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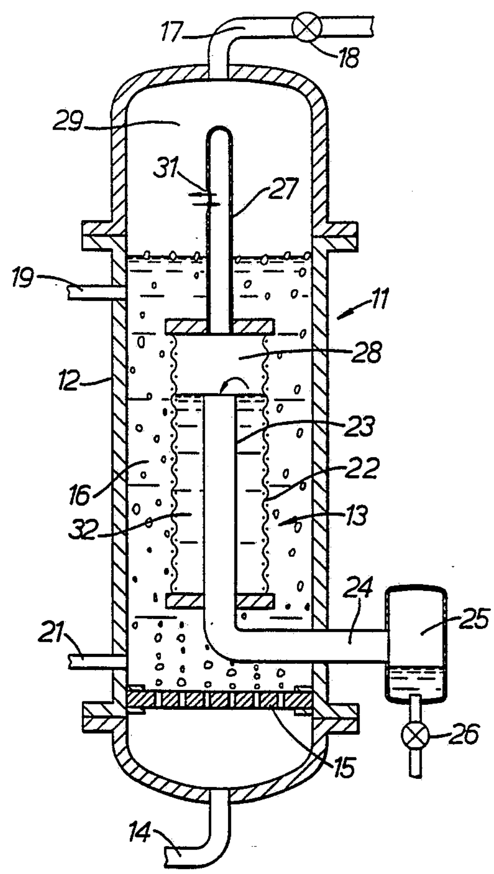
(54) Title: CATALYTIC MULTI-PHASE REACTOR

(57) Abstract

A reactor for conducting a continuous multi-phase catalytic reaction such as the conversion of syngas to higher hydrocarbon fuels. Gaseous reactants are introduced via a gas-permeable plate (15) into a slurry (16) which includes the product and a finely divided catalyst. The liquid product is separated from the remainder of the slurry by means of a filter unit (13) including a filter member (22). A pressure differential is established across the filter member (22) by means of a constant level device (23) within the filter unit which maintains a level of filtrate (32) within the filter unit (22) below the level of the slurry (16). The slurry (16) is maintained in a constant state of agitation by the introduction of the gaseous components as a steam of bubbles. Fluctuations in the pressure differential across the filter member (22) prevent the filter member from clogging and the gas spaces (28, 29) above the filtrate (32) and the slurry (16) are in communication.



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CATALYTIC MULTI-PHASE REACTOR

The present invention relates to a reactor for conducting a continuous multi-phase catalytic reaction and is particularly, though not exclusively, applicable to the catalytic conversion of syngas, produced by the reforming of methane, to hydrocarbon fuels, by a Fischer-Tropsh type of synthesis. Other reaction systems for which the apparatus would be suitable include various slurry reactions for the production of petrochemicals, the production of oxygenates from synthesis gas and dehydrogenation reactions.

Three-phase catalytic reaction systems are used in a number of chemical processes and their application in the petrochemical industry appears to be increasing. Of the three-phase systems in use, mechanically agitated, loop and bubble column slurry reactors contain small catalyst particles dispersed in the liquid. In most applications, the liquid will have to be separated from the slurry to remove liquid products or for catalyst regeneration purposes. In those cases where the liquid is an inert medium, occasionally, it may have to be replaced due to degradation or the build-up of impurities.

Mechanically agitated slurry reactors are particularly convenient for batch processes due to the low mass-transfer and heat resistance. These features also make them suitable for the determination of reaction kinetics in the laboratory. A serious disadvantage and limitation of this reactor type, however, is the difficulty in the separation of catalyst particles in any continuous operation.

Commercially, it is only mechanically agitated reactors that are used in the hydrogenation of double bonds in oils from cottonseed, soybean,corn, sunflower, etc. By employing a nickel catalyst, the products include margarine, shortening, soap and greases. The choice of reactor is based on the low diffusivities and high viscosities of the fatty oils. Fixed-bed operation has been proposed due to the advantage of completely catalyst-free products without filtration. A number of other hydrogenation reactions are also carried out in agitated reactors, e.g. the hydrogenation of nitro compounds.

The operation of bubble column slurry reactors is simple,since mechanically moving parts are avoided. Combined with the low diffusional resistance and efficient heat transfer, these reactors are attractive for many industrial processes. However, solid-liquid separation is usually performed outside the reactor in elaborate filtering and settling systems. The catalyst slurry is to be recycled to the reactor, sometimes with the use of a slurry pump. Thus, serious problems may been countered in the continuous operation of bubble column slurry reactors.

As world oil resources diminish it is becoming more attractive to use natural gas as an energy source and methods of upgrading this to higher hydrocarbon fuels are increasing in importance.

It is therefore an object of the invention to provide a reactor which allows continuous method of conducting a multi-phase catalytic reaction which does not suffer the drawbacks of the prior art.

It is a particular object of the invention to provide such a reactor which is well suited to use in H the conversion of natural gas via syngas to diesel fuel.

According to the invention, there is provided a solid/liquid slurry reaction apparatus which comprises: a reaction vessel arranged to receive the slurry; a filter member in contact with the slurry defining a filtrate zone which is separated from the slurry and having an outlet for filtrate product; means for establishing a mean pressure differential across the filter member; means for causing fluctuations or oscillations about the mean pressure differential; and means for introducing gaseous reactants or other components in the form of gas bubbles into the slurry.

Such a system is relatively simple yet effective. The separation step, generally considered to be particularly problematic, is achieved without undue complication and under proper operating conditions the filter member is self-cleaning.

Preferably, the pressure differential results from the hydrostatic pressure arising from the filter member being submerged in the slurry in the reactor. Preferably, communication between the space above the slurry in the slurry reactor and the space above the filtrate in the filtrate section prevents the build up of pressure differentials in excess of that corresponding to the hydrostatic pressure. The communication may be via a tube extending between the slurry section and the filtrate section and being open to each. The pressure fluctuations and oscillations may be caused by the turbulent motion of the slurry in the reactor. They may be transferred or enhanced, perhaps by resonance effects to the filtrate section, preferably via the tube.

Preferably, the amplitude or magnitude of the fluctuations or oscillations in the pressure differential across the filter member is about the same magnitude or greater than the mean value of the static pressure differential. Preferably the mean pressure differential across the filter member should be kept at a rather low level, typically less than 5 mBar (500Pa). The gas contact tube may, in addition to effecting the communication between the gas phase above the slurry and the internal parts of the filter member, also provide an easy escape route for gas which may have penetrated the filter membrane and which otherwise would have become entrapped in the filtrate section.

Gaseous products or components may be allowed to escape by any convenient means such as a separate outlet from the reaction vessel or simply via the tube. Experiments carried out suggest that if the gas contact tube is closed or severely choked, the filter member would rapidly become clogged. Of course, the contact tube will set a limit to the pressure drop across the filter member and thus prevent unwanted and damaging pressure build-ups, which otherwise would probably have occurred when there is a considerable pressure drop between internal parts of the reactor and the outlet side.

The reaction apparatus may include means for applying a pulsating pressure to the filtrate zone, either directly to the filtrate, or to the gas space above the filtrate. Preferably, the pulsating pressure is provided by the action of a reciprocating piston in a cylinder. This may be in place of or in addition to the above mentioned tube.

Preferably, the filter member is in the form of a filter unit defining internally the filtrate zone and which includes a filter element separating the filtrate zone and the slurry zone. Preferably, the filter element is generally cylindrical and its axis is generally vertical in use, though it may be inclined by as much as 10 or 30 to the vertical. It may be located within the reaction vessel or in a branch member of the reaction vessel in which at least a part of the slurry phase is allowed to circulate. Preferably, the filter element comprises a fined meshed screen, helically wound threads, fine vertical threads or sintered metal particles. The filter element material and catalyst are preferably selected so that the maximum hole or pore size in the filter element is of the same order of magnitude as the catalyst particle size. The particle size preferably being not less than half the pore size. However, it would be possible for the catalyst particle size to be larger than the maximum pore size with the pore size being of the same magnitude, or less. The means for introducing gaseous reactants or components may comprise any suitable means such as a bubble cap plate, a plurality of nozzles, a frit plate, etc, preferably located at the bottom of the reaction vessel. The reactants may be CO and H_2 for example from the reforming of natural gases, and the products may be methanol and higher hydrocarbons.

The pressure fluctuation value may be of the order of the pressure differential, for example from 10 to 200% of the pressure differential. The actual value of the pressure differential may be from 1 to 1000mBar, preferably 2 to 50mBar.

The pressure fluctuations may be provided by turbulent flow of the slurry in the reactor and/or by gas bubbles rising on the outside of the filter element, which may themselves give rise to turbulent flow conditions.

The vessel is preferably provided with an inlet and/or an outlet for liquid reactants or components. The filter unit member be wholly or partly filled with filtrate. Thus, the outlet from the filter unit may be connected to the tube from the filtrate section above the top of the filter unit. Alternatively, the outlet from the filtrate section may comprise a tube which is arranged to determine the level of the filtrate in the filtrate section. The filter unit may be vertically adjustable. Preferably the filtrate level is adjustable with respect to the reactor vessel.

Preferably, the reaction vessel is provided with means for heat transfer. This may comprise a plurality of vertically positioned tubes intended for circulation of a heat transfer medium.

The reactor vessel may, of course, include a plurality of filter units.

The invention is particularly well adapted for use in a method of converting natural gas (methane) to higher hydrocarbon fuels which involves initially burning reforming the methane to produce carbon monoxide and hydrogen, subjecting the CO and Hto catalytic conversion by a Fischer-Tropsch synthesis to form higher hydrocarbon fuels such as liquid paraffin waxes, and subsequently separating and/or cracking these products to produce the required range of hydrocarbons.

When diesel fuel is produced in this way it is vastly superior to conventional diesel in terms of its quality and properties. Firstly, it contains no sulphur, which is important from an environmental point of view. Secondly, it has a very high cetane number and can therefore be blended with lower grades of diesel fractions in order to produce a product which meets premium range standards. Thirdly, it contains virtually no harmful compounds that generate soot when burned and needs fewer additives for problem free use at low temperatures.

The invention may be carried into practice in various ways and some embodiments will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a schematic section through a three-phase slurry reactor for performing a method in accordance with the invention;

Figure 2 is a simplified schematic section through a part of a reactor showing an alternative system for achieving the fluctuations in pressure;

Figures 3, 4 and 5 are views similar to Figure 2 showing three ways of adjusting the pressure differential across the filter member; and

Figures 6 and 7 are two further alternative embodiments.

The reactor vessel 11 in Figure 1 comprises an outer casing 12 defining the reactor vessel 11 and within the casing 12 a filter unit 13. The housing 12 has a gas inlet 14 at the bottom which, in the case of a syngas conversion process, would constitute the reactant inlet. Above the gas inlet 14, there is a gas delivery device such as a gas-permeable frit plate 15 which supports the slurry 16 in the reactor vessel 11, and at the top of the casing 12, a gas outlet 17. The gas outlet 17 is controlled by a choke or valve 18. The casing also has an inlet 19 and an outlet 21 for the slurry.

The filter unit 13 comprises a generally vertical cylindrical filter element 22 in contact with the slurry 16. The filter element is in the form of a fine meshed screen though it could alternatively comprise helically wound metal threads, sintered metal particles or narrowly separated fine vertical threads. It houses a constant level device in the form of a vertical pipe 23 which terminates below the top of the filter unit 13. The pipe 23 leads to a filtrate outlet 24 which in turn leads to a collector 25 and to an outlet valve 26. A tube 27 extends from the space 28 within the filter unit 13 above the top of the pipe 23 to the space 29 within the top of the reactor 11 above the filtrate 16. An opening 31 in the tube 27 connects the two spaces 28,29.

In operation, gaseous reactants are introduced to the reactor vessel 11 via the inlet 14 and the plate 15. The reactants form bubbles in the slurry 16 which pass upwards past the filter unit 13. The slurry 16 consists of a liquid phase of the reaction products and a catalyst in finely divided form. The gaseous reactants react as they contact the catalyst, thus adding to the products in the slurry.

At the same time, the products pass through the filter element 22 to form a product filtrate 32 which is free of catalyst. Any gaseous products and unreacted reactants can be vented through the outlet 17 and subsequently treated and/or recycled. The product filtrate 32 leaves the filter unit 13 via the constant level device 23 and outlet 24 and is collected in the collector 25 for regulated continuous or periodic removal.

The difference in level between the slurry 16 and the product filtrate 32, determined by the constant level device, results in a pressure differential across the filter element 22. This helps to convey the liquid product through the filter element 22.

It might be expected that, under these conditions, the catalyst would clog the filter element, however, this is found not to be the case, provided that the pressure differential is not too great. The introduction of the reactants together with the connection of the gas spaces 28, 29, and the generally turbulent conditions in the reactor vessel 11 combine to cause fluctuations in the pressure differential across the filter element 22. These in turn cause fluctuations in the liquid flow through the filter element 22 resulting in an anti-clogging effect. This may be enhanced by the movement of the gas bubbles past the surface of the filter element 22.

An alternative embodiment is shown in Figure 2. In this case the filter unit 41 has no tube 27 connecting the space 28 to the space 29 in the reactor (not shown). Instead, a cylinder and piston assembly 42 is connected to the space 28. By reciprocating the piston, a pulsating pressure is produced resulting in the desired fluctuation in the pressure differential across the filter element 22. This arrangement can of course be used in conjunction with the embodiment shown in Figure 1. Communication between the spaces above the slurry and the filtrate may be provided by a tube (not shown) having a restriction or choke limiting the transmission of pressure pulses to the space above the slurry, which would otherwise have tended to eliminate the net effect of the reciprocating piston. The tube would nevertheless control the static pressure differential.

The constant level device 23 can be made adjustable in order to provide a degree of control over the pressure differential across the filter element 22. Three ways in which this can be achieved are shown in Figures 3, 4 and 5.

In the filter unit 51 of Figure 3, both the vertical pipe 52 and the tube 53 are slidably mounted with respect to the filter unit 51. In the filter unit 61 of Figure 4, the vertical pipe 62 is slidably mounted but the tube 63 is fixed relative to the filter unit 61. In the filter unit of Figure 5, the tube 73 is fixed, and the vertical pipe 72 is slidably mounted within a fixed sleeve 74. Thus, the level of the filtrate 32 remains fixed relative to the filter unit 71 as it is raised or lowered.

The variants shown in Figures 3 to 5 can be combined with either of the embodiments shown in Figures 1 and 2.

In the reactor 81 shown in Figure 6, the outlet 84 from the filter unit 83 has an upward loop 85 to ensure that the filter unit 83 is filled with liquid. In the reactor 91 shown in Figure 7, there is a tube 97 connecting the gas space in the reactor to the filtrate. The outlet 94 extends to the bottom of the filter unit 93 and there is an optional connection 96 between the outlet 94 and the space in the reactor. This connection 96 would tend to prevent any siphon effect and allow any gas remaining in the filtrate to escape. Again, the filter unit 93 will be filled with filtrate.

In all the illustrate embodiments, the geometries of the reactor, the communication means (eg. the tube 27) and the filtrate section may be varied in size and in order to optimise the pressure fluctuations by exploiting resonance-like effects.

The invention will now be further illustrated in the following Examples which were conducted on a laboratory scale.

EXAMPLE I

A stainless steel tube, with a diameter of 4.8cm and a height of approximately 2 meters was filled with a hydrocarbon liquid and a fine powdered catalyst. The tube was operated as a slurry bubble column by bubbling gas through the slurry.

A filter unit was placed in the upper part of the reactor. The filter unit was made of Sika stainless steel sintered metal cylinder Type R20 produced by the company Pressmetall Krebsöge Gmbh. The filter unit had an outer diameter of 2.5cm, a height of 25cm, and an average pore size of 20 µm.

In this particular experiment, the reactor was filled with a slurry consisting of a poly α-olefin liquid and approximately 10 weight % of a fine powdered cobalt on alumina catalyst. The particle size ranged from 30 to 150 µm. The catalyst was kept suspended by gas bubbling through the liquid. The gas was a mixture of H_2 CO and N_2 of varying composition, and was fed with a superficial gas velocity of 4cm/s. The temperature in the reactor was 230°C and the pressure was 30 bar ($3x10^6$ Pa).

The filtrate level inside the slurry was set approximately half way up in the valve.

The liquid formed by the Fischer-Tropsch reaction in the reactor was withdrawn through the filter unit. In addition, a poly α-olefin liquid fed to the reactor was also withdrawn through the filter unit. The liquid withdrawal varied from 320 to 2.5 g/h depending on the formation rate of the liquid product, and the feeding rate of the hydrocarbon liquid. The experiment lasted approximately 400 hours, and a total amount of liquid of 30 litres was withdrawn through the filter unit. The liquid level in the reactor was constant during the experiment, and no colour indicating presence of solid particles could be observed in the liquid.

EXAMPLE II

A glass tube, with a diameter of 22cm and a height of 2.5 meters was filled with hydrocarbon liquid (Monsanto heat transfer fluid, MCS 2313) and a fine alumina powder (average particle diameter approximately 75µm). The content of alumina was approximately 15% by weight. The tube was operated as a slurry bubble column (SBC) by bubbling gas through the slurry.

A filter member without a connection tube between the gas volume above the slurry phase and the gas volume above the product phase was placed in the upper part of the SBC. The filter member was made of a sika fil 10 stainless steel sintered metal cylinder produced by Sintermetallwerk Krebsöge GmbH. The sinter cylinder had an outer diameter of 2.5cm, a height of 20cm, and an average pore size of 10µm.

In this particular experiment the slurry level was set to be at the top of the sinter cylinder. The pressure amplitude in the SBC was measured to be 6mBar, the pressure drop across the sinter metal wall was approximately 3-4 mBar (300-400Pa). The temperature in the slurry was 20 ^{o}C, the pressure was 1 Bar (10^{5} Pa) and the gas velocity was approximately 6cm/s.

At the start of the experiment, the flow of the filtrate through the sinter metal cylinder was about 1000ml per minute. After 4 hours the flow was reduced to zero due to clogging of the sinter metal wall on the slurry side.

When a similar experiment was carried out in an apparatus in which communication between the gas volumes was provided by a piece of pipe acting as a connection tube, the initial flow rate was maintained essentially at the same level throughout the experiment.

CLAIMS

1. Solid/liquid slurry reaction apparatus which comprises a reaction vessel (11) arranged to receive the slurry (16) in a slurry zone; and means for introducing gaseous components in the form of gas bubbles into the slurry, characterised by: a filter member (13) in contact with the slurry (16) defining a filtrate zone which is separated from the slurry zone and having an outlet (23) for filtrate product (32); means for establishing a mean pressure differential across the filter member; and means for causing fluctuations or oscillations about the mean pressure differential.

2. Reaction apparatus as claimed in Claim 1, characterised in that the pressure differential results from the hydrostatic pressure arising from the filter member (13) being submerged in the slurry (16) in the reactor.

3. Reaction apparatus as claimed in Claim 1 or Claim 2, characterised in that the pressure fluctuations or oscillations are caused by the turbulent motion of the slurry (16) in the slurry zone.

4. Reaction apparatus as claimed in any preceding Claim, characterised in that a gas space (29) above the slurry zone is in communication with the filtrate (32) in the filtrate zone or with any gas space (28) above the filtrate zone (32).

5. Reaction apparatus as claimed in Claim 4,

characterised in that the communication is provided by a tube (27) extending between the slurry zone and the filtrate zone and being open to each.

6. Reaction apparatus as claimed in any preceding Claim, characterised in that the amplitude of the fluctuations or oscillations in the pressure differential across the filter member (13) is about the same magnitude or greater than the mean value.

7. Reaction apparatus as claimed in any preceding Claim, characterised by further including a separate outlet (17) for gaseous products or components from the reaction vessel (11).

8. Reaction apparatus as claimed in any preceding Claim, characterised in that means (42) for applying a pulsating pressure to the filtrate zone is provided.

9. Reaction apparatus as claimed in Claim 8, characterised in that the pulsating pressure is provided by the action of a reciprocating piston in a cylinder (42).

10. Reaction apparatus as claimed in any preceding Claim, characterised in that the filter member (13) is generally cylindrical and its axis is generally vertical in use.

11. Reaction apparatus as claimed in any preceding Claim, characterised in that the filter member (13) is located within the reaction vessel (11).

12. Reaction apparatus as claimed in any of Claims 1 to 7, characterised in that the filter member (13) is arranged in a branch member of the reaction vessel (11) in which at least a part of the slurry phase is allowed to circulate.

13. Reaction apparatus as claimed in any preceding Claim, characterised in that the filter member (13) is in the form of a filter unit defining internally the filtrate zone and which includes a filter element (32) separating the filtrate zone and the slurry zone.

14. Reaction apparatus as claimed in any preceding Claim, characterised in that the filter element (22) comprises a fine meshed screen, helically wound threads, fine vertical threads or sintered metal particles.

15. Reaction apparatus as claimed in any preceding Claim, characterised in that the means for introducing gaseous reactants or components comprises a frit plate (15) at the bottom of the reaction vessel (11).

16. Reaction apparatus as claimed in any preceding Claim, characterised in that the reaction vessel (11) is provided with an inlet (19) and/or an outlet (21) for liquid reactants or components which might optionally contain dispersed particulate matter such as finely divided catalyst.

17. Reaction apparatus as claimed in any preceding Claim, characterised in that the filter member (13) is arranged to be wholly or partly filled with the

filtrate product.

18. Reaction apparatus as claimed in Claim 17, characterised in that the outlet from the filtrate zone comprises a tube (23) which is arranged to determine the level of the filtrate in the filtrate (32) zone.

19. Reaction apparatus as claimed in any preceding Claim, characterised in that the filtrate level is adjustable with respect to the reactor vessel (11).

20. Reaction apparatus as claimed in any preceding Claim, characterised in that the filter member (13) is arranged to be vertically adjustable.

21. Reaction apparatus as claimed in any preceding Claim, characterised in that the reaction vessel (11) is provided with means for heat transfer.

22. Reaction apparatus as claimed in Claim 22, characterised in that the means for heat transfer is provided by a plurality of vertically positioned tubes intended for circulation of a heat transfer medium.

23. Reaction apparatus as claimed in any preceding Claim, characterised by a plurality of filter members within the reaction vessel.

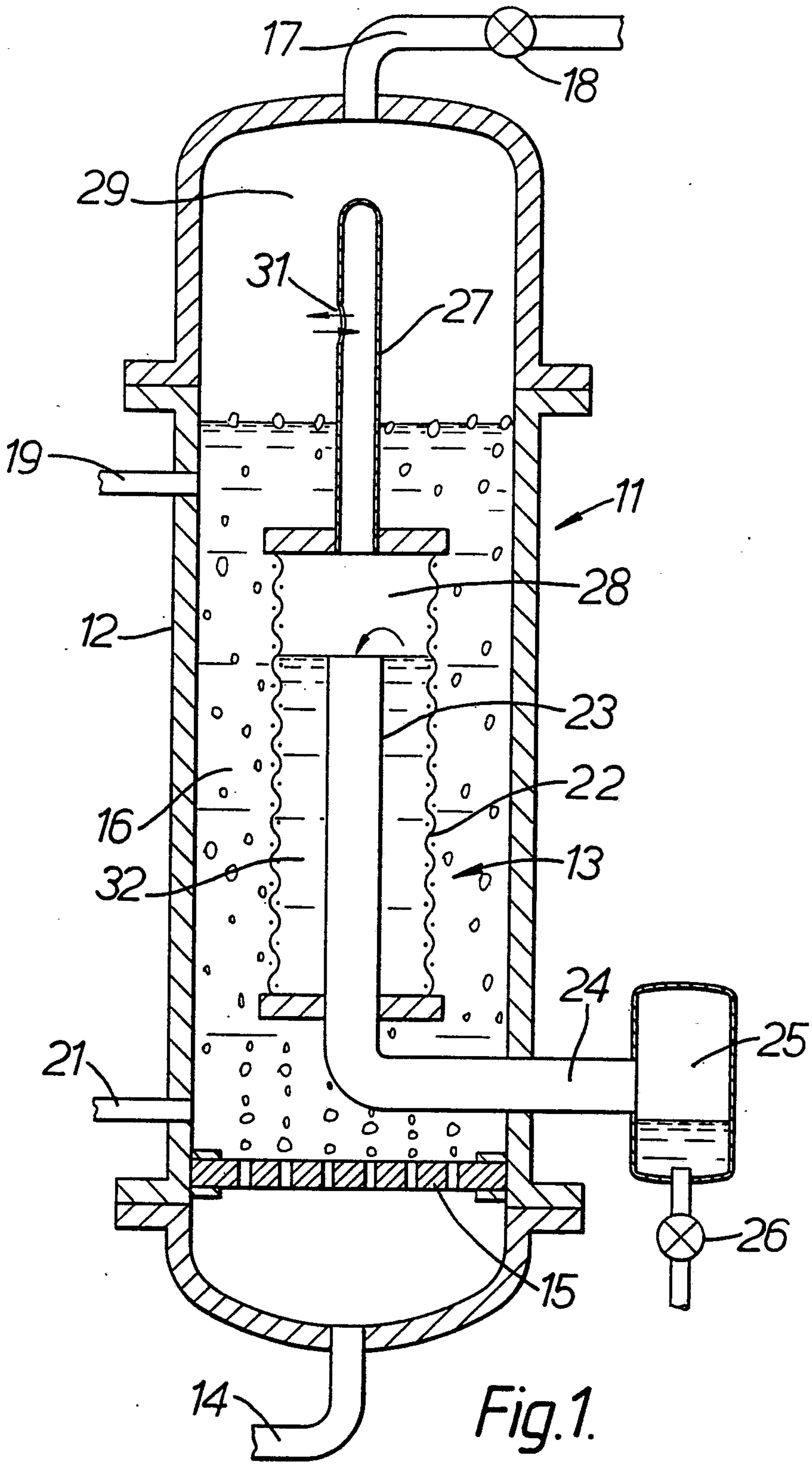

Fig.1.

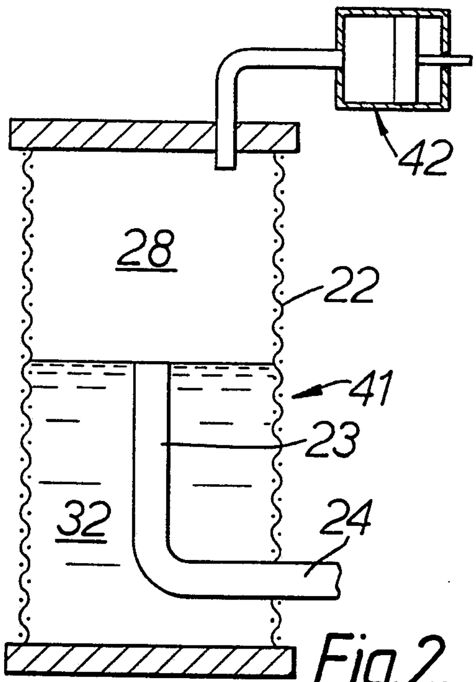

Fig.2.

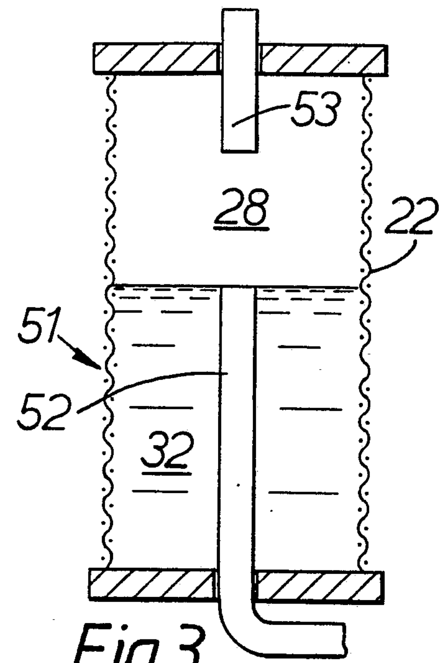

Fig.3.

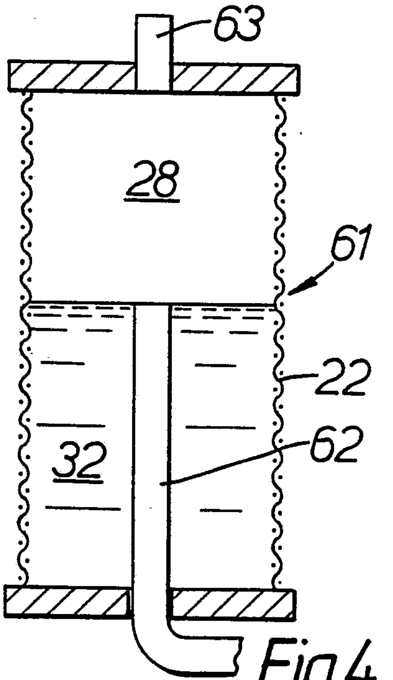

Fig.4.

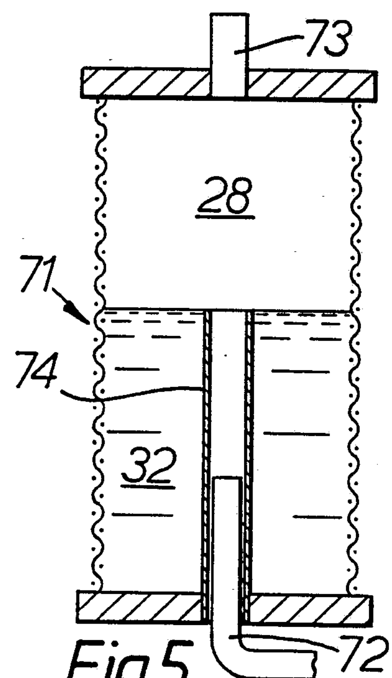

Fig.5.

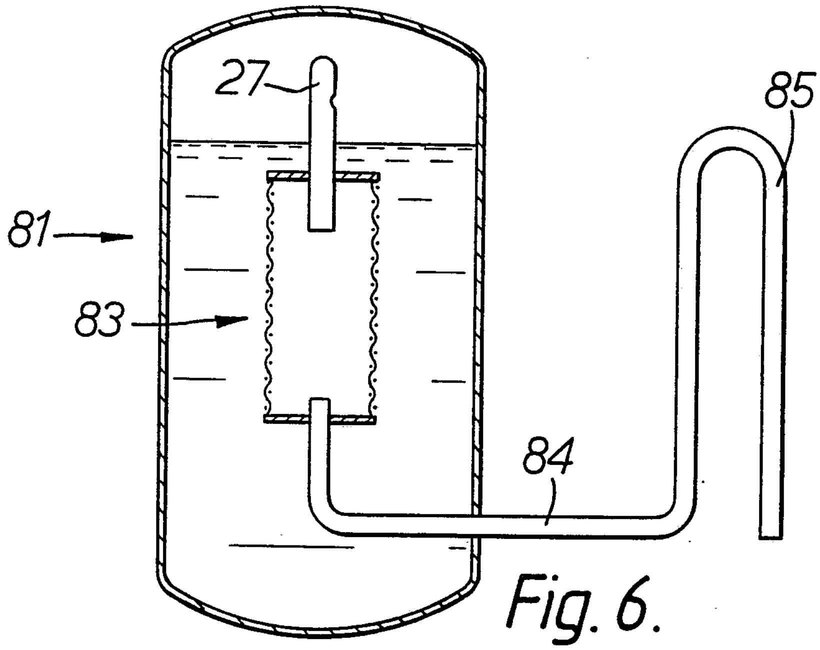

Fig. 6.

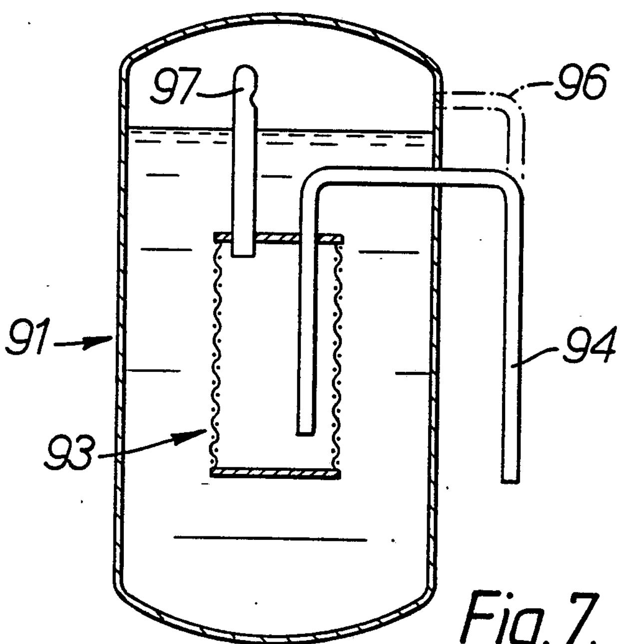

Fig. 7.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 93/00030

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: B01J 8/22, C07C 1/04, C10G 2/00
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)

IPC5: B01J, C07C, C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, 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	EP, A1, 0450859 (EXXON RESEARCH AND ENGINEERING COMPANY), 9 October 1991 (09.10.91) --	1
A	EP, A2, 0450860 (EXXON RESEARCH AND ENGINEERING COMPANY), 9 October 1991 (09.10.91) --	1
A	EP, A2, 0450861 (EXXON RESEARCH AND ENGINEERING COMPANY), 9 October 1991 (09.10.91) -- --------	1

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
24 May 1993	01 -06- 1993.
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Jack Hedlund Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

31/03/93

International application No.
PCT/NO 93/00030

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0450859	09/10/91	AU-B- 632412	24/12/92
		AU-A- 7401491	10/10/91
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