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(54) **Catalytic hydrocarbon conversion/synthesis**

(57) Hydrocarbons or bituminous shales or carbon monoxide are catalytically converted in the liquid phase in contact with hydrogen flowing upwardly through a series of successive stages (7,8,9,10), each containing a catalyst bed either semi-stationary or dispersed in the charge, the catalyst being maintained in each stage by an upward flow of hydrogen or hydrocarbon supplied (16,17,18,19) below a relatively large opening (20,21,22,23) in the partition wall (3,4,5) between two successive stages and periodically allowed to pass from one stage to the next lower stage through the said opening by discontinuing the said upward flow. The catalyst therefore flows in countercurrent to the reagents and is discharged at the base of the reactor vessel.

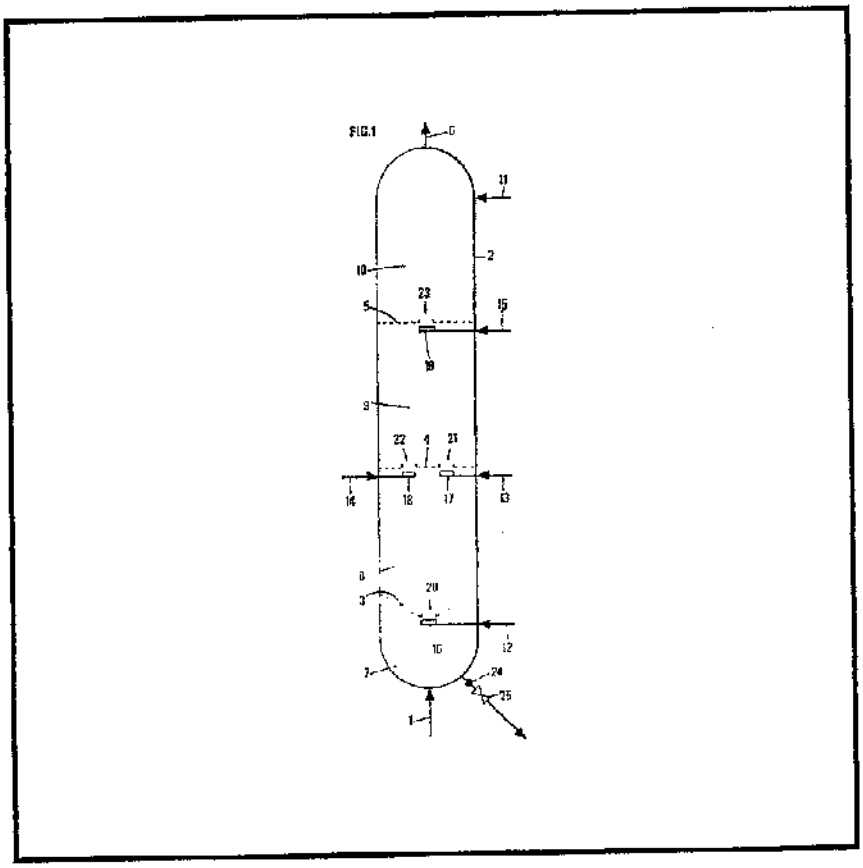

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FIG.1

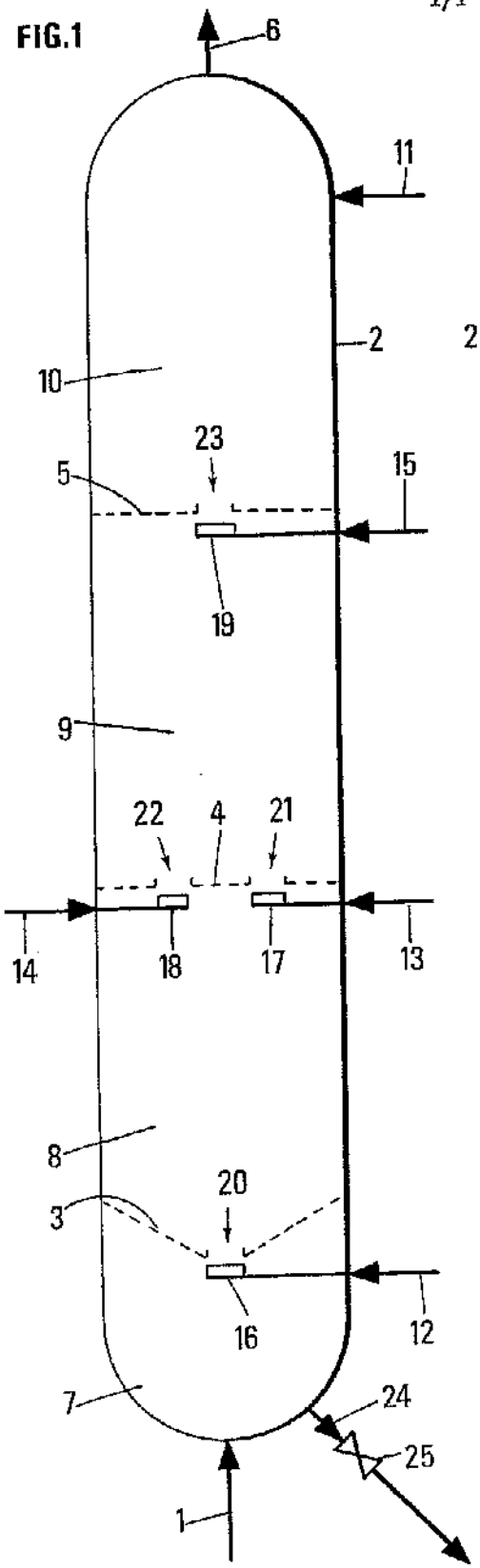


FIG.2

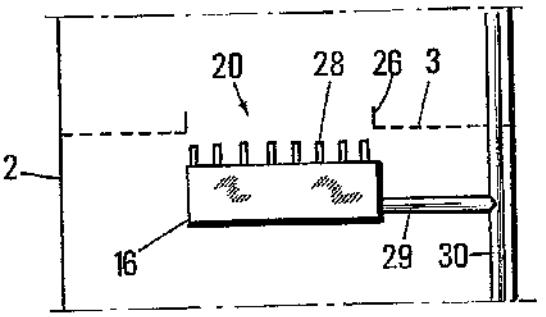


FIG.4

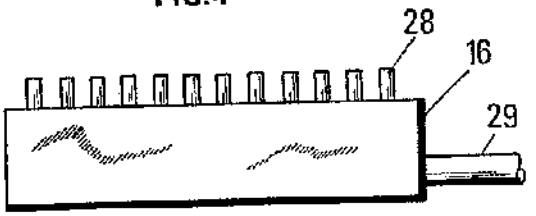
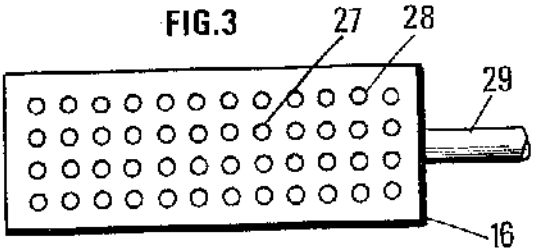


FIG.3



SPECIFICATION

Catalytic hydrocabon conversion

This invention concerns a liquid phase process and an apparatus for the catalytic conversion of hydrocarbons or carbon monoxide in the presence of hydrogen.

Various processes are known for the hydrotreatment of heavy hydrocarbon charges or of carbon monoxide, in the liquid phase, making use of a dispersed catalyst, and particularly a process wherein the catatlyst bed is in dispersed or expanded form, the dispersion or expansion being produced by the upward circulation of the liquid phase and/or hydrogen or a hydrogen-containing gas. An example of such a process is the H-oil process for a hydrocarbon liquid charge. This type of process does not provide for a satisfactory use of the catalyst; as a matter of fact, the catalyst withdrawn from the reactor is a mixture of very substantially deactivated catalyst, of moderately deactivated catalyst and of almost new catalyst and the sorting of the catalyst particles according to their deactivation degree is difficult to achieve.

According to an improvement to said technique (catalyst in a dispersed or expanded form), there is used a series of superposed beds of the same type. The fresh catalyst is introduced at the upper stage of the reactor, preferably after a previous sulfiding, while the stages located below contain a catalyst which is the more deactivated as it is at a lower stage. Periodically the catalyst of one stage n is allowed to go down to the next lower stage n + 1, while the less used catalyst of the upper stage n – 1 passes to the stage n, and similarly for all the stages. The catalyst of the last stage, at the bottom of the reactor, is discharged, while the fresh catalyst is introduced to the first stage No. 1 at the top of the reactor.

This procedure provides for an improvement of the utilization rate of a catalyst before discharge from the reactor. In addition, the fractionation of the reactor in a series of catalyst beds, improves the efficiency of the reactor. The main problem encountered in that type of reactor, concerns the transfer of the catalyst from one stage to the next stage below.

It has first been proposed to allow the catalyst to progressively go down through all the stages, but this has the major disadvantage of mixing, at each stage, a relatively active catalyst of stage n with a relatively less active catalyst of stage n + 1, which results in a relatively poor use of the catalyst.

It has also been proposed to transfer the catalyst periodically in separated charges or "batches", which obviates partially to the preceding disadvantage. But any one of these methods requires the use of valves, with or without hydrogen feed to the transfer duct, above the one or more valves. However, the use of such valves, as described for example in the US Patent No. 3 708 420, involves a risk of quick wear and deterioration of the valve sealing as a result of the possible presence of abrasive catalyst particles on the valve seat. The construction of the reactor with the positioning of the one or more valves inside the reactor poses difficult problems for their control, their maintenance and their exchange when in operation, as a result of the temperature and pressure conditions and of the corrosive action of the reaction medium. The construction of the reactor with the positioning of the one or more valves outside the reactor as indicated in US Patent No. 3 708 420, makes it necessary to bore holes at regular intervals in the wall of the reactor for the introduction of the valves and such holes are not desirable in the case of reactors operating both at high temperature and under pressure. Moreover, in the case of catalyst transfer through a duct external to the reactor, the charge is no longer in contact with a sufficient amount of catalyst in the main reaction zone, which disturbs the running of the plant. In addition, by-passing a section of the reactor by means of a lateral duct disturbs the pressure distribution and produces siphonages or even discontinues the catalyst fluidization in said section and, in any way, results in a substantial disturbance of the reactor operation. Finally, the lateral ducts include knees which interfere with the catalyst flow.

The present invention is based on the discovery that the catalyst transfer can be considerably improved by making use of the kinetic energy of a fraction of the gas and/or liquid in order to prevent or allow communication between the neighbouring stages. This simplifies the operation by avoiding mechanical displacement. Moreover, the use of a reactor in which the catalyst displacements are limited by partitions, results in a system equivalent to a reactor cascade either of the type with a bubbling bed or of the type with a semi-stationary bed, but with only one device for introducing the catalyst and for withdrawing the latter and a single zone for the disengagement of the liquid, gas and catalyst, if such a zone is required.

It is generally preferred to make use of bubbling beds instead of semi-stationary beds. By semi-stationary bed it is meant a catalyst bed subjected to an insufficient gas and liquid upward flow to produce the fluidization of the bed ; but these flow rates are however sufficient to displace the catalyst inside the bed. More precisely, the liquid and gas flow rates are then from 50 to 90 % of the flow rates required for obtaining the bed fluidization, usually called, in a conventionally manner in the art : "bubbling bed". The catalyst is generally used as extrudates, grains or particles.

The process according to the invention consists of passing the liquid phase (liquid charge or solvent for the reactants, according to the case) and a main stream of hydrogen or of a hydrogen-containing gas, upwardly through at least one catalytic reaction zone comprising several stages, the process being remarkable in that each stage contains a catalyst bed which may be either a semi-stationary bed or a bed at least a portion of which is in dispersed state in the liquid charge (ebullated bed), at least one intermediary stage being in permanent communcation respectively with the next lower stage and with the preceding upper stage on the one hand through several openings of small section and, on the other hand, through at least one opening of relatively large section, the catalyst passing from one stage to the next through said opening of relatively large section, of injecting at least one fluid selected from hydrogen, a hydrogen-containing gas and a liquid fluid upwardly below said openings of relatively large section at a flow rate and at a velocity sufficient to slow down or impede the passage of the catalyst from one stage to the next lower stage through said openings of relatively large section, and of periodically discontinuing or reducing the injection, below at least one of said openings of said relatively large section, to give passage downwardly to the catalyst through said opening of relatively large section. Preferably all the stages operate as abovementioned, with however a slight modification concerning the upper stage and the lower stage. The lower stage is in communication with a duct for withdrawing used catalyst, the latter being controllable through a hydrogen or a hydrocarbon diffuser, as in the other stages, through a valve or any other known device. The reaction product and the hydrogenation gas are withdrawn from the top of the reactor. The upper stage is periodically fed with fresh or regenerated active catalyst.

By relatively large opening is meant an opening through which the catalyst easily flows from one stage to an other, when the injection of hydrogen-containing gas and/or the injection of the liquid phase is discontinued below the concerned opening. An expert may easily determine from the above indications, when knowing the size of the catalyst particles, the practical dimensions to be used. Usually, the opening has a cross-sectional area of at least 3 cm^2, but preferably at least 5 cm^2. The maximum area of the cross-section depends on the reactor section. It is preferable not to exceed 50 % of the cross-sectional area of the reactor.

The remainder of the separating zone between the stages is provided with openings of small section as above-mentioned. Preferably these openings are holes through which the liquid and hydrogen flow upwardly but they do not give passage to the catalyst which flows in the opposite direction. The perforations are accordingly of relatively small size, usually smaller than 1 cm^2 of cross-sectional area. These perforations may be of various forms such as circular, rectangular or square, in the form of elongate slots, or grids, The preferred form is that of grids made of profiled metal bars separated by a space of, for example, from 0.1 to 10 millimeters. The section of the profiled bars may be advantageously triangular or parabolic. During their positioning, the so-achieved partitions are then so arranged in the reactor that the pointed portion be oriented downwardly.

The achievement of the partitions by means of the profiled bars, provides for a good compromise between the opening rate (% of the open surface as compared to the total surface), the rigidity and the small resistance to gases and liquids flow.

The shape of the one or more relatively large openings is either circular, square or rectangular or has any other form compatible with the nature of the separation zone. The periphery of the opening is advantageously provided with an upper edge whose height is higher than 5 mm and preferably higher than 20 mm.

The separating zones between the stages are horizontal or inclined with respect to a horizontal plane. In the case where the liquid and gas flow rates are insufficient to obtain a so-called "bubbling bed" but sufficient to obtain a semi-stationary bed, it is advantageous that the separating zones be inclined with respect to a horizontal plane by an angle equal to or close to the natural slope angle of the catalyst used.

The liquid which may be injected below a relatively large opening may be the charge itself or the solvent of said charge when it is in a gaseous state but there can be also injected a fraction of the liquid product from the reaction or a fraction of the solvent withdrawn at any level of the reactor.

The injection of hydrogen or of a hydrogen-containing gas and/or of a fraction of the liquid phase, takes place below each relatively large opening, usually from a distribution box (distribution zone) so achieved as to provide for a series of fluid jets at high velocity impeding the normal flow of the catalyst through said opening. As a preferred embodiment, the distributor may use hydrogen or a hydrogen-containing gas.

The distributor or distribution box may be devised as an assembly of tubes of appropriate diameter, connected at their lower end with a hydrogen gas distribution box. The hydrogen or hydrogen-containing gas pressure in the box is advantageously from 5 to 400 % higher than the operating pressure of the reactor. The diameter of the tubes producing the hydrogen gas jet is preferably from 0.25 to 1 cm. It is more advantageous to inject the gas or liquid at a higher flow rate from the periphery of the distributor than from the center thereof. Preferably in the

case of a distributor made of tubes, the diameter of the tubes at the periphery of the box on the first row and, optionally, on the second and third rows is from 2 to 20 % higher than the diameter of the tubes of the other rows. The tubes may be arranged in a parallel direction to one another or may be slightly divergent towards the exterior according to the more or less high tendency of the liquid phase to cause bubble trains to coagulate. The geometrical shape of the box is preferably the same as that of the relatively large opening controlled therefrom. Its surface area is usually at least 0.75 times the area of said opening ; it is preferably from one to ten times or better from 1.2 to 4 times that of the opening. The vertical distance between the lower level of the separating surface (excluding the edge) and the upper level of the tubes or of the box is usually from 0.15 to 40 cm (more particularly 1.5 to 10 cm).

The dispersed catalyst may fill the total volume available at each stage (expansion rate of 100 %) or only a portion of said volume. Expansion rates from 10 to 70 % are preferred. It is known that the expansion rate largely depends on the liquid flow rate. A portion of the catalyst may remain undispersed in the form of a relatively dense layer laying on the plates at each stage and thus forming a fraction of a semi-stationary bed.

The number of openings of relatively large section at each stage is at least 1 ; it may be greater and, for example, from 2 to 10 openings. The total area of these openings, at a given stage, preferably does not exceed 50 % of the cross-sectional area of the reactor.

The catalyst particles usually have an average diameter from 0.12 to 10 mm, these values being however not limitative.

A first type of reaction which can be conducted according to the process of the invention is the removal of pollutant compounds contained in various hydrocarbon cuts.

The hydrocarbon charges so treated according to the invention are then liquid hydrocarbons or hydrocarbon mixtures containing pollutants which may be of various natures.

In a particularly advantageous application, relatively heavy charges may be treated such, for example, as crude oil or distillation residues containing such impurities as sulfur and/or nitrogen compounds, asphalts, metal or organometallic compounds. The involved reactions are those applicable to heavy charges of this type, particularly desulfurization, denitrogenization, hydrocracking, hydrogenation and demetallization.

Another type of reaction is "the hydrogenation" or hydrogen treatment of coal or bituminous shales dissolved or dispersed in a flowing hydrocarbon solvent.

Another type is the hydrogen treatment of used oils to remove therefrom additives and organometallic particles and improve, by hydrogenation, their lubricating power and stability to oxidation and temperature.

The operating conditions of the above-described reactions are usually a temperature from 270 to 455°C, a pressure from 20 to 300 atmospheres and a hourly flow rate of the liquid charge or solvent from 0.1 to 15 volumes per volume of catalyst, although these values are not limitative and depend on the nature of the charge or the degree of severity required in the treatment to be performed.

The catalysts are often of a known type as already used in similar reactions, for example compounds of metals from group VI and/or VIII, used as such or deposited on carriers such, for example, as alumina, silica-alumina, silica, magnesia, bauxite, red-muds, clay, kieselgur, etc... Examples of metal compounds are molybdenum, tungsten, nickel, cobalt and/or iron oxides and preferably sulfides. These catalysts are of conventional type and may be prepared in a known manner.

The process according to the invention and the above-described apparatus are generally used for all catalytic or non-catalytic processes where it is desired to achieve a counter-current contact with a liquid fluid of a solid divided in particles of a size comparable to that of catalysts.

A particularly significant example is the synthesis of hydrocarbons or alcohols by reacting such gases as CO and H_2 in a flowing hydrocarbon liquid phase. Among these hydrocarbon synthesis reactions, there will be mentioned particularly the synthesis of methane or methanation.

For carrying out this reaction, the composition of the synthesis gas mixture expressed by the molar ratio hydrogen/carbon monoxide, is advantageously selected from 1/1 to 6/1. Preferably the ratio will be close to 2.5 to 3/1, which corresponds to the theoretical stoichiometry of the reaction. The liquid used as solvent for the gaseous reactants is, for example, injected at the bottom of the reactor through a duct such as duct 1 on Fig. 1, at a space velocity, for example, from 1 to 100 liter/liter of catalyst per hour. The gas reactants are injected through another duct, not shown on Fig. 1, and at different levels of the reactor, for example through such ducts as 12, 13 and 15. The liquid solvent must exhibit properties of both chemical inertia and thermal stability. Good results are obtained with saturated hydrocarbons, particularly with paraffinic hydrocarbons, in the liquid state under the reaction conditions, for example heptane, octane, dodecane, hexadecane or with mixtures of these hydrocarbons, for example liquid oil or paraffin cuts.

The pressure of the synthesis mixture hydrogen/carbon monoxide may vary from the

atmospheric pressure up to 80 bars or more, but the operating pressure will be preferably from 1 to 20 bars.

The hourly space velocity, expressed by the volume of synthesis gas mixture supplied, under normal conditions, per volume of reactor and per hour (VVH) may vary from 1 to 500. Preferably, VVH from 50 to 200 are used, which correspond to a space velocity of from about 500 to 1000 liter/liter of catalyst/h.

The reaction temperature may be selected from 100 to 450°C. The catalyst is a conventionfifil methanation catalyst and more particularl a catalyst based on nickel or a nickel compound deposited on a suitable carrier, for example, alumina or kiesulguhr.

Among the alcohol synthesis reactions, there will be mentioned particularly the methanol synthesis and the synthesis of higher homologous alcohols.

The liquid solvent, its flow rate (i.e. its space velocity) and the conditions of the injection of the liquid and gaseous fluids are substantially the same as those indicated above for the methantion reaction. In the present case, the gas reactants usually consist either of a mixture CO + H_2 or of a mixture CO_2 + CO + H_2 (synthesis gas). The operating conditions are well known. The temperature is, for example, from 150 to 350°C, the pressure being from 20 to 200 bars, the molar ratio H_2/CO or the molar ratio $H_2/CO + CO_2$ being from 1.5 to 10, with a space velocity from 1,000 to 10,000 m^3 (N.T.P.) of gas (mixture CO + H_2 or mixture CO + CO_2 + H_2) per m^3 of catalyst and per hour. As catalyst, there is used any conventional catalyst, for example based on at least one metal or compound of metal such as copper, cobalt, chromium, iron, vanadium, manganese, rare earth, zinc, alkali metals deposited or not on a carrier such as, for example, alumina.

The invention is illustrated by the accompanying drawings exemplifying embodiments thereof. The liquid charge and optionally also a hydrogen-containing gas are introduced through line 1 (Fig. 1). The mixture flows upwardly in the reactor 2 and passes through the grid 3, then the grid 4 and the grid 5. It issues through line 6.

A cyclone, not shown, provides for the removal of the liquid phase freed from catalyst when the disengagement zone is insufficient to achieve a perfect separation of the catalyst, the liquid and the gas. The equipment thus comprises, according to this figure, 4 stages 7, 8, 9 and 10. Fresh catalyst is introduced through line 11 and hydrogen or a hydrogen-containing gas through lines 12, 13, 14 and 15 feeding the distribution boxes 16, 17, 18 and 19. The grids 3, 4 and 5 are provided with so-called relatively large openings 20, 21, 22 and 23, centered above the distributors and provided with edges such as 26 (see Fig. 2). More and more used catalyst, for example, in the case of purification of heavy hydrocarbon charges, is present in stages 9, 8 and 7 respectively. The flow rate of liquid and gas and the diameter of the reactor are so selected as to maintain the catalyst in a dispersed or expanded state in stages 9 and 10 and at least partially in a semi-stationary state in stages 7 and 8.

This difference in the hydrodynamic state between the 4 stages results from the fact that, in the lower stages 7 and 8, the catalyst, whose composition is given in the following examples, became heavy, in the case of, for example, the purification of heavy hydrocarbon charges, with metals, mainly nickel and vanadium, and with coke and accordingly, its density became higher than that of the fresh catalyst of the upper stage (No. 10) and of the substantially unpolluted catalyst of the next lower stage (No. 9). Moreover, the hydrogen injection through such injectors as 16, 17, 18, increases the gas velocity in the upper portion of the reactor and facilitates the transition to the state of "bubbling bed" in the upper stages.

The catalyst does not flow from one stage to the other as a result of the kinetic energy of the hydrogen gas jets supplied by the distributors 16, 17, 18 and 19 and passing through the openings 20, 21, 22 and 23.

After a certain period of use, without interrupting the hydrocarbon and hydrogen flow introduced through line 1, the valve 25 on line 24 is opened for withdrawing the catalyst. When a portion or preferably the totality of the catalyst has left stage 7, the hydrogen or hydrogen-containing gas injection through line 12 is discontinued : the catalyst thus passes from stage 8 to stage 7 through the opening 20. Hydrogen is again injected through line 12 and the hydrogen feed is discontinued through line 13 and 14 to leave the catalyst flow down from stage 9 to stage 8. The procedure is similar for the upper stages 9 and 10.

It is also possible to discontinue the injection of hydrogen (or of a hydrogen-containing gas) simultaneously through lines 12, 13, 14 and 15 : the catalyst flows down from one stage to the next, but at each stage, a catalyst mixing occurs to a certain extent and this must be preferably avoided.

The design of the apparatus would be exactly the same in the case of a liquid stream used instead of hydrogen or of a hydrogen-containing gas and flowing through pipes 12, 13, 14 and 15 for impeding the catalyst flow through openings 20, 21, 22 and 23.

Figs. 2 to 4 show, in detail, portions of the apparatus. Particularly Fig. 3 is a view from below of the distribution box ; a side view of the same box is shown on Fig. 4.

These Figs. No. 2, No. 3 and No. 4 show the position of such tubes as 27 and 28 in a

distribution box of rectangular shape 16 corresponding to a rectangular opening 20 (on Fig. 2), in a grid 3 (on Fig. 2) formed of profiled metal bars of triangular section ; 26 (on Fig. 2) designates the edge of the opening, 28 (on Figs. 3 and 4) shows one of the tubes located at the external periphery of the box; these tubes have a diameter slightly larger than that of the other tubes such as 27 (on Fig. 3) located more inside. Pipe 29 of Figs. 2, 3 and 4 is used for feeding the distribution box either from a high pressure pipe 30 internal to reactor 2 (see Fig. 2), or through a passage-way through the reactor wall.

In other cases, the distribution box may be simply constructed from a box having a perforated face or provided with a fritted surface or with any other means for obtaining fluid jets of high velocity.

The present process may also be performed in several reactors with dispersed catalyst and/or a semi-stationary bed of the type described, these reactors being optionally associated in series or in parallel. It is also possible to provide one or more stationary bed reactors, following one or more reactors with dispersed or semi-stationary catalyst beds of the described type, these stationary bed reactors being optionally used to complete the reaction or to proceed to a different reaction, for example saturating hydrogenation, hydrodesulfidation, hydrodenitrogenization, hydrocracking, catalytic cracking, hydrorefining or hydrofinishing.

—*EXAMPLE 1*

By way of example, for making obvious the performances obtained by the reactor of the invention, the treatment was performed on a straight run residue of heavy Iran type, whose properties are mentioned in Table I, in three different tests, all involving the same amount of catalyst and the same flow rate of fresh hydrocarbon.

The catalyst used in the three series of tests is of the cobalt-molybdenum alumina type. It is presulfided before being introduced into the reactors used in the 3 tests. Its total pore volume is 0.50 cc/g. it contains by weight, 3 % of cobalt oxide and 14 % of molybdenum oxide. It is in the form of extrudates of a 1.4 mm diameter and an average length of 8 mm.

The first test which will be called " Case A" concerns the use of the catalyst in a single stage bubbling bed, not in conformity with invention.

The second test, which will be called "Case B" provides for the use of a catalyst in a reactor according to the invention comprising 4 stages of substantially the same volumes. Hydrocarbons withdrawals at the level of each bed, indicate the advance rate of the reaction and the accumulation of vanadium onto the catalyst. The results are reported in Table II. The stages are indicated with reference numbers 1, 2, 3 and 4, while following the upward flow of the hydrocarbons. The catalyst flows downwardly.

The reactor used in each of the two tests ("Case A" and "Case B") has a ratio H/D = 13 (height/diameter). The total pressure is 90 bars at the reactor outlet. In "Case A" the flow rate of the hydrogen gas is 1480 liters NTP of gas per liter of charge at 15°C. The total amount of the gas is injected at the bottom of the reactor, in admixture with the charge. In "Case B", 1000 liters of hydrogen gas per liter of charge are injected at the bottom of the reactor and, in addition, 120 liters of hydrogen per liter of charge are injected between each stage, through diffusers or distribution boxes. From the above-defined hydrodynamic conditions, it results that the bed is a semi-stationary bed in the lower stages 1 and 2 and a ebullated bed in the upper stages 3 and 4. In the two tests ("Case A" and "Case B"), the average temperature is 390°C.

In "Case B", the reactor exhibits the further following characteristics :

—Two so-called "large" openings in each partition between two stages, cross-sectional area of each opening : 15 cm^2 ; shape of the opening : rectangular.

—Diameter of the so-called small section openings : about 0.3 cm^3 in the form of grids made from profiled metal bars spaced at a distance of about 4 mm.

—Height of the edges 26 of Fig. 2 : 25 mm.

—Distribution box similar to that of Figs. 4 and 5 ; diameter of the tubes located above the periphery of the distribution box : 0.5 mm ; diameter of the other tubes : 0.45 mm ; cross-sectional area of each distribution box equal to about 2 times the surface of the so-called "large" opening controlled therefrom.

—Average vertical distance between the lower level of the separating surface (excluding the edge) and the upper level of the tubes : 20 cm.

In the third test, the same catalyst amount as the two other tests is used in a stationary bed, in a conventional down flow operated reactor having a ratio H/D = 4. The gas and liquid flow rates and the pressures are the same as those used for the first two tests. The average temperature of the reactor is 370°C, corresponding for the catalyst and the charges to a normal temperature of the cycle beginning. The characteristics of the obtained products are reported in Table III.

From the observation of the discharged catalysts and of the products obtained, it is apparent that the staged reactor according to the invention ("Case B") is much more efficient than a single stage reactor as that of "Case A". It provides for a better use of the catalyst issuing from

the reactor with a higher methane content for the same rate of addition of new catalyst.

Moreover, the comparison of Table II ("Case B") and Table III shows that in the reactor according to the invention, there is obtained, at an average temperature of 390°C, the removal of sulfur, nitrogen and metals and a reduction of Conradson carbon similar to those obtained in a conventional reactor with a stationary bed, at 370°C, at the beginning of the cycle, the other conditions being substantially unchanged. However, in the case of a stationary bed catalyst, the metals (Ni and V) deposited on the catalyst will progressively deactivate said catalyst, and it is consequently necessary to progressively increase the average temperature of the reactor. After about 1200 hours, the catalyst contains about 20 % of (Ni + V) and it is neceesary to stop the operation of the plant, to discharge the used catalyst and to replace it with a new charge of catalyst. The reactor, designed in accordance with the invention, has the advantage of being kept in operation, due to the possibilities of introducing new catalyst and of withdrawing used catalyst.

TABLE I

CHARACTERISTICS OF THE STRAIGHT RUN RESIDUE OF "HEAVY IRANIAN" TYPE.

Cut	350°C +	
Density (d)	0.970	g/cm^3
Sulfur (S)	2.6	% by weight
Nitrogen (N)	4200	ppm (part per million)
Conradson carbon	10.7	% by weight
Asphaltens	4.15	% by weight
Nickel	75	ppm
Vanadium	200	ppm

TABLE II

OBTAINED PRODUCTS		CASE A	CASE B			
		1 SINGLE STAGE	1st STAGE	2nd STAGE	3rd STAGE	4th STAGE
Properties of the 180°C+ cut						
Density	g/cc	0.95				0.920
Sulfur	% b.w.	0.93	1.83	0.75	0.54	0.47
Nitrogen	ppm	3570				3192
Conradson carbon	% b.w.	7.0				5.8
Vanadium	ppm	101	135	91	73	66
Vanadium on the catalyst in % of new catalyst		16.6	22.2	11.5*	4.1*	1.2*
Temperature	°C	390	405	405	388	365
Average temperature	°C	390	390°C			
Total performances						
Hydrodesulfidation	% b.w.	64.2	81.9			
Hydrodenitrogenization	% b.w.	15	24			
Vanadium removal	% b.w.	49.5	67			
Ratio of added catalyst to the fresh charge mass	% b.w.	0.6 kg/t	0.6 kg/t			
Ratio of the hourly flow rate of the fresh charge by weight to the catalyst weight		0.83*	0.83 h^{-1}			

* Calculated from hydrocarbon analyses.

TABLE III

Third test

Fixed bed reactor

Properties of the produced 180°C+ cut

Density	0.940	g/cm³
Sulfur	0.44	% b.w.
Nitrogen	3150	ppm
Conradson carbon	5.6	% b.w.
Vanadium	56	ppm
Hydrodesulfidation	83	% b.w.
Hydrodenitrogenization	25	% b.w.
Vanadium removal of the cycle beginning	72	% b.w.
Average temperature of the reactor	370°C	
Ratio : hourly flow rate by weight of fresh charge/catalyst weight	0.83 h^{-1}	

—*EXAMPLE 2*

This example relates to the manufacture of methane from hydrogen and carbon monoxide. As liquid solvent there is used a hydrocarbon cut of naphthenic and paraffinic type whose boiling point is in the range from 350 to 450°C. The average temperture for performing the reaction is 340°C. The solvent temperature at the inlet of the reactor is 320°C ; the solvent temperature at the outlet of the reactor is 350°C. The average temperature of the gas-solvent mixture is 300°C. The operation is conducted under a pressure of 40 bars. The space velocity of the solvent is 20 l/l catalyst/hour and the space velocity of the gas ($CO + H_2$) is 3,000 l/l catalyst/hour. There is used a catalyst consisting of nickel deposited on kieselguhr (50 % by weight of nickel) as extrudates of a 2 mm diameter and a 5 mm length. The ratio H_2/CO is 2.5.

In test called "Case A_1" the catalyst is used as a "bubbling bed" in a single stage, not in conformity with the invention.

In a second test which will be called "Case B_1", the catalyst is used in a reactor according to the invention comprising 4 stages substantially of the same volumes (same characteristics as the "Case B" reactor of Example 1). The reactor used in each of these two tests (Case A_1 and Case B_1) has a ratio H/D = 13 (height/diameter). In test "Case A_1", the total amount of the gas is injected at the bottom of the reactor. In the test "Case B_1" there is injected, on the one hand, 2,700 liters of gas per liter of catalyst per hour and 300 liters of gas per liter of catalyst and per hour through the diffusers or distribution boxes. In each of the 4 stages, the catalyst is in a "ebullated bed".

In the two tests, the solvent withdrawn from the top of the reactor passes through an exchanger, which lowers its temperature to 300°C, and then reaches a separator, surmounted with a cooler whereby the temperature of the reaction gas is decreased to about 40°C.

In "Case A_1", there is obtained, at the top outlet of the reactor a gas whose composition by volume is as follows (expressed as dry gas) :

Methane	85	%
Ethane	6	%
CO	2	%
CO_2	3.5	%
H_2	3.5	%

In "Case B_1", there is obtained, at the top outlet of the reactor, a gas whose composition by volume is as follows (expressed as dry gas) :

Methane	:	90	%
Ethane	:	3	%
CO	:	1	%
CO_2	:	3	%
H_2	:	3	%

—*EXAMPLE 3*

This example concerns the manufacture of methanol from hydrogen and carbon monoxide. The liquid solvent is the same as in example 2. The average temperature of the reaction is 230°C. The temperature of the solvent at the inlet of the reactor is 220°C ; the temperature of the solvent at the outlet of the reactor is 240°C. The average temperature of the gas-solvent mixture is 200°C.

The operating pressure is 100 bars. The space velocity of the solvent is 15 l/l. catalyst/hour and the space velocity of the gas (CO + H_2) is 6,000 l/l. catalyst/hour. The catalyst consists of balls of a diameter from 2.5 to 3.5 mm, said catalyst containing by weight :

40 % of CuO
20 % of ZnO
10 % of alumina
30 % of secar cement, used as binder.

In a test called "Case A_2", the catalyst is used in a bubbling bed of a single stage, not in conformity with the invention.

In a second test, which will be called "Case B_2", the catalyst is used in a reactor according to the invention comprising 4 stages of substantially the same volumes (same characteristics of the reactor as in "Case B" of Example 1). The reactor in these two tests (Case A_2 and Case B_2) has a ratio of its height to its diameter : H/D = 13. In test "Case A_2", the totality of the gas is injected at the bottom of the reactor. In test "Case B_2" there is injected on the one hand 5,400 liters of gas per liter of catalyst and per hour and 600 liters of gas per liter of catalyst and per hour through the diffuser or distribution boxes. The catalyst is present as a ebullated bed in each of the 4 stages.

In the two tests, the volume withdrawn from the top of the reactor passes through an exchanger which decreases its temperature to about 200°C and then reaches a separator overtopped with a cooler whereby the temperature of the reaction gas can be decreased to about 30°C.

In the test "Case A_2", the conversion rate of CO is 47 % and there is obtained a mixture containing by weight 99 % of methanol and 1 % of higher homologous alcohols (ethanol, n-propanol, isopropanol, n-butanol and isobutanol). In test "Case B_2", the conversion rate of CO is 50 % and there is obtained a mixture also containing by weight 99 % of methanol and 1 % of higher homologous alcohols.

CLAIMS

1. A liquid phase process for the catalytic conversion of hydrocarbons or carbon monoxide in the presence of hydrogen, comprising passing a liquid phase and hydrogen or a hydrogen-containing main gas stream upwardly through at least one catalytic reaction zone comprising several superposed stages, in which each stage contains a catalyst bed that may be either a semi-stationary bed or a bed at least a portion of which is an ebullated bed, at least one intermediary stage being in permanent communication with the next lower stage and with the preceding upper stage through, in each case, two or more openings of small section and at least one opening of relatively large section, the latter being intended to allow periodical passage of the catalyst from one stage to another, periodically injecting upwardly, below said openings of relatively large section,at least one fluid selected from hydrogen, a hydrogen-containing gas and a liquid hydrocarbon at a flow rate and a velocity sufficient to slow down or impede the passage of the catalyst from one stage to the next lower stage through the said openings of relatively large section, and discontinuing or periodically reducing the injection below at least one of the said openings of relatively large section to allow the catalyst to pass downwardly through the said opening of relatively large section.

2. A process according to Claim 1 in which all the intermediary stages operate as indicated in Claim 1, the uppermost stage periodically receives fresh catalyst and at least a portion of the used catalyst present in the lower stage is periodically discharged.

3. A process according to Claim 1 or 2 in which each opening of relatively large section has a cross-sectional area of at least 2 cm^2, the total area of the cross-sections being not higher than 50% of the cross-sectional area of the reaction zone.

4. A process according to Claim 3 in which the said openings of small section are all of a

cross-sectional area lower than 1 cm^2.

5. A process according to Claim 4 in which the injection of the said fluid is performed from a distribution zone located from 0.15 to 40 cm below the relatively large opening, the area of the said distribution zone amounting to at least 0.75 times the area of the relatively large opening associated with it, the liquid hydrocarbon being selected from at least a portion of the initial charge or of the reaction product or of an intermediary effluent of the charge subjected to the said catalytic process.

6. A process according to Claim 5 in which the fluid is injected under a feeding pressure from 5 to 400% higher than the operating pressure of the reaction zone.

7. A process according to any one of the preceding claims in which the catalyst is in an ebullated state at each stage.

8. A process according to any one of Claims 1 to 7 as applied to the hydrotreatment of hydrocarbons or bituminous shales.

9. A process according to any one of Claims 1 to 7 as applied to the synthesis of hydrocarbons by action of hydrogen on carbon monoxide.

10. A process according to any one of Claims 1 to 7 as applied to the synthesis of at least one primary alcohol selected from methanol and higher homologous alcohols.

11. Apparatus for carrying out a process according to Claim 5, comprising :

(a) an elongate and substantially vertical enclosure divided into stages through separating partitions, which are horizontal or inclined to a horizontal plane and provided with relatively small openings in the form of holes or clearances, the cross-sectional area of each relatively small opening being lower than 1 cm^2, at least a portion of each of the separating partition between the stages also comprising at least one relatively lare opening whose unitary area is at least 5 cm^2, the total area of these relatively large openings being not in excess of 50% of the total cross-sectional area of the reactor, the separating partitions of the stages comprising an edge in the vicinity of the relatively large openings, the said edge protruding above the separating partitions and having a height higher than 5 mm;

(b) means for injecting a liquid charge and hydrogen at the bottom of the apparatus;

(c) means located below each relatively large opening for injecting upwardly gas or liquid and comprising an assembly of substantially vertical tubes whose lower end is connected to a gas-distributing box, the diameter of each tube being from 0.25 mm to 1 cm, the tubes located above the vicinity of the periphery of the gas-distributing box having a diameter 2 to 20 % greater than the diameter of the tubes located above the center of the distributing box, the geometrical shape of the distributing box being further substantially the same as that of the relatively large opening controlled from it, the cross-sectional area of the box being from 1 to 10 times that of the relatively large opening, the vertical distance between the lower level of the separating surface of each partition separating the stages (excluding the said edge) and the upper level of the tubes being in the range 0.14 to 40 cm;

(d) means for introducing active catalyst at the top of the apparatus;

(e) means for withdrawing used catalyst from the bottom of the apparatus; and

(f) means for withdrawing the reaction products from the top of the apparatus.

12. A process as claimed in Claim 1 carried out substantially as hereinbefore described in any one of Examples 1 to 3.

13. Apparatus as claimed in Claim 11 substantially as hereinbefore described with reference to the accompanying drawings.

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