therefor, in which the above drawbacks have been eliminated or have at least been reduced.

In particular, it is an object of the invention to provide a reactor the active catalyst of which is largely efficient in use, while the catalyst bed in the reactor only offers a relatively low flow resistance to the gas flow.

It is a further object of the invention to provide a reactor which is particularly suitable for being operated in a countercurrent mode.

The invention is based on a better insight into the mechanism that plays a role in the mixing of a gas and a liquid in a manner suitable for carrying out a reaction. It has hitherto been believed that gas and liquid must be in contact with each other over the full height of the catalyst bed in order that a sufficient supply of materials to be reacted is provided over the full height of the catalyst bed. According to the invention, however, it has been found that this is not necessary, but that it is sufficient when the gas and the liquid meet each other intermittently, and preferably in a regular manner, so that the liquid can become saturated with gas at each meeting point.

To that end, according to the invention a reactor of the above type has the characteristics set forth in claim 1.

In one embodiment the agglomerates have the form of lumps of catalyst granules adhered together, which adhering may have been effected by cementing or sintering. The lumps may be neatly stacked, but the lumps may also be poured loose into the catalyst bed.

In another embodiment the agglomerates are provided by packing the catalyst granules in packs together in a packing permeable to gas and liquid, e.g. a metal gauze.

According to the inventive concept a separation is automatically effected between the gas phase, on the one hand, and the liquid phase, on the other. Because of the capillary action the liquid will preferably stay in the relatively small spaces between the catalyst granules, and the gas will preferably stay in the relatively large spaces between the agglomerates. Thus, no pushing occurs, and the flow resistance remains low. An additional advantage thereof is that the granular size has become less critical and may in general be smaller than is now conventional, since a reduction of the granular size now influences the flow resistance to a lesser extent.

When the liquid leaves an agglomerate and moves to a next agglomerate, the liquid passes one of the above relatively large spaces between the agglomerates where it comes into contact with the gas. Although the residence time of the liquid in that space is rather short, this time is sufficient for the gas to dissolve in the liquid. The amount of the gas dissolved in the liquid is sufficient to feed the reaction of the gas with the liquid during the residence time of the liquid in the next agglomerate, after which, in a next one of the above spaces, the gas in the liquid is "refreshed", and the above cycle may be repeated.

U.S. patent 4,105,587 describes a process for producing alumina catalyst particles, of which dry steaming a dough-like mixture is presented as the essential step. The dough-like material contains particles the dimensions of which vary over some orders of magnitude: the maximum dimensions of the particles is about 1.5 mm, while at least 95 wt.% of the particles have dimensions less than 0.15 mm. This has the result that the smaller particles will take a position in the spaces between the larger particles. Furthermore, during the production process the dough-like material is subjected to an extrusion step under high pressure, which has the result that the particles will be deformed and the resulting agglomerates ("interconnected pack") will be highly densified. Consequently, the capillary channels between the particles in the agglomerates, indicated in the above publication by the term "macropores", have dimensions in the range up to 15 microns.

Such agglomerates are not suitable for use in a countercurrent reactor.

U.S. patent 4,604,261 describes a conventional multiphase solid bed reactor for trickle-flow in which the catalyst bed is subdivided into several beds. This reactor has a complex double-walled structure in which the gas is supplied via an annular space so as to be introduced from the side into the beds. In each bed both the gas and the liquid must always flow in the spaces between the catalyst granules, which has the above drawbacks.

Further aspects, features, and advantages of the invention will be explained in more detail by the following description of preferred embodiments of a reactor with reference to the drawing. In this drawing:

Fig. 1 diagrammatically shows a side view of a reactor with a catalyst bed;

Fig. 2 shows a detail of a catalyst bed;

Fig. 3 diagrammatically shows the construction of a catalyst bed according to the principle of the invention;

Fig. 4 diagrammatically shows a catalyst bed according to the principle of the invention, on a smaller scale than Fig. 3, to illustrate the course of the different flows:

Figs. 5A and 5B show graphs to explain the advantages of a countercurrent mode; and

Figs. 6, 7, 8 show different embodiments of a catalyst bed according to the principle of the invention.

In the figures the same or comparable parts are denoted by the same reference numerals.

Fig. 1 diagrammatically shows a reactor 1 containing a catalyst bed 2, which reactor 1 is provided with a gas supply line 3 and a liquid supply line 4 and with a gas discharge line 5 and a liquid discharge line 6. Since the gas supply line 3 and the liquid supply line 4 are located at both sides of the catalyst bed 2, the reactor 1 is intended to be operated in a countercurrent mode; the directions of flow of the gas and the liquid through the catalyst bed 2 are denoted by arrows F_G and F_F, respectively.

The catalyst bed 2 contains granular catalyst material, as shown in more detail in Fig. 2, in which the individual catalyst granules are denoted by reference numeral 11. In general, the granules 11 have shapes comparable with each other, such as a sphere, an elongated cylinder or a flat cylinder (pill), the dimensions of each of which granules may be in the order of 1 mm. In Fig. 2 the catalyst granules 11 are depicted as more or less spherical. As also shown in Fig. 2, the catalyst granules are generally positioned in a random manner with respect to each other, and these catalyst granules supporting each other define therebetween a capricious pattern of capillary channels 12. Typically, the dimensions of the granules 11 are in the millimeter range, more in particular about 1 - 3 mm, and the capillary channels 12 have diameters which are in the millimeter range, more in particular about 0.1 - 3 mm.

Each granule 11 contains pores 13 associated with the specific surface area of the relevant catalyst. The dimensions of the pores 13 are in the nanometer range and are typically in the order of about 10 - 100 Å. It is within these pores 13 that the reaction to be catalyzed substantially takes place.

The catalyst granules 11 may be made of a support material, e.g. a ceramic material or a metal for a proper heat conduction, to which a thin layer of the actual catalyst material is applied, which layer bounds each capillary channel 12. In a preferred embodiment, which is particularly suitable for the desulfurization of oil by means of hydrogen gas, the catalyst granules 11, however, are integrally made of catalyst material, such as a porous matrix impregnated with active material. An example thereof is γ-alumina having in at least part of the pores W, Co, Mo, Ni, or Mn atoms as active material, or combinations of these atoms.

In a conventional reactor the whole catalyst bed 2 is formed by granules 11 poured loose on a support or into a container. On the other hand, in the reactor 1 according to the invention, as diagrammatically illustrated in Fig. 3, the granules 11 are collected in agglomerates 20. Although this is not shown in Fig. 3 for simplicity's sake, the granules 11 contain pores 13, as known per se and described above in more detail with reference to Fig. 2.

In the agglomerates 20 the distances between the granules 11 are relatively small, by which in the agglomerates 20 capricious patterns of capillary channels 12 are always defined, the dimensions of which are typically in the millimeter range. Between the agglomerates 20 the distances are relative large, by which gas passageways 21 are defined between the agglomerates 20. Typically, the dimensions thereof are preferably in the centimeter range, more in particular in the range of 0.3 - 3 cm. Typically, the granules 11 in the agglomerates 20 have dimensions in the order of about 1 mm, while the dimensions of the agglomerates 20 are typically in the range from about 1 cm to about 30 cm. It will therefore be clear that in Fig. 3 the dimensions of the granules 11 and the agglomerates 20 are not given in the correct ratio, for clearness' sake.

During operation, the granules 11 will be moistened by liquid, and because of the occurring capillary forces the capillary channels 12 will always be filled with the liquid at least substantially completely. Under the action of gravity, the liquid in these capillary channels 12 will then move downwards. At the lower end of each agglomerate 20 liquid leaves and falls through an interagglomerate space 21 to a next agglomerate 20. At the same time the gas flows through the passageways 21, which flow, because of the relatively large dimensions of the passageways 21, takes place practically without loss of pressure. This is illustrated in more detail in Fig. 4, in which the liquid flow is denoted by arrows L and droplets 22, and in which the gas flow is denoted by arrows G and dotted lines 23. The agglomerates 20 are depicted as rectangular blocks, and the catalyst bed 2 is depicted in layered form, namely built up from layers A, in which the agglomerates 20 are located beside each other at the same level, alternated with layers B, in which there are no agglomerates 20.

Thus, according to the concept underlying the invention the gas and the liquid flow countercurrently via different paths without hindering each other. Where the liquid traverses an interagglomerate space 21 when passing from one agglomerate 20 to the next one, the liquid comes into contact with gas which can dissolve in the liquid. The liquid then flows, with a specific amount of gas dissolved therein, through the capillary channels 12 of the next agglomerate 20, the dissolved amount of gas being sufficient to feed the reaction to be catalyzed in the next agglomerate 20.

This may be illustrated by the following calculating example. The solubility of hydrogen in a heavy oil is at a reaction temperature of ca. 350°C about 0.1 - 0.15 Nl/kg per bar pressure. At a partial hydrogen pressure of 50 bar, therefore, about 6 Nl or 0.3 moles of hydrogen is dissolved per kg of oil. In a hydrodesulfurization process, in which 4 moles of hydrogen are required to remove 1 mole of sulfur, this dissolved amount of hydrogen is sufficient to remove about 0.07 moles of sulfur per kg of oil, or about 0.2 wt.% of sulfur. If, for instance, it is desirable to reduce the sulfur content of an oil from 2 wt.% to 0.2 wt.%, it follows from the above that 9 successive steps are necessary in which hydrogen is always dissolved in the oil, assuming that the oil is always saturated with hydrogen, and that this hydrogen is always consumed completely.

It will be clear, however, that during the course of the reaction the hydrogen concentration falls, and that therefore, the driving force behind the reaction decreases. It is desirable to maintain a sufficiently high driving force, so that it is recommendable to use more reaction stages and to saturate the oil more often. When the number of resaturation stages is multiplied by ten to about 100, in each reaction stage the hydrogen concentration in the oil will remain higher than about 90% of the saturation concentration, which is deemed sufficient. In a commercial reactor having a height of about 20 m this implies a vertical dimension of the agglomerates 20 in the order of 20 cm, which is much larger than the granular size of a conventional fixed bed catalyst. The above calculating example illustrates that it is not necessary to contact the gas and the liquid with each other on a distance scale in the order of the granular size, as has hitherto been the starting point when designing a reactor.

As already stated with reference to Fig. 1, the reactor 1 is particularly suitable for being operated in a countercurrent mode. The significance of such a mode will now be elucidated with reference to Figs. 5A and 5B, which graphically show the relation between the concentration of the sulfur (S) in the oil (Fig. 5A) and the concentration of H_2S in the gas phase (Fig. 5B) as a function of the location in the reactor bed, expressed in percentages, in the desulfurization of an oil containing 2 weight percent of sulfur, by means of a hydrogen gas flow of 50 bar in a ratio of 220 Nl per kg of oil.

Fig. 5A illustrates that the desulfurization reaction is a second order reaction. The H_2S formed in the desulfurization is entrained with the gas (H_2), so that the concentration of H_2S is highest in the outlet zone of the gas. In the case of a concurrent mode (full line in Fig. 5B) the oil in the greater part of the reactor bed is in an environment having a relatively high concentration of H_2S, which counteracts the desulfurization reaction. Moreover, the desulfurization reaction is then counteracted most strongly in the outlet zone of the oil, in which the easily removable sulfur parts have already been removed and the most difficultly removable sulfur parts are still to be removed, which exactly requires the greatest possible reaction force.

On the other hand, in the countercurrent mode (dotted line in Fig. 5B) the H_2S formed is entrained by the gas flow to the oil inlet zone of the reactor bed and discharged from there. Fig. 5B clearly shows that then the oil in the greater part of the reactor bed is in an environment having a relatively low concentration of H_2S.

In this connection it must be considered that the oil is actually a mixture of different components, the desulfurization rates of which are different. The components that can be most easily desulfurized (highest desulfurization rate) are already desulfurized in the oil inlet zone of the reactor bed. Because of these factors the concentration of H_2S is relatively high in the oil inlet zone and considerably falls as the oil advances in the reactor bed, in such a manner that, on average, the concentration of H_2S is less than in the concurrent mode.

An important consequence thereof is that the components that can be difficultly desulfurized (lowest desulfurization rate) are hardly impeded by the counteraction of H_2S at the end of the reactor bed in the very pure H_2 atmosphere, as is actually the case in the concurrent mode. Consequently, in the countercurrent mode the concentration of sulfur in the oil remaining at the end of the reactor bed is considerably less than in the concurrent mode. Because at the end of the reactor bed the concentration of H_2S is low, there is also the possibility to use a catalyst material which, on the one hand, is very active, but, on the other hand, is very sensitive to sulfur and/or H_2S. Exactly because of that sensitivity such an active catalyst material normally cannot be used in conventional reactors.

A comparable situation occurs in hydrocracking. The by-product of the conversion of nitrogen-containing organic substances, e.g. ammonia, exerts a strong counteraction on hydrogenation reactions and, in particular, on hydrocracking reactions. In order to avoid that at the downstream end of a reactor operating in concurrent mode such a reaction is suppressed almost completely, the ammonia formed must be removed between successive stages. In order yet to obtain a sufficient hydrocracking conversion, the loss of intrinsic reactivity must moreover be compensated by using relatively high temperatures or by having recourse to catalysts having a very high intrinsic acidity (zeolites), which, admittedly, retain sufficient activity in the presence of ammonia, but, on the other hand, are poorly accessible to large molecules.

For the hydrogenation of aromatic hydrocarbons a countercurrent mode is likewise desirable, not only from a kinetic viewpoint (counteraction by H_2S and ammonia), but also from a thermodynamic viewpoint, since in the outlet zone of the reactor the partial hydrogen pressure is very low, because of the combined effects of pressure drop, hydrogen consumption, and the formation of other gas components.

Another important aspect resides in the fact that hydrogen-consuming reactions, such as in hydrocracking, are very exothermic. In a concurrent mode the reaction heat released is entrained by the reaction products towards the outlet of the reactor, which results in a sharp temperature rise in that direction. In order to keep this rise within limits, it is necessary to provide the reactor bed with cooling agents. In a countercurrent mode the reaction heat released is transported by the reaction products in two opposite directions, which results in a flatter temperature profile.

Different embodiments of a catalyst bed according to the principle of the invention will now be described.

It is possible to individually prepare and place the agglomerates 20 in a reactor. Thus, for instance, it is possible to prepare an agglomerate 20 by placing catalyst granules 11, e.g. by pouring them loose, in a container 30, e.g. in the form of a vertical cylinder or a horizontal tube, having side walls 31, a lower wall 33, and optionally, an upper wall 32, which optional upper wall 32 and lower wall 33 are permeable to liquid. Fig. 4 shows an example thereof, with the side walls 31 given in closed condition. It is not necessary, however, that the side walls 31 are closed. because it can de demonstrated that, as a result of the capillary action of the capillary channels 12, the liquid will not leave an agglomerate 20 at the side, but only at the lower end. A comparable effect is known in everyday life from water in a sponge.

An example of a suitable material for producing a container 30 is a metal gauze. The containers 30 can be stacked with interposition of spacers, but it is also possible to place the containers 30 on racks which are attached in the reactor or, if the containers 30 are in the form of tubes having a length which corresponds to the width of the reactor, to directly attach the tubes to the inner wall of the reactor.

Since the precise manner of attachment in a reactor is not essential and, after the foregoing, several appropriate methods of attachment will be clear to those skilled in the art, the positioning of the containers 30 will not be described in more detail.

Although a reactor as described above with reference to Fig. 4 already offers the essential advantages of the invention, the positioning of the containers 30 in the reactor is rather difficult. An improvement in this respect is provided by the reactor illustrated in Fig. 6, in which the agglomerates 20 have been prepared by placing catalyst granules 11 on a liquid-permeable bottom plate 41, e.g. made of a gauze. The bottom plate 41 is horizontally arranged in a reactor and efficiently has horizontal dimensions which correspond to those of the reactor for simple attachment thereof.

The bottom plate 41 is provided with substantially vertical walls 42 to separate bottom plate parts with granules 11 (the agglomerates 20) from bottom plate parts without granules (the gas passageways 21). These vertical walls have a height defining the height of the catalyst layers A, and may have the form of vertical tubes, so that the gas passageways 21 in the catalyst layers A have the form of vertical cylinders, but these vertical walls may also extend in the horizontal direction over the full length of a bottom plate 41.

The bottom plate 41 defines with two vertical walls 42 containers 44 comparable to the containers 30 discussed above. Between two adjacent containers 44 the bottom plate 41 may be continuous, as illustrated at the top of Fig. 6; the vertical walls 42 are then placed on the bottom plate 41 separately or in pairs. In a simple structural variant the bottom plate 41 and the vertical walls 42 are integrally formed from a gauze or a perforated plate by bending it in the form of a wave or block, as shown at the bottom of Fig. 6.

Each container 44 encloses a space 45 for receiving catalyst granules 11. These containers 44 can be easily filled by pouring an appropriate amount of granules 11 on the horizontally arranged plates 41. For various reasons, inter alia to prevent waste, it is recommendable to provide the bottom plate 41 with a top plate 43 which may be quite flat and may rest on the upper sides of the side walls 42.

The bottom plate 41 and the top plate 42 can be considered to be a sandwich 40 with interspaces 45 for receiving catalyst granules 11 to form the agglomerates 20. The sandwich 40 can be easily filled by putting it on its side, in such a manner that the cross-section as shown in Fig. 6 is horizontally directed, followed by pouring granules 11 into the spaces 45.

It will be clear that the side walls 42 may also be associated with the top plate 43, which is equivalent to mounting the sandwich 40 upside down.

A further saving is obtained by making the top plate 43 identical with the bottom plate 41 and mounting it on the bottom plate 41 in alignment but upside down, as shown for the second sandwich 40 in Fig. 6. It is not necessary then to make two different parts.

Another manner of individually making and placing the agglomerates 20 in a reactor is to place catalyst granules 11 in fully closed containers 50 provided with a liquid-permeable outer wall 51, e.g. of a gauze or a perforated plate. Such containers 50 may be systematically stacked in the reactor, but the favorable effect according to the invention may also be obtained in a very easy manner by pouring these containers 50 loose into the reactor. The containers 50 may be identical with the containers 30 discussed before, or they may have the form of cubes, blocks, or other regular or irregular polyhedrons. In principle, the containers 50 need not have any symmetry, and they need not be equal to each other. Preferably, the containers 50 are more or less spherical, as illustrated in Fig. 7, thus ensuring at all times that an agglomerate 20 is always bounded by some gas passageways 21. Admittedly, a reactor thus filled has no regularly filled catalyst bed, but the lack of regularity does not detract from the advantages offered by the invention, while an additional advantage is that the reactor can be filled in a simple, rapid, and thus inexpensive manner.

In the embodiments discussed before the agglomerates 20 are always defined by enclosing a specific amount of catalyst granules 11 in an at least partially liquid-permeable casing. The agglomerates, however, may also be self-supporting by adhering together a specific amount of catalyst granules 11, e.g. by sintering, cementing, surface peptization, etc. Such a self-supporting agglomerate can be suitably made in the form of a sphere, cube, block, disk, ring, etc. Fig. 8 shows an agglomerate 20 the outward form of which is comparable to that of the embodiment illustrated in Fig. 7, in which the container 51 is therefore quite absent. The self-supporting agglomerates can be placed in the reactor in the same way as in the case of the agglomerates enclosed in a container, effectively by pouring them loose.

The embodiment as illustrated in Fig. 6 may likewise be self-supporting by adhering together granules 11 to obtain agglomerates in the form of plates of a suitable thickness, in which plates openings are left to form passageways for the gas. If these plates are provided at the top and/or bottom with suitable projections, e.g. ridges of a suitable height, of which the ridges at the top may have another orientation than ridges at the bottom, then the plates can be directly stacked, because the projections function as spacers for defining the gas passageways between the successive plates.

An additional advantage of the embodiments as illustrated in Figs. 4 and 6, in which modules filled with granules 11, whether self-supporting or not, are placed over each other, is that the catalyst materials of the different modules may have compositions different from each other, of which modules particularly those at the discharge side of the liquid phase may contain a very active material highly sensitive to sulfur and/or H_2S.

Summarizing, the invention provides a catalyst means which, because of the unique structure of the catalyst granules collected in agglomerates, has an intrinsic phase-separating action, which has the result that a liquid phase will preferably be present in recesses 12 defined in the agglomerates and a gas phase will preferably be present in the spaces 21 between the agglomerates 20. Thus, the reactor according to the invention is excellently suitable for being operated in a countercurrent mode at only a slight loss of pressure.

It will be clear to those skilled in the art that within the framework of the present invention various modifications are possible without departing from the scope of protection of the claims.

Thus, for instance, it is possible that the capillary channels in the agglomerates are distributed regularly, instead of capriciously.

Furthermore, it is possible that agglomerates in the form of plate-shaped modules (self-supporting or sandwich containers) have horizontal dimensions smaller than those of the reactor, thus providing tile-shaped modules of, e.g., 20 cm x 20 cm, which can be stacked according to interlocking patterns. Such tile-shaped modules can be transported more easily.

Moreover, it is possible that catalyst granules are adhered together to form miniagglomerates, and that the miniagglomerates are combined to maxiagglomerates, e.g. by placing them in containers.

CLAIMS

1. A gas/liquid countercurrent reactor (1) at least partially filled with catalyst granules (11), which is designed for flowing at least one gas and at least one liquid in opposite directions and catalytically reacting them with each other;
wherein the catalyst granules (11) are porous, and contain pores (13) the dimensions of which are substantially in the nanometer range;
wherein the dimensions of the catalyst granules (11) are substantially in the range from about 0.5 mm to about 3 mm;
wherein the catalyst granules (11) are collected in agglomerates (20), the dimensions of which are substantially in the range from about 1 cm to about 30 cm;
wherein in the agglomerates (20) capillary channels (12), the dimensions of which are substantially in the range from about 0.1 mm to about 3 mm, are defined between the granules (11);
and wherein between the agglomerates (20) gas passageways (21) are defined, the dimensions of which are substantially in the centimeter range;
in order to ensure that during operation of the reactor (1) the gas flow (S) will substantially move via the gas passageways (21) between the agglomerates (20), and to ensure that the transport of the liquid (L) will substantially take place by flow in the capillary channels (12) between the granules (11) in the agglomerates (20).

2. A reactor according to claim 1, wherein the dimensions of the pores (13) of the catalyst granules (11) are substantially in the range from about 5 to 500 Å, preferably in the range from about 10 to 100 Å.

3. A reactor according to claim 1, wherein in each agglomerate (20) the dimensions of at least 90% of the

granules (11) are in the range from about 0.5 to 2 mm, which granules (11) are substantially uniform.

4. A reactor according to claim 1, wherein in each agglomerate (20) at least 20% of the pore volume is present in pores (i.e. capillary channels (12)), the dimensions of which are above 0.1 mm.

5. A reactor according to claim 1, wherein the typical dimensions of the gas passageways (21) between the agglomerates (20) are substantially in the range from about 0.3 cm to about 3 cm.

6. A reactor according to any of the preceding claims, wherein in the agglomerates (20) the catalyst granules (11) are adhered together, e.g. cemented or sintered together.

7. A reactor according to any of claims 1-5, wherein the catalyst granules (11) are packed in an at least partially liquid-permeable casing (30; 44; 51).

8. A reactor according to claim 7, wherein the casing (30; 44; 51) is made of a gauze or a perforated plate, preferably of metal.

9. A reactor according to claim 8, wherein a horizontal plate (41) is provided with vertical walls (42) for defining gas passage openings (21).

10. A reactor according to claim 9, wherein the vertical walls (42) are formed by profiling the plate (41).

11. A reactor according to claim 8, 9 or 10, wherein the casing (44) is made as a sandwich (40) of two preferably profiled plates (41, 43).

12. A reactor according to at least any of the preceding claims, wherein the agglomerates (20) are poured loose into a catalyst bed (2).

13. An agglomerate (20) of catalyst granules (11) for use in a reactor (1) according to any of the preceding claims, which catalyst granules (11) are porous, and contains pores (13), the dimensions of which are substantially in the nanometer range;
wherein the dimensions of the catalyst granules (11) are substantially in the range from about 0.5 mm to about 3 mm;
wherein the dimensions of the agglomerates (20) are substantially in the range from about 1 cm to about 30 cm; and
wherein in the agglomerates (20) capillary channels (12), the dimensions of which are substantially in the range from about 0.1 mm to about 3 mm, are defined between the granules (11).

14. An agglomerate (20) according to claim 13, wherein the dimensions of the pores (13) of the catalyst granules (11) are substantially in the range from about 5 to 500 Å, preferably in the range from about 10 to 100 Å.

15. An agglomerate (20) according to claim 13, wherein the catalyst granules (11) are adhered together, e.g. cemented or sintered together.

16. An agglomerate according to claim 13, wherein the catalyst granules (11) are packed in an at least partially liquid-permeable casing (30; 44; 51).

17. An agglomerate according to any of claims 13-16, wherein the agglomerate substantially has the form of a tile having openings extending therethrough.

18. An agglomerate according to any of claims 13-16, wherein the agglomerate substantially has a spherical form, the diameter of which is in the range from 0.3 to 30 cm.

19. A process for catalytically reacting at least one gas and at least one liquid with each other in a reactor (1) at least partially filled with catalyst granules (11), which catalyst granules (11) are porous, and contain pores (13), the dimensions of which are substantially in the nanometer range; wherein the dimensions of the catalyst granules (11) are substantially in the range from about 0.5 mm to about 3 mm; wherein the catalyst granules (11) are placed in the reactor in such a manner that the catalyst granules (11) are collected in agglomerates (20), the dimensions of which are substantially in the range from about 1 cm to about 30 cm; wherein in the agglomerates (20) capillary channels (12), the dimensions of which are substantially in the range from about 0.1 mm to about 3 mm, are defined between the granules (11); and wherein between the agglomerates (20) gas passageways (21) are defined, the dimensions of which are substantially in the centimeter range;
and wherein the gas (G) and the liquid (L) are flowed countercurrently in the reactor (1), the gas (G) via the gas passageways (21) between the agglomerates (20) und the liquid (L) substantially in the capillary channels (12) between the granules (11) in the agglomerates (20).

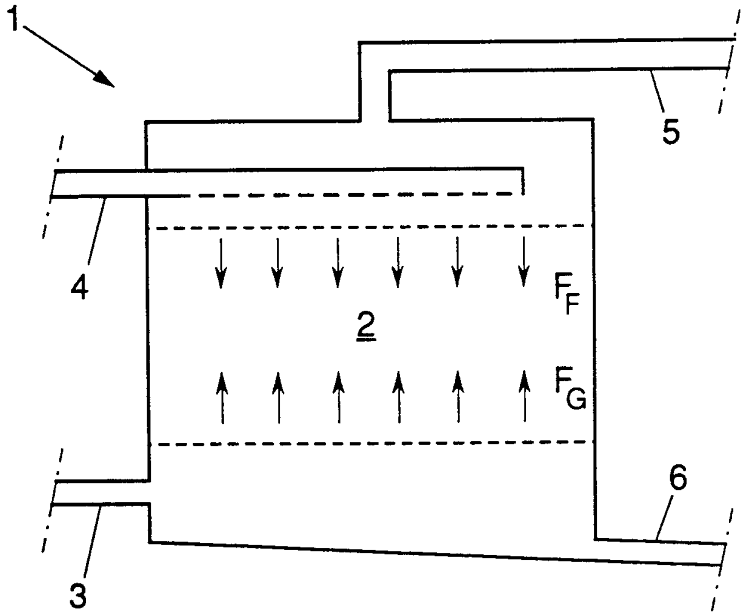

FIG. 1

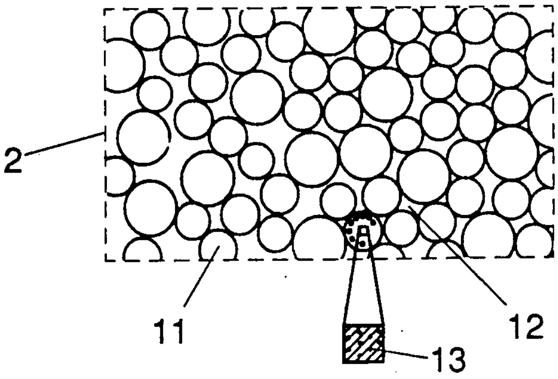

FIG. 2

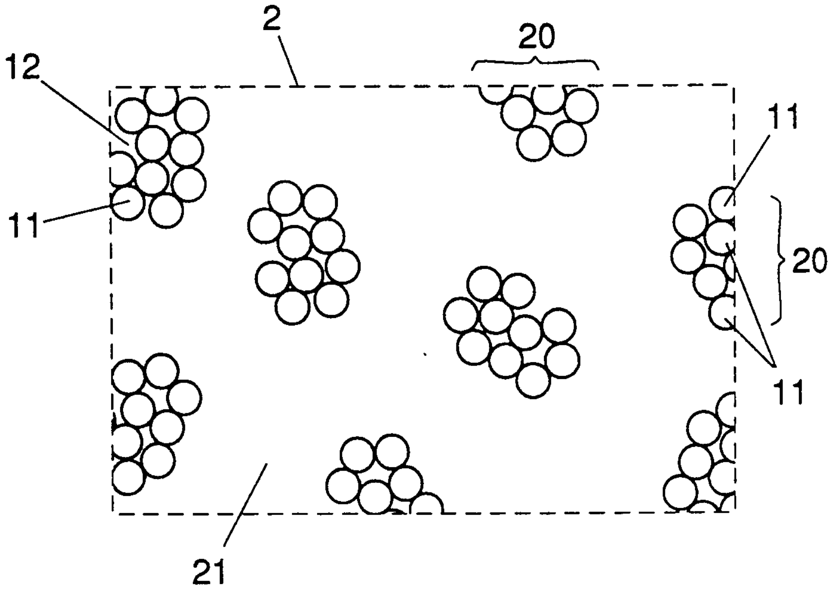
2
12
20
11
11
20
11
21

FIG. 3

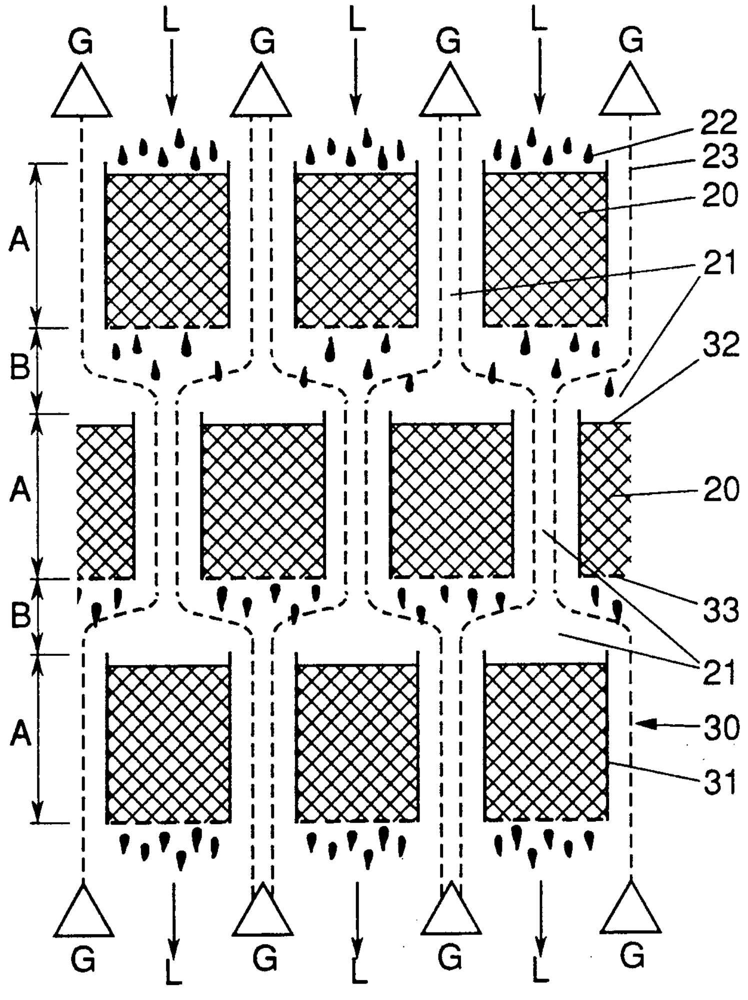
G
L
G
L
G
L
G
22
23
20
A
21
21
B
32
A
20
33
B
21
A
30
31
G
L
G
L
G
L
G

FIG. 4

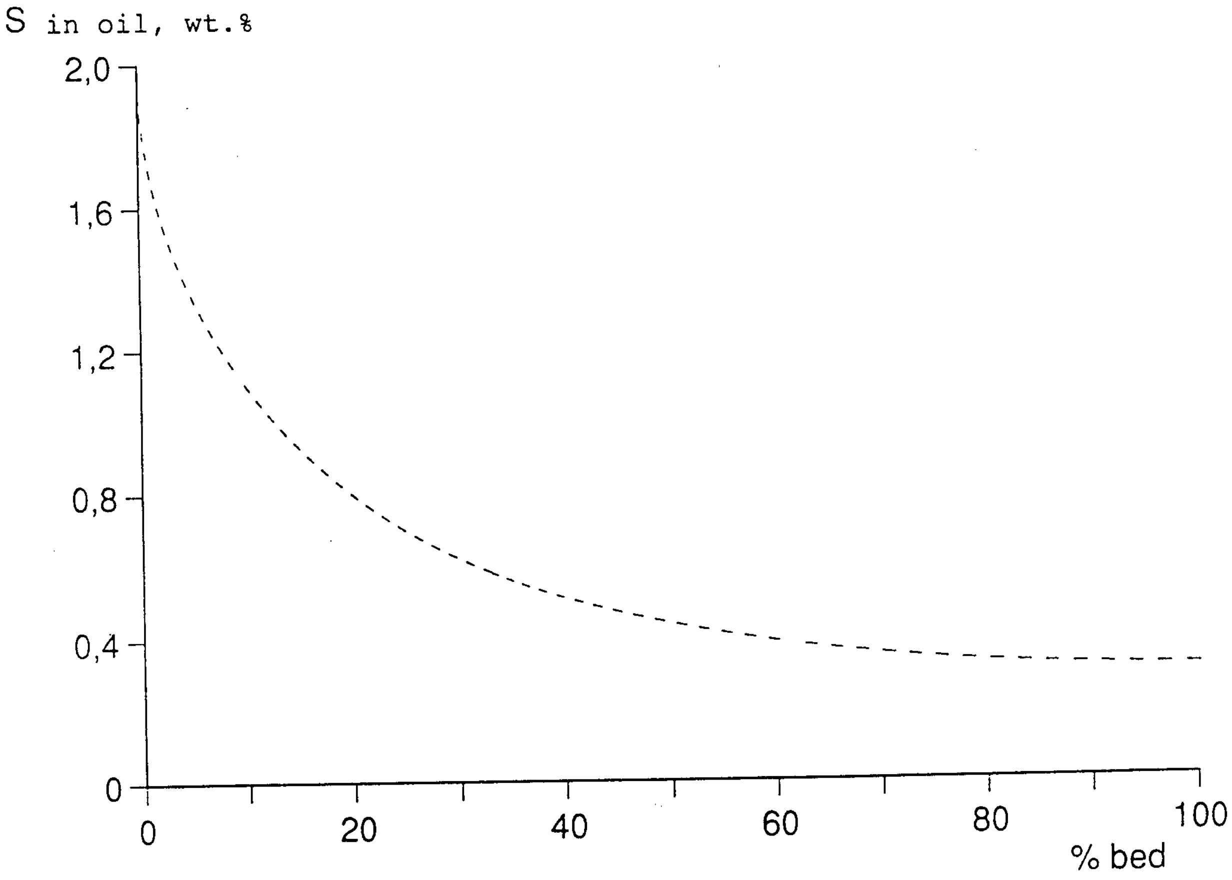
S in oil, wt.%
2,0
1,6
1,2
0,8
0,4
0
0
20
40
60
80
100
% bed

FIG. 5A

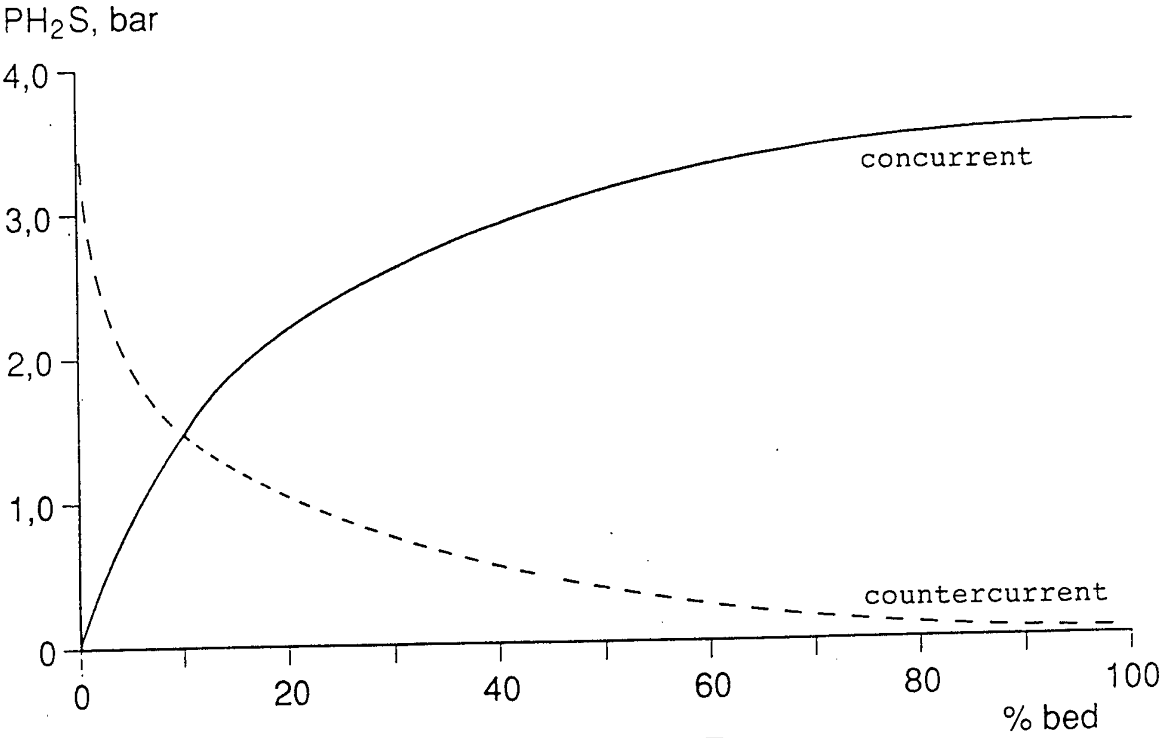
PH_2S, bar
4,0
3,0
2,0
1,0
0
0
20
40
60
80
100
% bed
concurrent
countercurrent

FIG. 5B

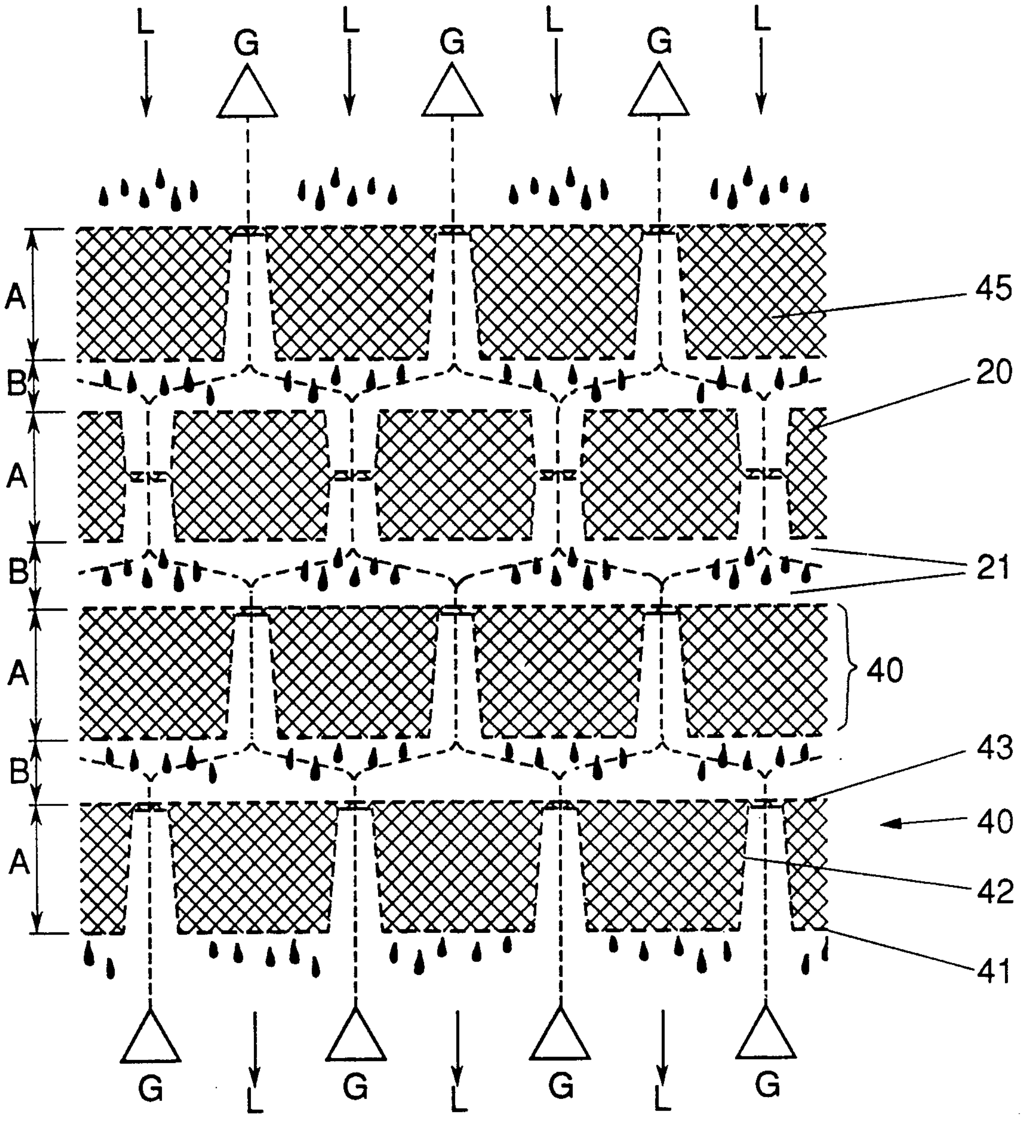

FIG. 6

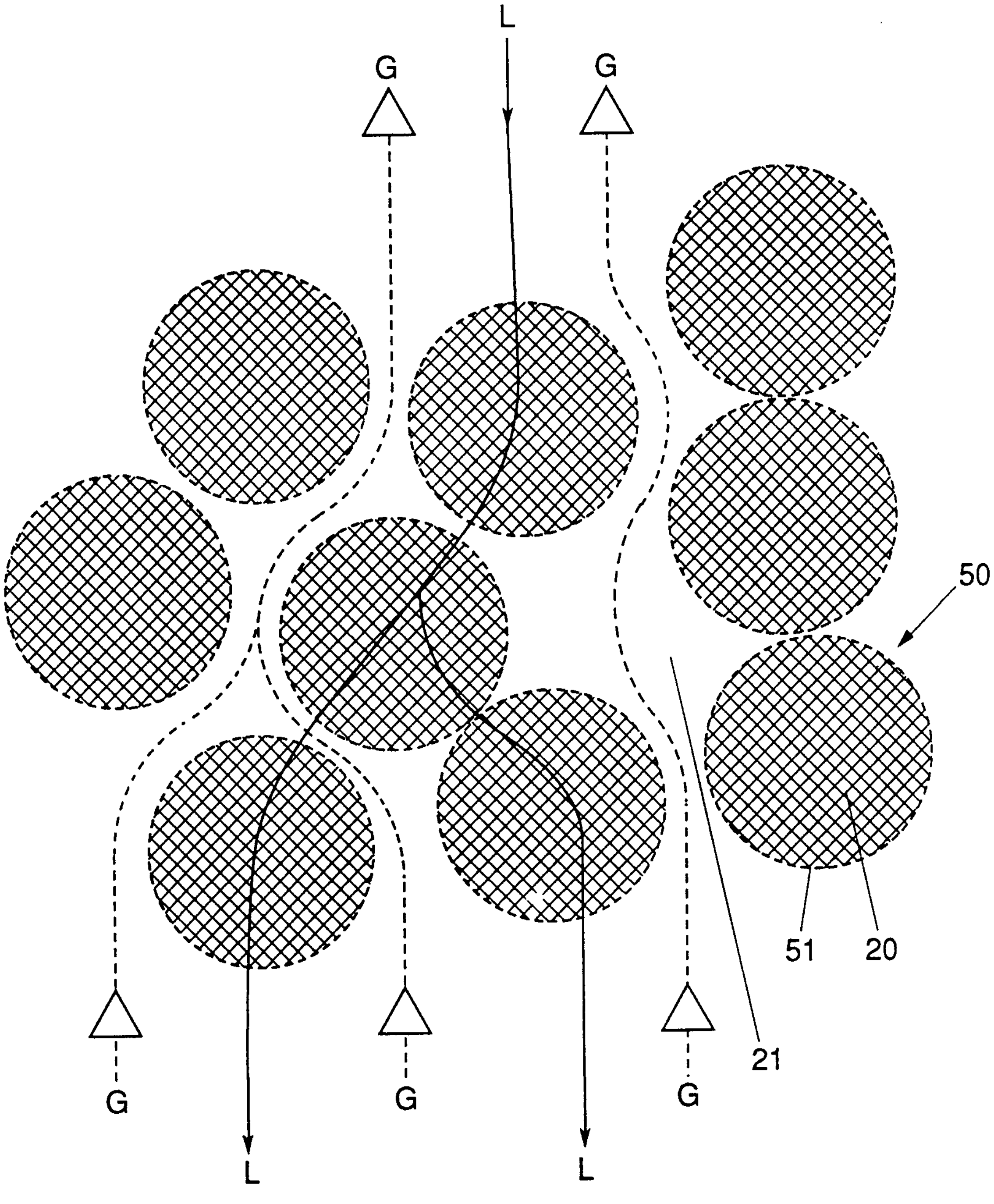

FIG. 7

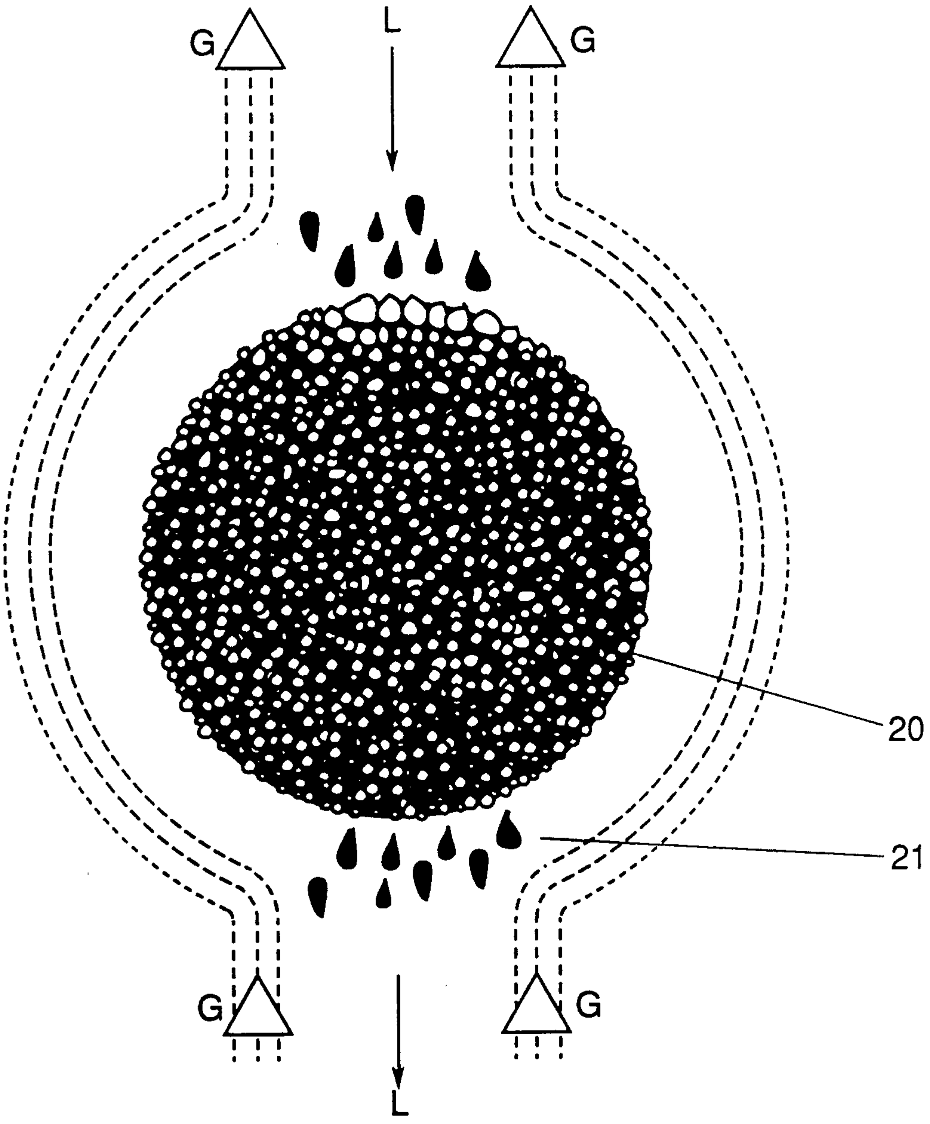

FIG. 8

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 95/00056

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J8/02 B01J8/00 B01J35/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J C10G 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 105 587 (CHEVRON RESEARCH COMPANY) 8 August 1978 cited in the application see column 1, paragraph 1 see column 1, paragraph 4 see column 2, paragraph 4 - column 3, paragraph 1 see column 4, paragraph 4 see column 5, paragraph 4 - column 6, paragraph 2 ---	1,2,6, 13-15, 17-19
A	US,A,3 846 337 (UNION OIL COMPANY OF CALIFORNIA) 5 November 1974 see column 2, line 48 - column 3, line 17 see column 3, line 63 - column 4, line 12 see column 4, line 62 - column 5, line 2 see column 8, line 36 - line 65 --- -/--	1,6,13, 15

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

☒ Patent family members are listed in annex.

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

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

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

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search 9 May 1995	Date of mailing of the international search report 24.05.95
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Stevnsborg, N

INTERNATIONAL SEARCH REPORT

Internat ' Application No
PCT/NL 95/00056

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 604 261 (MOBIL OIL CORPORATION) 5 August 1986 cited in the application see the whole document ---	1,7,8, 11-13, 16,19
A	EP,A,0 217 487 (MOBIL OIL CORPORATION) 8 April 1987 see the whole document ---	1,7-13, 16,19
A	US,A,2 877 099 (SOCONY MOBIL OIL COMPANY) 10 May 1959 see the whole document -----	1,7,8, 11-13, 16,19

1

INTERNATIONAL SEARCH REPORT

Internat· ' Application No
PCT/NL 95/00056

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4105587	08-08-78	NONE		
US-A-3846337	05-11-74	US-A-	3867279	18-02-75
US-A-4604261	05-08-86	NONE		
EP-A-0217487	08-04-87	US-A-	4597854	01-07-86
		AU-B-	591676	14-12-89
		AU-A-	5836886	22-01-87
		CA-A-	1254163	16-05-89
		JP-A-	62018492	27-01-87
US-A-2877099	10-03-59	NONE		