(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 131 912**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **84108167.2**

(22) Date of filing: **12.07.84**

(51) Int. Cl.⁴: **C 10 G 49/10**
C 10 G 47/24

(30) Priority: **16.07.83 JP 129789/83**

(43) Date of publication of application:
23.01.85 Bulletin 85/4

(84) Designated Contracting States:
BE DE FR GB IT NL

(71) Applicant: **RESEARCH ASSOCIATION FOR PETROLEUM ALTERNATIVES DEVELOPMENT**
4-2, 1-chome Uchikanda
Chiyoda-ku Tokyo(JP)

(72) Inventor: **Okimoto, Kazuaki**
No. 1720, Kamiizumi Sodegaura-machi
Kimitsu-gun Chiba-ken(JP)

(72) Inventor: **Muto, Hideru**
No. 216, Imazuasayama
Ichihara-shi Chiba-ken(JP)

(74) Representative: **Türk, Dietmar, Dr. rer. nat. et al,**
Redies, Redies, Türk & Gille Patentanwälte
Brucknerstrasse 20
D-4000 Düsseldorf 13(DE)

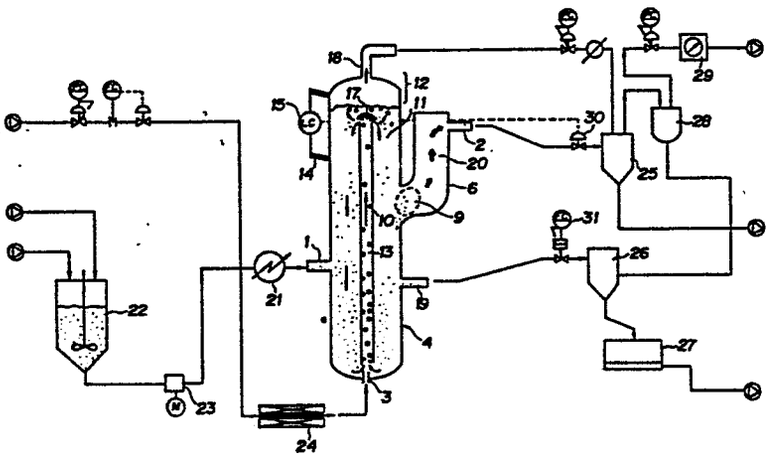
(54) A method for the hydrogenation treatment of heavy oils.

(57) The invention provides an efficient process for the catalytic hydrogenation reforming of a heavy oil, in which the slurry of a feed heavy oil and catalyst particles is introduced into a reaction vessel (4) and ascends in the vessel as being carried by the hydrogen-containing gas introduced into the vessel at the bottom gas inlet port (3). When the slurry reached the upper part of the vessel, the slurry is freed from the gaseous material and then descends in the vessel through a gravity-difference separation zone (9) formed in contact with the inner walls of the vessel, in which the descending velocity of the slurry is so low that the catalyst particles gravitationally settle in the slurry and are separated from the liquid portion and the liquid portion thus freed from the catalyst particles is discharged through the liquid discharge port (2) provided at the side wall of the vessel at such a space velocity as not to disturb free settling of the catalyst particles in the separation zone. The slurry containing the thus increased amount of the catalyst particles descends to the bottom of the vessel and is again carried up by the gas through the upflow zone formed in the central portion of the vessel.

EP 0 131 912 A1

./...

FIG. 1



0131912

A METHOD FOR THE HYDROGENATION TREATMENT OF HEAVY OILS

BACKGROUND OF THE INVENTION

The present invention relates to a novel method for the treatment of a heavy oil, hydrogen-containing gas and catalyst particles for the hydrogenation treatment. More particularly, the invention relates to an efficient method for the hydrogenation treatment of a heavy oil by contacting with catalyst particles and a hydrogen-containing gas.

As is well known, one of the processes widely used for the cracking treatment of heavy oils is the suspended bed process by virtue of the advantageous feature of the process that the solid-liquid or solid-gas contacting in the suspended bed process in general can be performed by use of extremely fine particles as one of the contacting materials. Conventional suspended bed processes, however, have a problem that the fine solid particles are carried by the liquid under treatment or by the exhaust gas to escape out of the system and the effluent particles are deposited and accumulated in the subsequent pipings and valves as well as even in the pumps to cause interruption of the process operation and eventual breakdown of the apparatuses. Another problem in the conventional suspended bed processes is the difficulty in the control of the residence time of the solid particles, e.g. catalyst, in the system which is the reason for the difficulty in improving the efficiency of the process operation. A measure usually undertaken in this connection is the periodical or continuous discharge of a part of the slurried

suspension of the solid particles followed by the separation and recycling or removal and discard of the solid particles of, for example, catalyst out of the system by use of a cyclone, wire nets and the like. The necessity of conducting such a procedure out of the system is of course industrially disadvantageous due to the energy consumption for maintaining the temperature of the process or the large investment for the auxiliary apparatuses therefor. While it is necessary to return the thickened slurry containing the solid particles to the contacting vessel such as the reactor when separation of the solid particles has been undertaken in a cyclone and the like equipment for separation installed out of the system, thickened slurries sometimes cause plugging of the pipings to make a serious trouble in operation. In this connection, a proposal has been made in, for example, Japanese Patent Publication No. 1700/1975 to provide a device for the separation of the catalyst particles inside the contacting apparatus per se but no quite satisfactory results can be obtained with such an apparatus when the solid particles are very fine.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a novel and improved method for the contacting treatment of a heavy oil with a hydrogen-containing gas and catalyst particles in a suspended bed process in which the contacting efficiency of the heavy oil, hydrogen-containing gas and catalyst particles is remarkably improved and, simultaneously, the catalyst particles are prevented from

being carried out of the system by the oily material and gas discharged out of the system by use of a specific apparatus and by conducting the process under specific operational conditions.

Thus, the method of the present invention for the hydrogenation treatment of a heavy oil comprises, in the catalytic hydrogenation treatment of a heavy oil by contacting with a hydrogen-containing gas and catalyst particles in a fluidized state, supplying the feed heavy oil and the particles of a hydrogenation catalyst into a reaction vessel having a separation zone by the difference in the specific gravities and kept at a temperature in the range from 250 to 600 °C and under a pressure in the range from atmospheric pressure to 350 kg/cm^2; introducing a hydrogen-containing gas into the reaction vessel at the bottom thereof in such a rate that 100 to 2000 Nm^3 of hydrogen is supplied to the reaction vessel per kl (kiloliter) of the heavy oil to cause contacting of the heavy oil, catalyst particles and hydrogen in a fluidized state by the upward flow of the hydrogen-containing gas; separating the gaseous material inside the reaction vessel; then separating a part of the oily material from the suspension of the catalyst particles in the heavy oil within the separation zone by the difference of specific gravities inside the reaction vessel in the substantial absence of the gaseous material; and taking the hydrogenated oily material out of the reaction vessel at a liquid-hourly space velocity in the range from 0.2 to 10 $hour^{-1}$.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is a flow diagram to practice the method of the invention including a reaction vessel illustrated by a schematic cross section.

FIGURES 2 to 10 are each a schematic illustration of the reaction vessel used in the method of the invention.

FIGURES 11 and 12 are each a graphic showing of the experimental results obtained in Examples 3 and 4 and in Example 5, respectively.

DETAILED DESCRIPTION OF THE INVENTION

In the following, the above described method of the present invention is described in detail with reference to the accompanying drawing, of which FIGURE 1 is a flow diagram of the process according to the invention including a reaction vessel of a typical type.

In the first place, the heavy oil and the catalyst are respectively introduced into the slurry tank 22 in which a slurry is prepared by suspending the catalyst particles in the heavy oil. It is preferable in order to prevent settling of the catalyst particles in the slurry that the slurry in the slurry tank 22 is agitated by use of a screw-type stirrer or the slurry is circulated by use of a slurry pump through a circuit (not shown in the figure). The nature of the heavy oil to which the inventive method is applied is not particularly limitative provided that the heavy oil is in a liquid state and flowable at the reaction temperature. The catalyst is also not limitative in respect of the particle size distribution and fine particles having

a particle diameter of 10 to 300 μm can be used. The content of the catalyst particles in the slurry may range from a low concentration of 1% by weight to a very high concentration of 50% by weight. Even the finest particle size distribution of the catalyst and the highest concentration of the catalyst in the slurry as mentioned above can satisfactorily be used in the inventive method because of the easiness in the separation of the catalyst particles from the oily material. The slurry of the catalyst prepared in the slurry tank 22 is sent to the slurry preheater 21 by means of the slurry pump 23 and the preheated slurry is introduced into the reaction vessel 4 through the inlet port 1 for the slurry or heavy oil.

The inlet port 1 for the slurry or heavy oil may be provided at any portion of the reaction vessel 4 but it should preferably be on the side wall of the reaction vessel 4 as is shown in FIGURE 1 in most cases.

Along with the introduction of the slurry as described above, a hydrogen-containing gas is introduced into the reaction vessel 4 through a gas inlet port 3 provided on the lower portion or, preferably, at the bottom of the reaction vessel 4. The gas inlet port 3 should preferably be provided in such a disposition that the gas is introduced into the reaction vessel 4 in an upward flow. It is also preferable that the gas is preheated at a certain temperature in a preheater 24 prior to the introduction into the reaction vessel 4 through the gas inlet port 3.

At the start of the introduction of the slurry and

the hydrogen-containing gas into the reaction vessel 4 as is described above, it should be noted that the liquid discharge port 2 is kept closed in the initial stage of the introduction of the slurry and opened only after the surface level of the slurry in the reaction vessel 4 has reached a certain height. The surface level of the slurry in this case should leave a sufficient unoccupied space in the upper part of the reaction vessel 4 in order to avoid possible carrying of the catalyst particles or the liquid material by the separated gas taking place when the surface level of the slurry in the reaction vessel 4 is heaved too high. Control of the level of the slurry can be performed by means of a level controller 15 through the side duct 14 on the reaction vessel 4.

The slurry introduced into the reaction vessel 4 at the inlet port 1 is brought into contact with the hydrogen-containing gas coming from the gas inlet port 3 and they ascend in the reaction vessel 4 while keeping contact with each other. The reaction vessel 4 is provided with an upflow zone 13 so that the slurry is sucked into this upflow zone 13 at the bottom thereof and ascends therethrough by being carried by the hydrogen-containing gas.

Such an upflow zone 13 can be formed in a variety of ways and the simplest way therefor is a mere blowing of the hydrogen-containing gas upwardly from the gas inlet port 3 at the bottom of the reaction vessel 4 although a more reliable formation of the upflow zone 13 can be achieved by installing an upright tubular body 10 inside the reaction vessel 4 as is shown in FIGURE 1.

As is mentioned before, the reaction vessel 4 in the inventive method is provided with a separation zone by the difference of specific gravities and such a separation zone 9 is formed at the shoulder joint of a side arm 6 of the reaction vessel 4 communicating therewith as is shown in FIGURE 1.

In the reaction vessel 4 illustrated in FIGURE 1, the slurry introduced into the reaction vessel 4 at the slurry inlet port 1 is sucked into the upright tubular body 10 forming the upflow zone 13 through the gap between the bottom of the reaction vessel 4 and the lower end of the upright tubular body 10 and ascends therethrough by being carried by the upward flow of the gas. The upright tubular body 10 has a circular or rectangular cross section and the length thereof is of course smaller than the height of the reaction vessel 4. It is optional that a plural number of such tubular bodies are installed inside a reaction vessel 4. The diameter of the upright tubular body 10 or bodies is limited only by the requirement that a downflow zone 11 for the slurry should be kept between the tubular body 10 and the side walls of the reaction vessel 4. The vertical disposition of the upright tubular body 10 should provide a gap of a suitable width between each of the upper and lower ends thereof and the top wall or the bottom of the reaction vessel 4, respectively. In particular, the upper end of the tubular body 10 should be sufficient apart from the top wall of the reaction vessel 4 to form a sufficiently wide gas separation zone 12 in the upper part of the vessel 4 in order to prevent

the overflowing slurry at the upper end of the tubular body 10 from entering the gas exhaust port 18. The gap width between the lower end of the tubular body 10 and the bottom of the reaction vessel 4 should be determined to ensure highest efficiency for the entrainment of the slurry coming down in the downflow zone 11 to the bottom into the tubular body 10 by the upward flow of the gas.

The tubular body 10 should have its lower end opening just above the gas inlet port 3 and be installed in an upright disposition in order to facilitate the efficient upward flow of the gas introduced into the reaction vessel 4 at the gas inlet port 3. When the process of the inventive method is performed in a reaction vessel 4 provided with the tubular body 10 at the preferred disposition, the catalyst particles in the slurry ascends inside the tubular body 10 together with the upward flow of the hydrogen-containing gas and overflows at the upper end of the tubular body 10 into the gas separation zone 12. The velocity of ascending and overflowing of the slurry containing the catalyst particles can readily be controlled within a desirable range because the velocity of ascending and overflowing the slurry depends on the flow velocity of the hydrogen-containing gas.

When a plurality of the upright tubular bodies 10 are installed inside a reaction vessel 4 as is mentioned above, a preferable design of the reaction vessel 4 is that a plurality of the gas inlet ports 3 are provided in the same number as that of the tubular bodies 10.

The slurry overflowing at the upper end of the

tubular body 10 forming the upflow zone 13 is brought into the open space of the gas separation zone 12 where separation takes place between the slurry and the gaseous material carrying the slurry and the thus separated gaseous material is discharged out of the reaction vessel 4 through the gas exhaust port 18.

The installation of a baffle plate 17 illustrated in FIGURE 1 is effective in preventing the liquid and the catalyst particles from being carried by the exhaust gas into the gas exhaust port 18 as a result of the deflection of the overflowing slurry from upward to horizontal direction by impinging at the baffle plate 17. The exhaust gas discharged through the gas exhaust port 18 can be recycled and reused, if desired, either as such or after purification in a refiner (not shown in the figure).

On the other hand, the slurry, i.e. the mixture of the heavy oil and the catalyst particles, freed from the gaseous material in the gas separation zone 12 descends in the reaction vessel 4 along the direction of the gravity. In the reaction vessel 4 illustrated in FIGURE 1, the descending slurry flows down through the downflow zone 11 formed between the upright tubular body 10 and the side walls of the reaction vessel 4. The reaction vessel 4 shown in FIGURE 1 is provided with a side arm 6 communicating therewith at a certain height of the side wall and the shoulder joint portion of the side arm 6 forms a gravity-difference separation zone 9. The shoulder joint of the side arm 6 is at a position lower than either one of the upper end of the tubular body 10

and the liquid discharge port 2 so that the slurry overflowing at the upper end of the tubular body 10 does not directly reach the liquid discharge port 2 but first descends as a downflow.

The downflow of the slurry on its descending way reaches the gravity-difference separation zone 9 formed at or in the vicinity of the shoulder joint of the side arm 6 where separation of the slurry takes place into a liquid flow substantially freed from catalyst particles and a flow of a thickened slurry, i.e. a slurry containing an increased amount of the catalyst particles. The former flow freed from catalyst particles reaches the liquid zone 20 through the shoulder joint of the side arm 6 and is discharged out of the reaction vessel 4 through the liquid discharge port 2. The downflow of the thickened slurry is continued as such to reach the bottom of the reaction vessel 4. In the course of the transit of the descending slurry through the shoulder joint of the side arm 6, few solid particles enter the liquid zone 20 through the gravity-difference separation zone 9 at the shoulder joint leaving the downflow of the slurry because the velocity of the slurry in the downward direction is much larger than that in the horizontal direction. Therefore, no or very few catalyst particles are discharged out of the reaction vessel 4 as being carried by the liquid discharged from the liquid discharge port 2 when the discharge of the liquid is performed by controlling the upward linear velocity of the liquid in the liquid zone 20 not to exceed the free-settling velocity of the

catalyst particles in the liquid so that the liquid discharged out of the reaction vessel 4 and collected in the liquid receiver tank 25 is substantially free from the catalyst particles. The rate of discharging of the liquid is not particularly limitative but desirably within the above mentioned limitation in order to minimize the amount of the catalyst particles carried by the liquid. The rate of the liquid discharge can readily be controlled by adjusting the opening of the valve at the liquid discharge port 2 and controlling the feed rate of the slurry from the slurry inlet port 1 or the discharge rate of the slurry out of the slurry discharge port 19.

On the other hand, the downward flow of the thickened slurry descending in the reaction vessel 4 through the downflow zone 11 reaches the bottom of the reaction vessel 4 as a flow of a relatively moderate velocity after cease of the turbulent and stirring state immediately following the overflowing at the upper end of the tubular body 10.

When the reaction vessel 4 in the inventive method has been filled with the slurry to an adequate level, the supply of the slurry at the slurry inlet port 1 may be terminated and, instead, the feed heavy oil alone without the catalyst is introduced into the reaction vessel 4 at the same inlet port 1 so that the reaction is catalyzed by the catalyst particles under convectional circulation in the reaction vessel 4. In this case, the reaction can be continued toward the end of the catalyst life without introduction of a fresh portion of the catalyst

or without discharge of the worn-out catalyst. When introduction of the slurry containing the catalyst particles is steadily continued, on the other hand, the steady state in the reaction vessel 4 can be maintained by continuously discharging the slurry or the catalyst particles to balance the continuous introduction of the catalyst particles. The discharge of the slurry in this case is preferably performed at a relatively lower portion of the reaction vessel 4 where the concentration of the catalyst particles in the slurry is relatively high by providing a slurry discharge port 19 on the lower portion of the reaction vessel 4 as is shown in FIGURE 1.

The catalyst particles having reached the bottom of the reaction vessel 4 after continuous descending movement through the downflow zone 11 are entrained by the upward flow of the gas and again brought into the tubular body 10 through the gap between the lower end of the tubular body 10 and the bottom of the reaction vessel 4 to ascend therein and overflow at the upper end of the tubular body 10.

In the inventive method, the slurry containing the catalyst particles circulates inside the reaction vessel 4 along the above described circuit on the way of which the catalyst particles, the feed heavy oil and the hydrogen-containing gas are brought into intimate contact with each other and the gaseous and liquid materials after the reaction are efficiently discharged out of the reaction vessel 4 without carrying the catalyst particles.

FIGURE 2 is a schematic cross section of the reaction

vessel 4 of a somewhat different structure used in the inventive method. The structure of this reaction vessel 4 is similar to that of the reaction vessel 4 illustrated in FIGURE 1 in the lower portion but quite different in the upper portion. The reaction vessel 4 has no side arm for forming the gravity-difference separation zone. Instead, the reaction vessel 4 has a much larger diameter in the upper part than in the lower part. Further, the upright tubular body 10 is double-walled in the upper part thereof.

Preparation of the slurry of the catalyst particles in the feed heavy oil in the slurry tank 22 and introduction of the slurry into the reaction vessel 4 are carried out in about the same manner as in the reaction vessel 4 illustrated in FIGURE 1. The slurry inlet port 1 may be at any position including the upper part, side walls and bottom of the reaction vessel 4.

In the next place, the slurry introduced into the reaction vessel 4 is lifted up through the upright tubular body 10 installed at the center of the vessel 4 as being carried by the hydrogen-containing gas blown thereinto from the nozzle of the gas inlet port 3 at the center of the bottom of the reaction vessel 4 and the slurry is discharged out of the tubular body 10 at the upper end thereof. The configuration and dimensions of the tubular body 10 may be the same as in the tubular body illustrated in FIGURE 1 except that the upper part thereof is double-walled. It is also optional to provide two or more of the tubular bodies according to need.

The diameter of the tubular body 10 is not particularly limitative excepting the limitation that a sufficiently wide downflow zone 11 for the descending slurry is kept between the outer surface thereof and the inner side walls of the reaction vessel 4. The tubular body 10 should be installed in such a disposition that the lower end thereof opens just above the gas inlet port 3 and the tubular body 10 is held substantially upright in order to facilitate the upward flowing of the gas ascending therein after introduction from the gas inlet port 3. It is essential that the outer tube 33 of the double-walled portion of the tubular body 10 is protruded above the liquid surface of the slurry held in the reaction vessel 4.

When the process of the inventive method is performed by use of the above described reaction vessel 4 provided with the partly double-walled tubular body 10 at the specified position, the catalyst particles in the slurry ascends in the tubular body 10 as being carried by the upward flow of the hydrogen-containing gas and overflows out of the upper end of the inner tube of the tubular body 10 into the gas separation zone 12. The ascending and overflowing velocity of the slurry containing the catalyst particles can readily be controlled by adequately controlling the flow velocity of the hydrogen-containing gas.

When a plurality of the upright tubular bodies 10 are installed in a reaction vessel 4 as is mentioned above, a preferable design of the reaction vessel 4 is that a plurality of the gas inlet ports 3 are provided in the

same number as that of the tubular bodies 10.

When the tubular body 10 is double-walled in the upper part thereof as is illustrated in FIGURE 2, it is further preferable to provide a baffle plate 17 positioned inside the outer tube of the double-walled portion of the tubular body 10 but above the surface level of the slurry inside the tubular body 10.

The slurry ascending through the upflow zone 13 overflows out of the upper end of the tubular body 10 and is discharged to the gas separation zone 12 where separation of the gaseous material takes place from the slurry. The gaseous material liberated in the gas separation zone 12 is discharged out of the reaction vessel 4 through the gas exhaust port 18. The baffle plate 17 positioned above the surface level of the slurry is effective to prevent the liquid and solid particles from being carried by the gas discharged out of the reaction vessel 4. The gas discharged through the gas exhaust port 18 can be recycled and reused, if desired, either as such or after purification in a refiner (not shown in the figure).

It is essential that the reaction vessel 4 has a sufficiently large horizontal cross section in the upper part in comparison with the lower part. When the cross section is not large enough in this part, no satisfactory solid-liquid separation can be achieved in the slurry because the slurry overflowing out of the tubular body 10 continues to be in a turbulent and stirring state so that a considerable amount of the catalyst may be lost through the liquid discharge port 2. At any rate, the

cross section of the reaction vessel 4 in the upper part thereof should be sufficiently large to ensure absence of turbulent flow of the slurry without the gaseous material in the discharge of the liquid.

The slurry ascending through the lift zone 13 overflows out of the upper end of the tubular body 10 into the gas separation zone 12 where the gaseous material is separated from the slurry. The slurry, i.e. the mixture of the heavy oil and the catalyst particles, freed from the gaseous material in the gas separation zone 12 descends in the reaction vessel 4 along the direction of the gravity. By virtue of the sufficiently large cross section of the reaction vessel 4 in the upper part thereof, the catalyst particles always remain in the vicinity of the tubular body 10 forming the upflow zone 13 of the slurry and never reach the side walls of the reaction vessel 4 so that the liquid substantially free from catalyst particles can be discharged out of the liquid discharge port 2 provided on the side wall of the reaction vessel 4.

The liquid discharge port 2 may be provided at any height of the side wall of the reaction vessel 4 below the surface level of the liquid in the gas-separation zone 9 held therein but it is preferable to provide the liquid discharge port 2 at a height as close as possible to the surface level of the liquid in the gas-separation zone 9 since the concentration of the catalyst particles in the slurry descending in the reaction vessel 4 is gradually increased by the settling of the catalyst

particles as the slurry flows down. It is important to minimize the linear velocity of the slurry under discharge out of the reaction vessel 4 so as to decrease the amount of the catalyst particles carried by the outward flow of the slurry. In this connection, it is preferable that the liquid discharge port 2 has a cross section as large as possible. A preferable design of the reaction vessel 4 in this part is illustrated in FIGURE 3 in which a plurality of the liquid discharge ports 2 are provided circumferentially around the reaction vessel 4 or liquid discharge ports 2 each having a horizontally extending slot-like opening are provided so that the overall cross sectional area through which the liquid is discharged can be increased.

In the reaction vessel 4 illustrated in FIGURE 2, the regions encircled by the dot lines correspond to the gravity-difference separation zone 9 which is desirably formed in contact with the walls of the reaction vessel 4 because of the possibility of eliminating the flow of the mixture of the liquid and catalyst particles and decreasing the loss of heat energy through the vessel walls. When the liquid is discharged through the liquid discharge port 2 under control of the discharge velocity out of the gravity-difference separation zone 9 not to exceed the free-settling velocity of the catalyst particles in the liquid, the discharged liquid is substantially free from catalyst particles so that no or very few catalyst particles are found in the liquid discharged out of the reaction vessel 4 and received in the liquid receiver tank 25.

The thus thickened slurry, i.e. the slurry containing an increased amount of the catalyst particles after discharge of the particle-free liquid, in the gravity-difference separation zone 9, on the other hand, descends along the funnel-like inclined surface of the vessel wall. The reaction vessel 4 is provided at a height lower than the middle thereof with a slurry discharge port 19 where the concentration of the catalyst particles in the slurry is relatively high. When the overall concentration of the catalyst particles in the slurry held in the reaction vessel 4 is excessively high, a part of the slurry is taken out through the slurry discharge port 19 so as to decrease the overall amount of the catalyst in the reaction vessel 4.

A further different embodiment of the inventive method is described with reference to FIGURE 4 which schematically illustrates a cross sectional view of the reaction vessel 4 used therefor. As is understood by the comparison of FIGURE 2 and 4, the outer configuration of the reaction vessel 4 is substantially the same as that in FIGURE 2. In this case, however, no upright tubular body 10 in FIGURE 2 is provided therein. When the ratio of the horizontal cross sectional areas of the upper part of the larger diameter and the lower part of the smaller diameter is the same as in FIGURE 2, the turbulent and stirring state in the slurry caused by the bubbling of the hydrogen-containing gas at the center portion of the slurry surface may propagate to the gravity-difference separation zone 9 around the periphery of the vessel so that the solid-liquid

separation between the heavy oil and the catalyst particles by the gravity difference would be incomplete. Accordingly, the above mentioned ratio of the cross sectional areas should be substantially larger than in the vessel in FIGURE 2. It is also essential in this case that the gravity-difference separation zone 9 is formed in contact with the inner surface of the reaction vessel 4.

It is important that the linear velocity of the liquid flow at the liquid discharge port 2 should be as small as possible in order to minimize the amount of the catalyst particles carried by the liquid flow. Such a condition can be achieved by increasing the cross sectional area for the outflow of the slurry. The disposition of the liquid discharge ports illustrated in FIGURE 3 is applicable also to this case. Alternatively, a baffle plate 32 is provided as is illustrated in FIGURE 5 to face the opening of the liquid discharge port 2. A preferable configuration of the baffle plate 32 is a section of a cylinder surface with the lengthwise sides held vertically, which may be in contact with the inner surface of the vessel walls as is illustrated in FIGURE 6. It is of course optional according to need that two or more of such baffle plates are provided circumferentially along the inner surface of the reaction vessel 4.

A still different embodiment of the inventive method is described with reference to FIGURE 7 which illustrates a schematic cross sectional view of the reaction vessel 4 used therefor. The outer configuration of the reaction vessel 4 is basically the same as that illustrated in

FIGURE 2 but no upright tubular body 10 in FIGURE 2 is provided in this case. The difference from the reaction vessel 4 illustrated in FIGURE 4 or 5 is in the form of the baffle plate 32. The baffle plate 32 in this reaction vessel 4 is protruded above the surface of the slurry into the gaseous phase of the gas separation zone 9 to partition the foam-breaking zone and the gravity-difference separation zone 9 so that the efficiency of the solid-liquid separation in the gravity-difference separation zone 9 is increased because the turbulence or agitation in the surface portion of the slurry caused by the destruction of the foams and liberation of the gas does not propagate to the separation zone 9.

Further, the lower end of the baffle plate 32 is outwardly broadened in a funnel-like shape. It is advantageous that the broadened lower end of the baffle plate 32 is larger than the cross section of the lower part of the reaction vessel in respect of the diameter (when the cross section is circular) or the longer side (when the cross section is rectangular) since the bubbles of the hydrogen-containing gas ascending in the reaction vessel are prevented from entering the gravity-difference separation zone 9 even when the ascending bubble column has a somewhat increased diameter so that the turbulence of the slurry in the gravity-difference separation zone 9 can be minimized. It is necessary in this case that a sufficient gap is retained between the funnel-like lower end of the baffle plate 32 and the inner walls of the reaction vessel since otherwise the narrow gap may

readily be clogged by the deposition of the catalyst particles to disturb smooth circulation of the slurry inside the reaction vessel 4. It is important also in this case that the gravity-difference separation zone 9 is formed in contact with the inner walls of the reaction vessel 4 so that the loss of heat energy from inside of the reaction vessel 4 is greatly decreased.

The linear velocity of the liquid discharged out of the liquid discharge port 2 should be as small as possible in order to minimize the amount of the catalyst particles carried by the discharged liquid. The linear velocity of the discharged liquid can be decreased by increasing the cross section through which the liquid is discharged so that it is preferable as is shown in FIGURE 9 to provide a plurality of the liquid discharge ports 2 or to have the liquid discharge port 2 extending circumferentially in a slot-like form. The procedure for the operation using the reaction vessel illustrated in FIGURE 7 is substantially the same as with the reaction vessel 4 illustrated in FIGURE 1.

FIGURE 10 is a schematic cross sectional view of a reaction vessel used in a further different embodiment of the inventive method. The outer configuration of this reaction vessel is much the same as that illustrated in FIGURE 7. Different from the reaction vessel 4 in FIGURE 7, the baffle plate 32 in this reaction vessel 4 is divided into four parts. The first baffle plate at the lowermost position has a conical form with its vertex facing upward. The second baffle plate is in a funnel-

like from with its upper and larger periphery fixed to the inner surface of the reaction vessel 4. The third baffle plate is in a reversed funnel-like form above the second while the cylindrical fourth baffle plate is positioned above the third of which the upper and smaller opening is thrusted into the fourth having a larger diameter. The configuration of the upper part of this fourth baffle plate 32 may be the same as that in FIGURE 7. At any rate, the upper end of the fourth baffle plate 32 is protruded above the surface of the slurry into the gaseous space of the gas separation zone 9 so as to partition the foam-breaking zone and the gravity-difference separation zone 9. Such a disposition of the fourth baffle plate 32 is advantageous because the turbulence in the surface of the slurry caused by the breaking of foams and separation of the gas does not propagate to the separation zone so that the efficiency of the solid-liquid separation in the gravity-difference separation zone 9 is not decreased. The cross sectional form of each of the baffle plates may be either circular or rectangular according to the design of the reaction vessel 4. It is important also in this case that the gravity-difference separation zone 9 is formed in contact with the inner walls of the reaction vessel 4 so that the loss of heat energy from inside of the reaction vessel 4 is greatly decreased.

The heavy oil to which the inventive method is applicable includes various kinds of heavy hydrocarbon oils such as the residual oils by atmospheric pressure distillation of crude oil, residual oils by reduced-

pressure distillation of atmospheric residue, shale oils, tar sand oils and the like. As the hydrogen-containing gas in the present invention, the gas in which the purity of hydrogen is more than 75 mole % can be preferably used. The catalyst may be a conventional hydrogenation reforming catalyst having a particle size distribution in the range from 40 to 300 μm and the concentration of the catalyst particles in the slurry may range from a very low value of 1% by weight to a very high value of 50% by weight according to desire. Thus, the advantageous features of the inventive method are obtained by the use of such very fine catalyst particles and such an extremely high concentration of the catalyst in the slurry by virtue of the easiness of the solid-liquid separation of the catalyst particles from the oily product after the hydrogenation.

As is understood from the above given description of the inventive method, the feed heavy oil, catalyst particles and hydrogen-containing gas pertaining to the hydrogenation reforming are brought into very good contact with each other as a result of the circulatory flow of the slurry caused in the reaction vessel and the separation of the effluent gas, hydrogenated oil and catalyst particles is very complete. In particular, the discharge of the hydrogenated oil can be performed easily and at a high rate because of the completeness of the separation of the catalyst particles from the liquid.

The conditions of the operation in the hydrogenation reforming of a heavy oil according to the inventive method may be about the same as in the conventional hydrogenation

reforming reactions. Some of the reaction parameters include the temperature in the range from 250 to 600 °C, pressure in the range from atmospheric to 350 kg/cm^2G, liquid-hourly space velocity (LHSV) in the range from 0.2 to 10 $hour^{-1}$, ratio of hydrogen/heavy oil in the range from 100 to 2000 Nm^3/kiloliter, etc. Further, the residence time of the oil in the reaction vessel 4 should be in the range from 0.1 to 5 hours and the highest fraction of the catalyst in the reaction vessel 4 should be 50% by weight although these parameters may be determined according to need. The residence time and fraction of the catalyst can be controlled by adequately adjusting the concentration of the feed slurry and the discharge rate of the slurry while the residence time of the oil can be controlled by the adjustment of the feed rate of the feed slurry and the discharge rate of the hydrogenated oil.

As is mentioned before, a part of the slurry circulating in the reaction vessel 4 is taken out of the slurry discharge port 19 and received in the slurry receiver tank 26 through the flow control valve 31 followed by the separation of the catalyst particles from the slurry in the centrifugal separator and the like machine 27. The thus separated catalyst particles of the spent catalyst after use are washed with a solvent such as naphtha to remove the oily matter and heavy metal-containing materials adhering thereto and the coked material deposited on the catalyst particles can be removed by burning. The thus regenerated catalyst particles can be reused for the

preparation of the slurry after removal of the undersized fine particles finer than 40 μm.

As a result of the very little intermixing of the catalyst particles in the discharge oil, the post-treatment of the product oil by the hydrogenation reforming is very easy and the process can be continuously run over a long period of time because the lines are never clogged by the deposition of the catalyst particles and the slurry can be supplied or discharged at any time without interrupting the operation.

In addition, the method of the present invention provides a possibility of using catalyst particles having a relatively fine particle size distribution by virtue of the completeness in the separation of the catalyst particles from the product oil. As a result thereof, the reactivity of the catalytic hydrogenation reforming can be enhanced and the volume of the hydrogen-containing gas required for the fluidization of the catalyst particles can be smaller than in the conventional methods. Therefore, the volume of the circulating hydrogen gas can be greatly reduced in comparison with the conventional methods and the efficiency of the hydrogenation reforming can also be improved. Furthermore, catalysts of fine particle size distribution such as the spent catalyst from the process of catalytic cracking can be used in the inventive method contributing to the reduction of the running cost of the process. In addition, a relatively low concentration of the slurry introduced into the reaction vessel is sufficient to build up and maintain a higher concentration of the slurry cir-

culating in the reaction vessel so that the contacting area for the reaction can be sufficiently large.

In the following, the method of the present invention is described in more detail by way of examples.

Examples 1 and 2

A heavy oil was subjected to a hydrogenation reforming treatment in the suspended bed type process using the reaction vessel 4 and the flow system illustrated in FIGURE 1. The feed heavy oil was a residual oil of Arabian heavy oil by reduced-pressure distillation at 525 °C$^+$ of which the properties are shown in Table 1 below. The reaction conditions are shown in Table 2.

As is shown in Table 2, 93 to 95% and 70 to 75% of the contents of the metals and asphaltene in the feed heavy oil could be removed by the treatment. Such a good removal was obtained presumably as a result of the extended residence time of the oil in the reaction vessel by virtue of the suppression of excessive cracking. The consumption of hydrogen was low at about 200 Nm^3/kl in each of Examples 1 and 2. The concentration of the catalyst particles in the discharged liquid could be as low as 0.1% by weight or less by keeping the linear ascending velocity of the liquid at 0.01 cm/second.

Table 1

Properties of starting heavy oil

Specific gravity, 15/4 °C		1.0216
Kinematic viscosity, centistokes	100 °C	1400
	120 °C	-
	150 °C	-
Fluidity point, °C		+45.0
Sulfur, % by weight		4.85
Nitrogen, % by weight		0.325
Metals, p.p.m.	Vanadium	110
	Nickel	34
	Iron	15
Residual carbon, % by weight		20.5
Total carbon, % by weight		84.6
Total hydrogen, % by weight		9.9
Composition analysis, % by weight	Asphaltene	7.5
	Resinous matter	20.9
	Aromatics	52.9
	Saturated compounds	18.7

Table 2

Example No.			1	2
Catalyst			*1 Silica-alumina type	*2 Cobalt-molybdenum type
Reaction conditions	Temperature, °C		450	440
	Pressure, kg/cm^2G		70	70
	LHSV, $hour^{-1}$ *3		0.5	0.5
	Concentration of catalyst, % by weight		30	30
	Staying time of catalyst, hours		10	10
Linear ascending velocity of liquid, cm/second *4			0.01	0.01
Results of reaction	Hydrogen consumption, $Nm^3/k\ell$		180	185
	Properties of product oil	Metals removed, %	95	93
		Asphaltene removed, %	70	75
		343°C⁻ decomposition, % by weight	57	44
		525°C⁻ decomposition, % by weight	82	72
		Yield of medium fraction, % by weight	25	26
		Desulfurization, %	57	85

*1 : A silica-alumina type catalyst supporting nickel and vanadium; particle size distribution 40 to 150 μm; average particle diameter 67 μm

*2 : An alumina catalyst supporting cobalt and molybdenum, particle size distribution 40 to 150 μm; average particle diameter 68 μm

*3 : LHSV = (feed rate of oil) / (volume of reaction vessel)

*4 : The value at the liquid zone 20

Example 3

The hydrogenation reforming treatment of heavy oil was conducted in substantially the same manner as in Example 1 using the same feed heavy oil and catalyst but with modified severity of the reaction conditions. The results are shown in FIGURE 11.

Example 4

The hydrogenation reforming treatment of heavy oil was conducted in substantially the same manner as in Example 2 using the same feed heavy oil and catalyst but with modified severity of the reaction conditions. The results are shown in FIGURE 11.

Example 5

The hydrogenation reforming reaction was performed using the same feed heavy oil and catalyst as used in Example 1 under the reaction conditions of the reaction temperature at 440 °C, LHSV of 0.5 $hour^{-1}$, catalyst concentration of 30% by weight, residence time of catalyst of 10 hours and a variable pressure. Each of the yields in the product oil was determined as a function of the reaction pressure to give the results shown in FIGURE 12.

In each of the above described Examples 1 to 5, the content of the catalyst particles in the product oil as carried by the discharged liquid was 2% by weight or smaller. The reaction was continuously run for 1000 hours in each of the Examples with absolutely no troubles of clogging with cokes and the like.

WHAT IS CLAIMED IS:

1. A method for the catalytic hydrogenation reforming treatment of a heavy oil by bringing the heavy oil into contact with a hydrogen-containing gas in the presence of catalyst particles in a fluidized state which comprizes:
introducing the heavy oil and particles of a hydrogenation catalyst into a reaction vessel having a separation zone by the difference in the specific gravities and kept at a temperature in the range from 250 to 600 °C and under a pressure in the range from atmospheric pressure to 350 kg/cm^2;
introducing a hydrogen-containing gas into the reaction vessel at the bottom thereof at such a rate that from 100 to 2000 Nm^3 of hydrogen is supplied to the reaction vessel per kiloliter of the heavy oil to cause contacting of the heavy oil, catalyst particles and hydrogen in a fluidized state by the upward flow of the hydrogen-containing gas;
separating the gaseous material from the mixture of the heavy oil, catalyst particles and hydrogen-containing gas in the reaction vessel;
then separating a part of the oily material from the suspension of the catalyst particles in the heavy oil within the separation zone by the difference of specific gravities inside the reaction vessel in the substantial absence of the gaseous material; and
taking the thus hydrogenation-treated oily material out of the reaction vessel at a liquid-hourly space velocity in the range from 0.2 to 10 $hour^{-1}$.

2. The method for the catalytic hydrogenation reforming treatment as in Claim 1, wherein the purity of the hydrogen in the hydrogen-containing gas is more than 75 mole %.

3. The method for the catalytic hydrogenation reforming treatment as in Claim 1, wherein the heavy oil is one or more kinds of oils selected from the group consisting of the residual oils by atmospheric pressure distillation of crude oil, residual oils by reduced-pressure distillation of atmospheric residue, shale oils, and tar sand oils.

4. The method for the catalytic hydrogenation reforming treatment as in Claim 1, wherein the particle size distribution of the catalytic particle is from 40 to 300 μ.

5. The method for the catalytic hydrogenation reforming treatment as in Claim 1, wherein the concentration of catalyst particles in the slurry is from 1 to 50% by weight.

FIG. 1

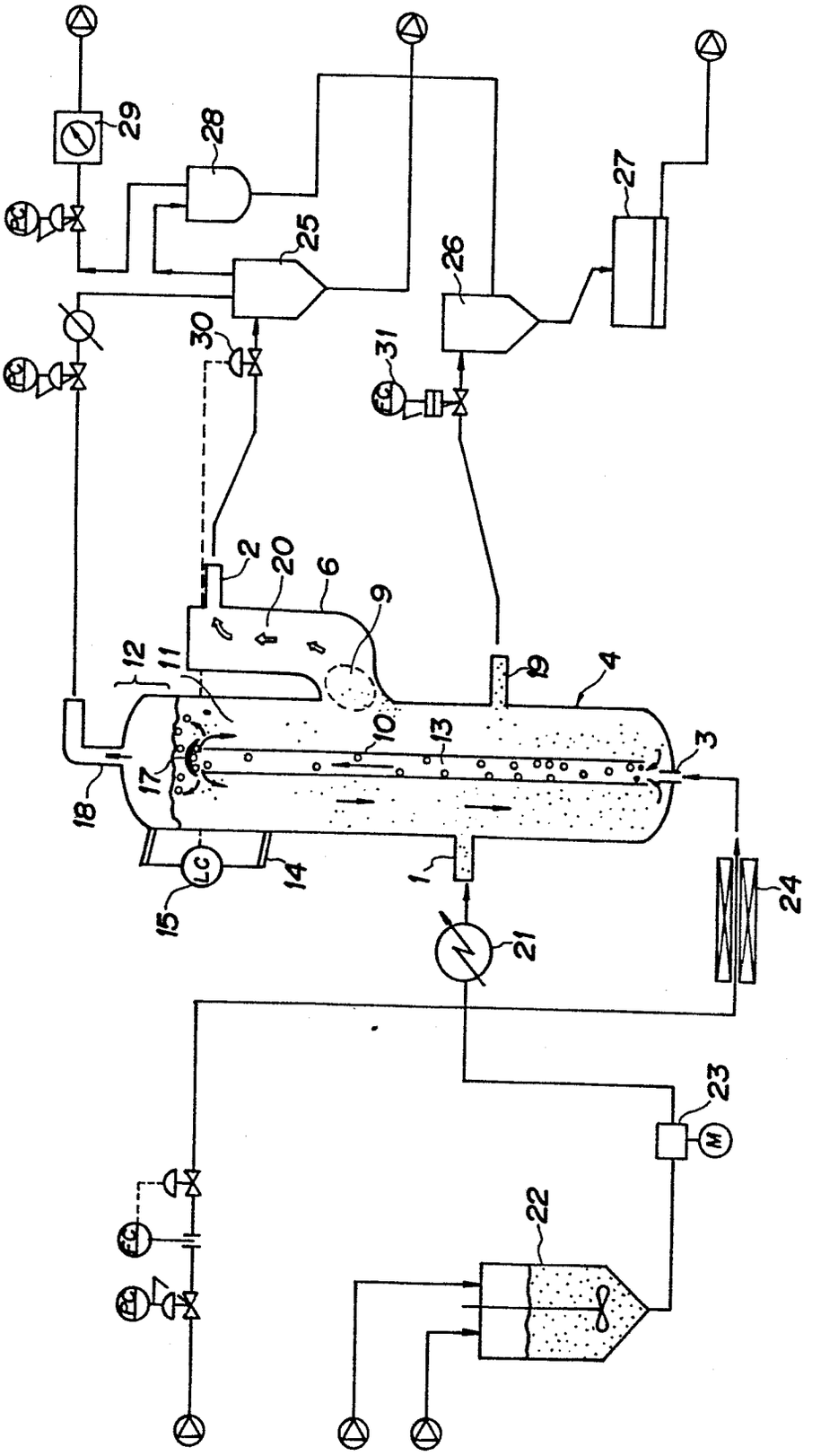

29
28
27
25
26
30
31
2
20
6
9
12
11
19
4
10
13
3
17
18
LC
14
15
1
21
24
23
M
22

FIG. 2

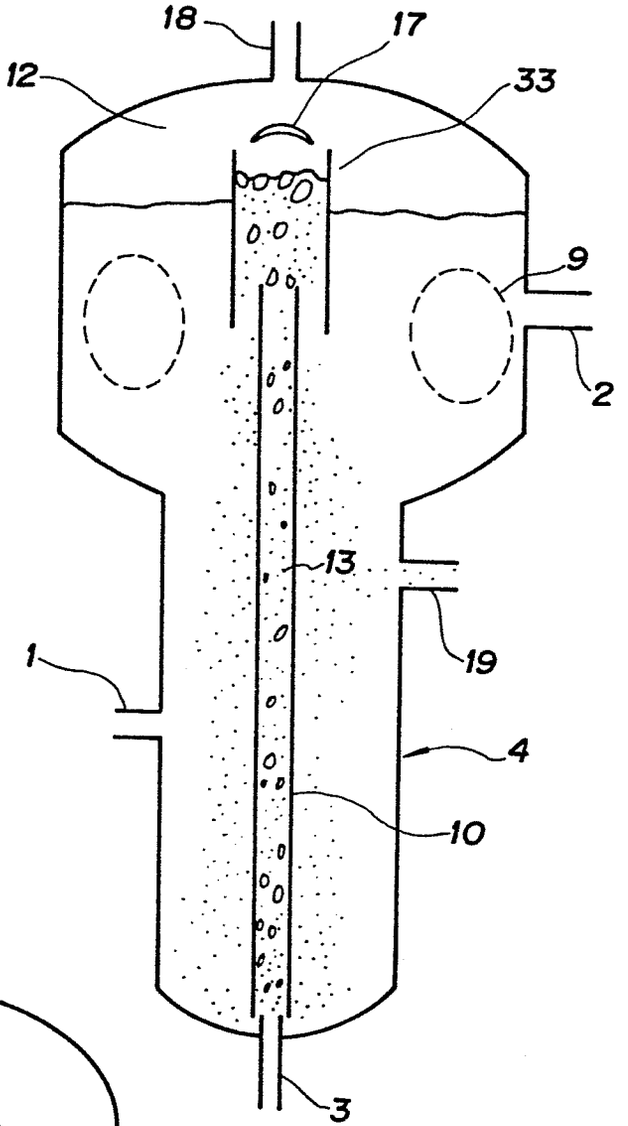
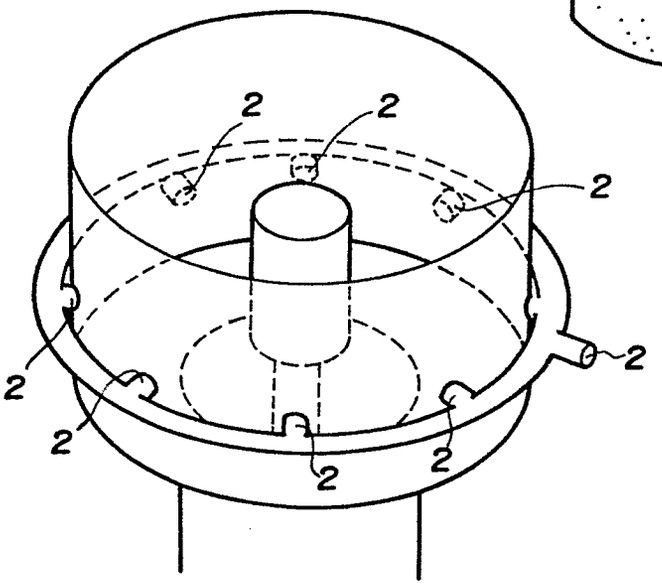


FIG. 3



0131912

FIG. 4

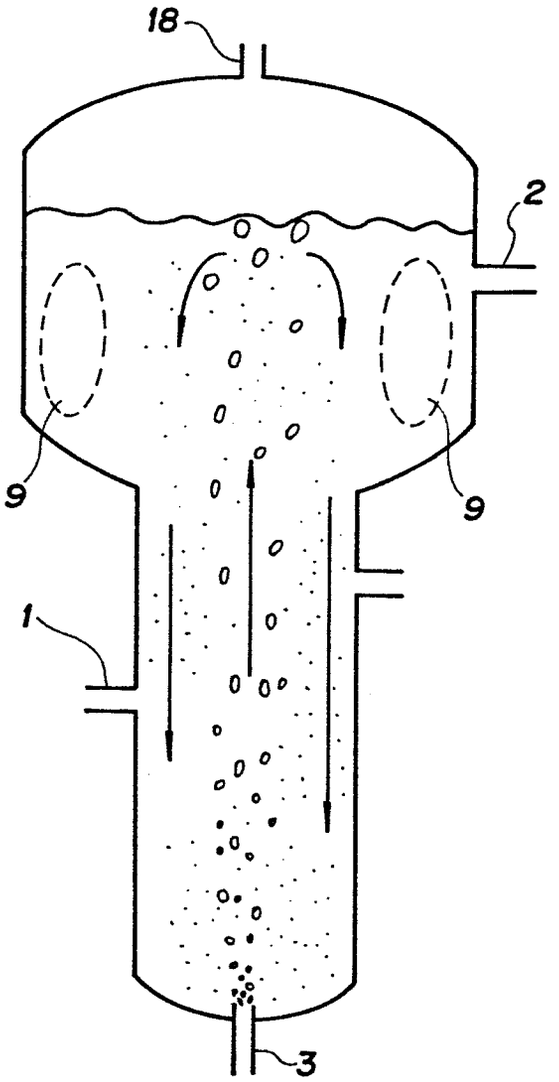


FIG. 5

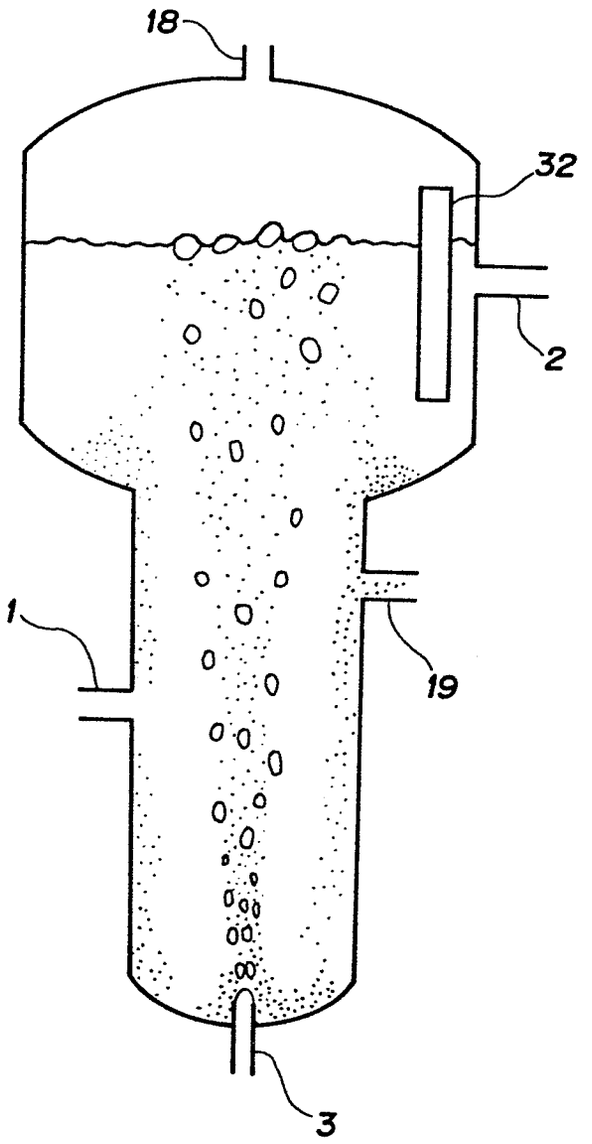


FIG. 6

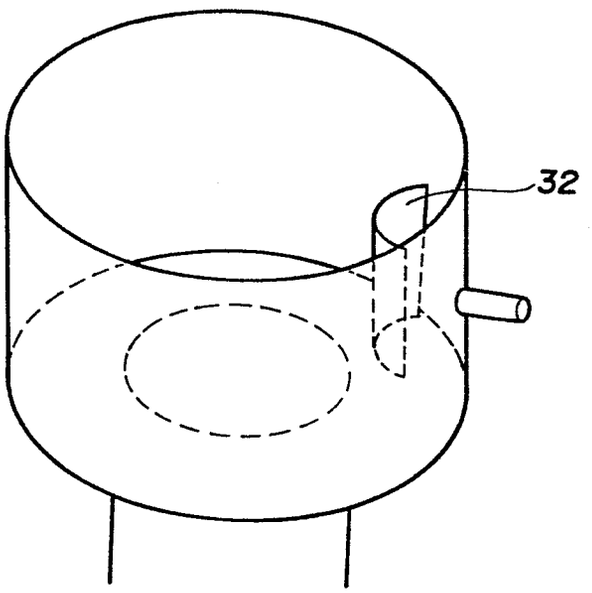


FIG. 8

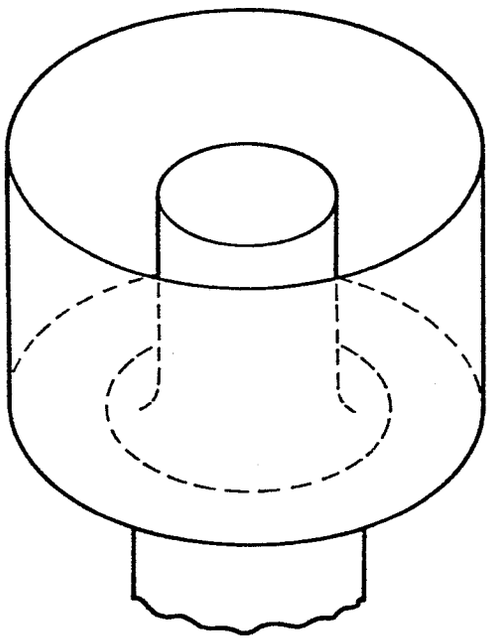


FIG. 7

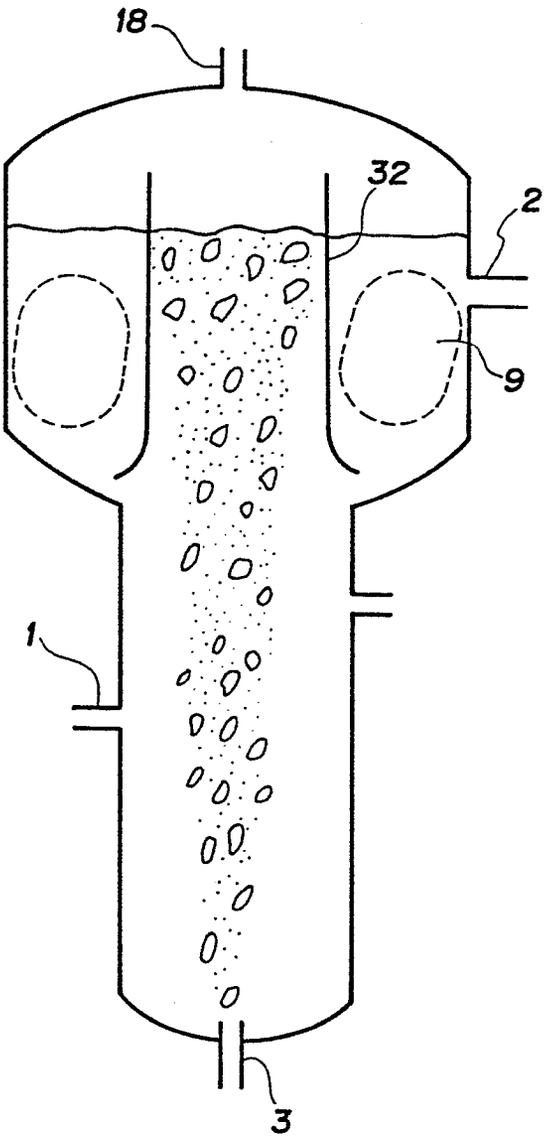
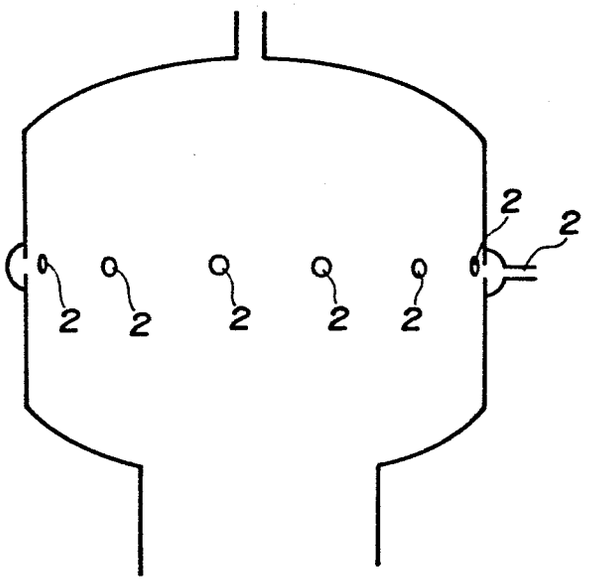


FIG. 9



0131912

FIG. 10

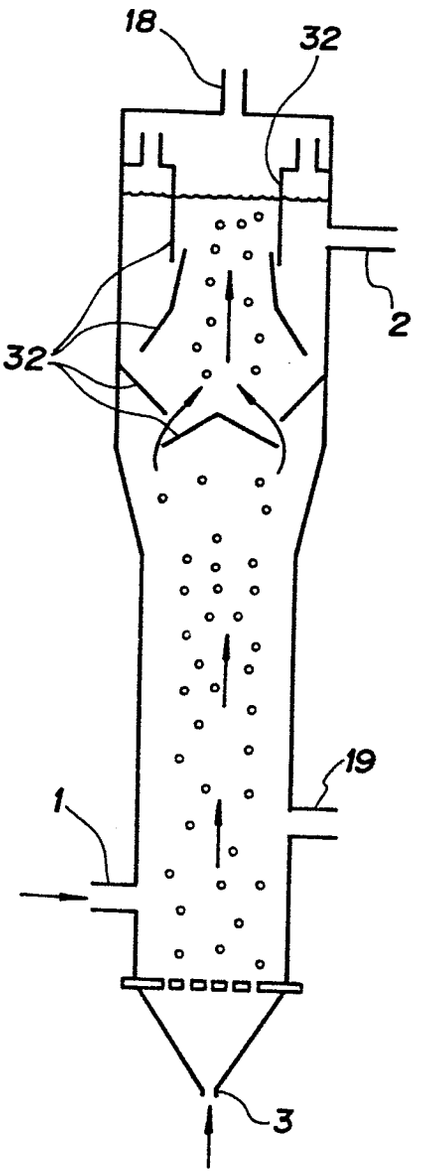


FIG. 11

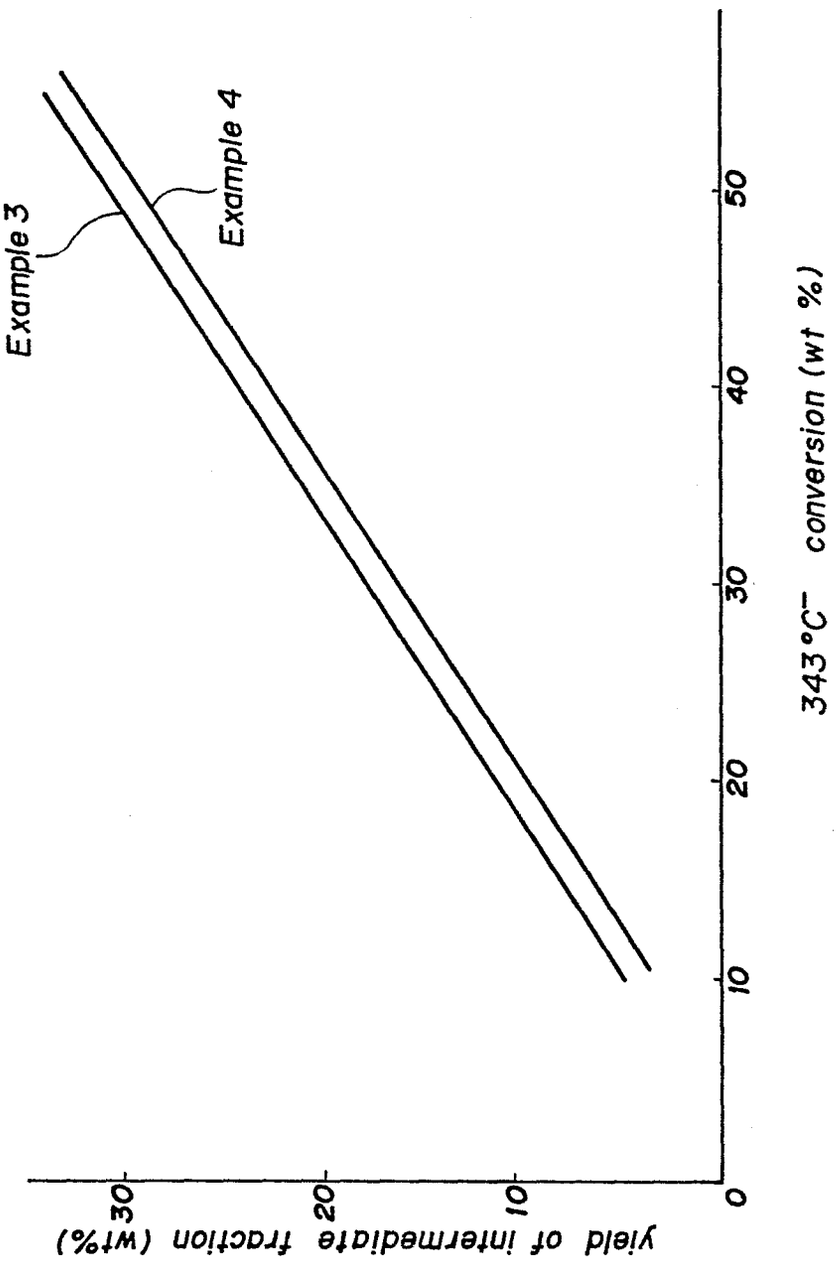
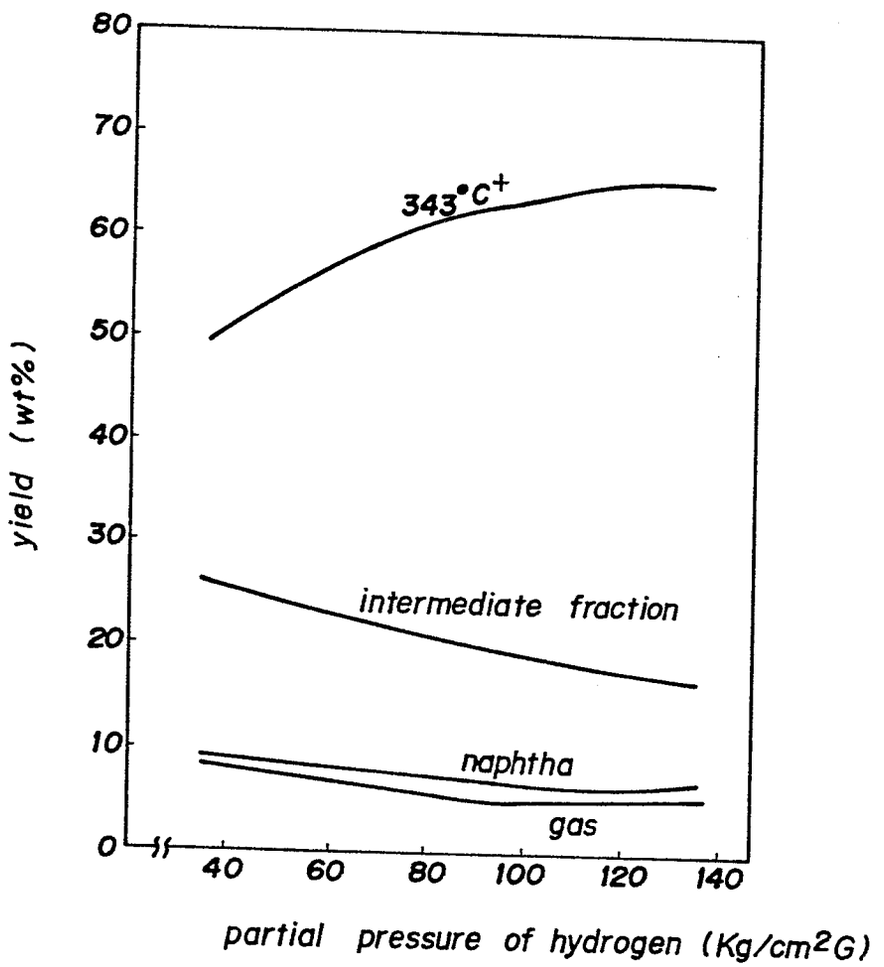

yield of intermediate fraction (wt%)
0
10
20
30
343°C⁻ conversion (wt %)
10
20
30
40
50
Example 3
Example 4

FIG. 12


80
70
60
50
40
30
20
10
0
343°C+
intermediate fraction
naphtha
gas
40
60
80
100
120
140
yield (wt%)
partial pressure of hydrogen (Kg/cm2G)

European Patent Office

EUROPEAN SEARCH REPORT

0131912
Application number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 84108167.2

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
A	GB - A - 1 331 778 (HYDROCARBON RESEARCH INC.) * Claims; page 2, lines 68-113 * --	1,3,5	C 10 G 49/10 C 10 G 47/24
A	US - A - 4 221 653 (CHERVENAK et al.) * Claims 1-7; column 2, line 32 - column 3, line 33 * --	1,3,5	
A	US - A - 3 896 024 (NACE) * Claims; column 1, line 27 - column 2, line 68 * ----	1,3,5	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 10 G 47/00
C 10 G 49/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	23-10-1984	STÖCKLMAYER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503 03 82