United States Patent

[11] **3,607,000**

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[54] INTERNAL BYPASS FOR A CHEMICAL REACTOR

13 Claims, 8 Drawing Figs.

[52] **U.S. Cl.** 23/1, 23/288, 208/216
[51] **Int. Cl.** C10g 23/02
[50] **Field of Search** 208/213, 146, 216; 23/288, 1 R, 1 G, 1 E, 1 B; 210/20

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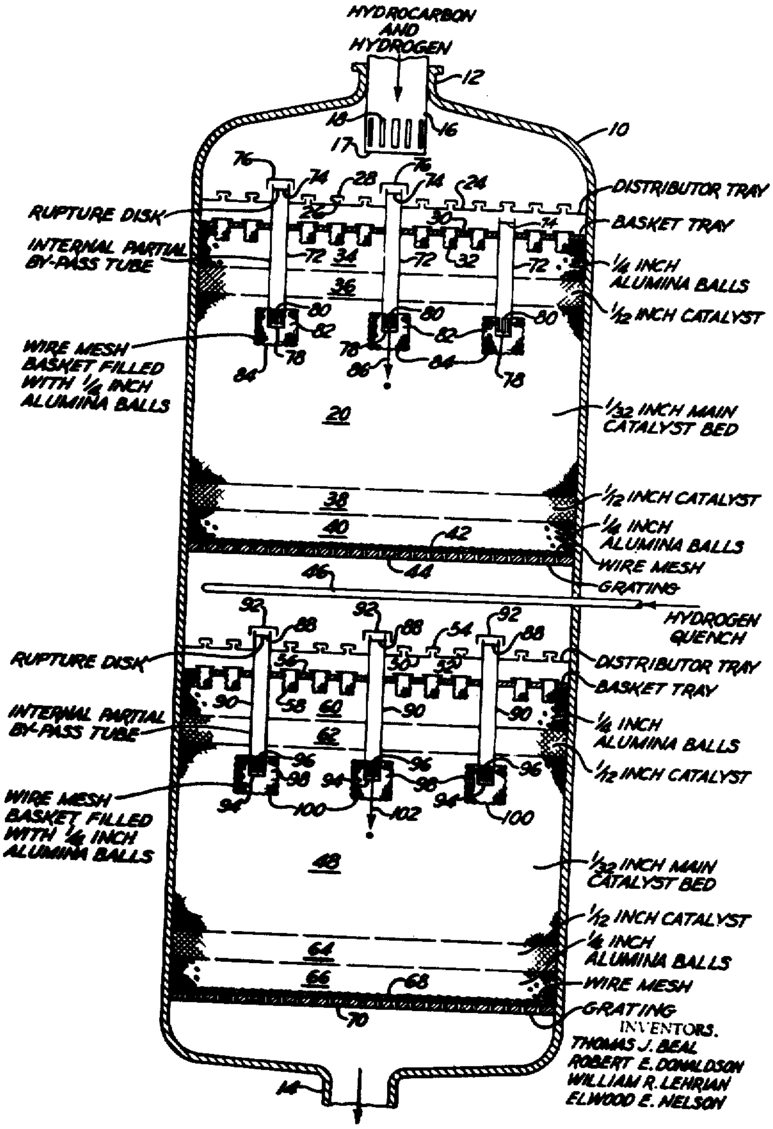
ABSTRACT: In a reactor containing a fixed bed of catalyst an internal bypass for reactants is provided to bypass the portion of the bed which is contaminated and offers the greatest pressure drop without changing the direction of flow of the reactants. The internal bypass is of particular advantage in a hydrodesulfurization process utilizing very small catalyst particles wherein pressure drop is critical and wherein an external bypass which changes flow direction might impart a greater pressure drop than it conserves by avoiding a contaminated section of catalyst.



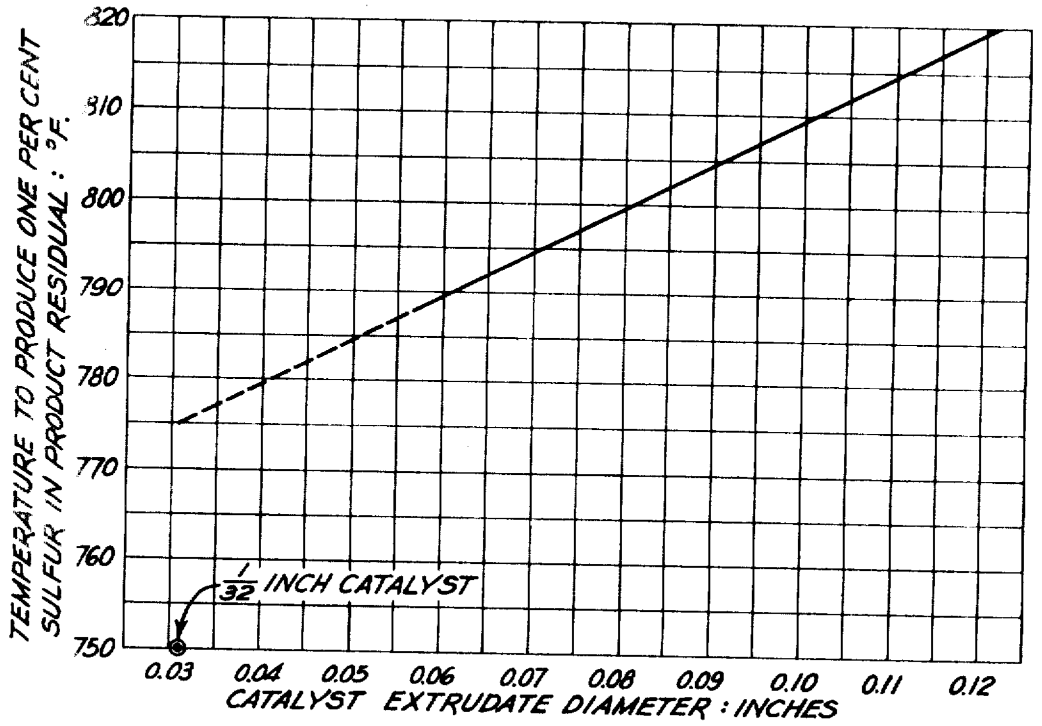


Fig. 1

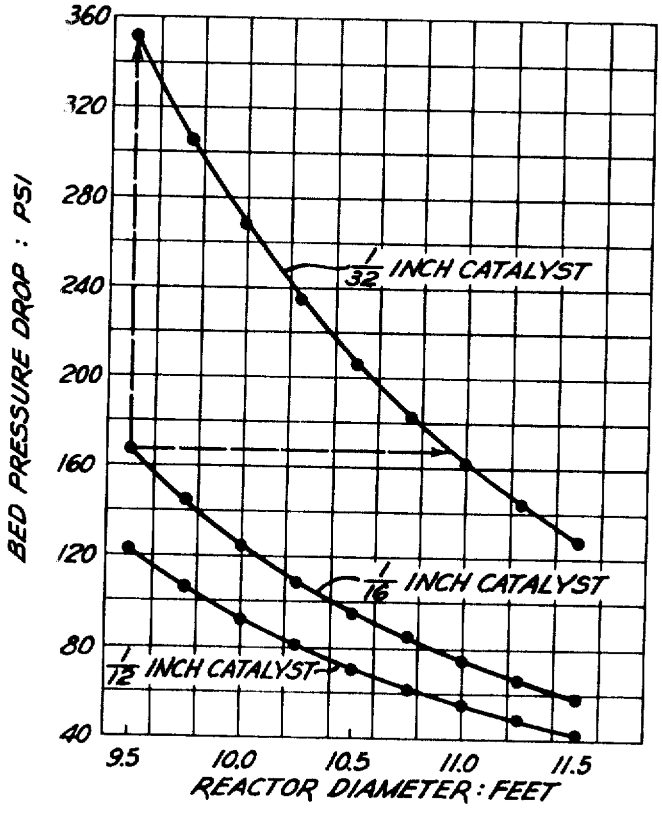


Fig. 2

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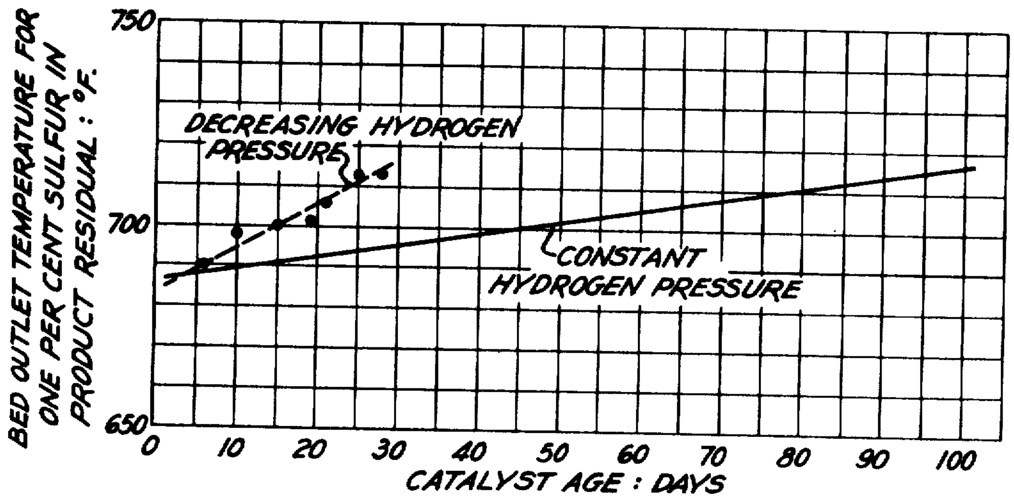

Fig. 3

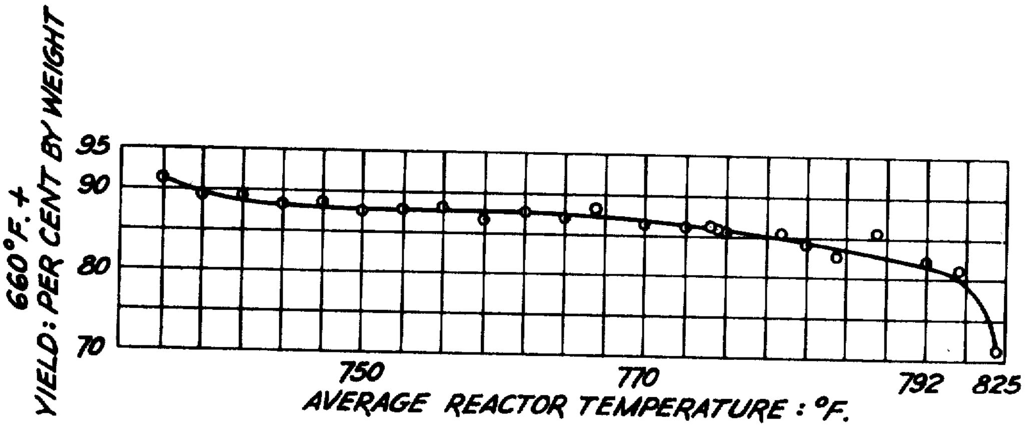

Fig. 4

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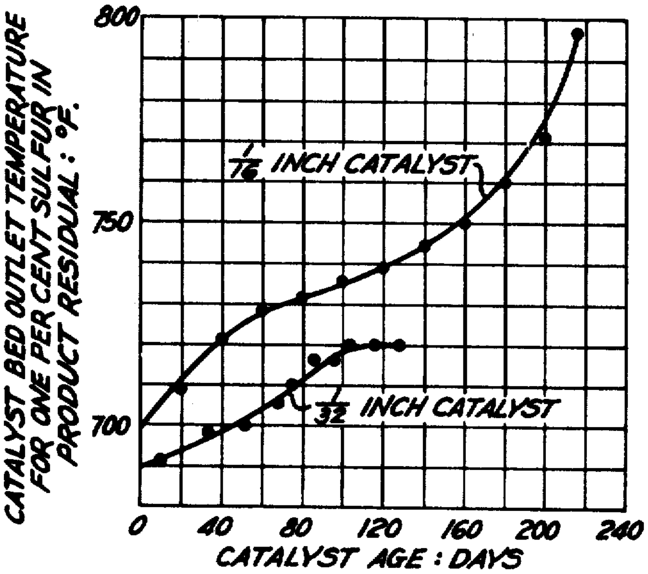

Fig. 5

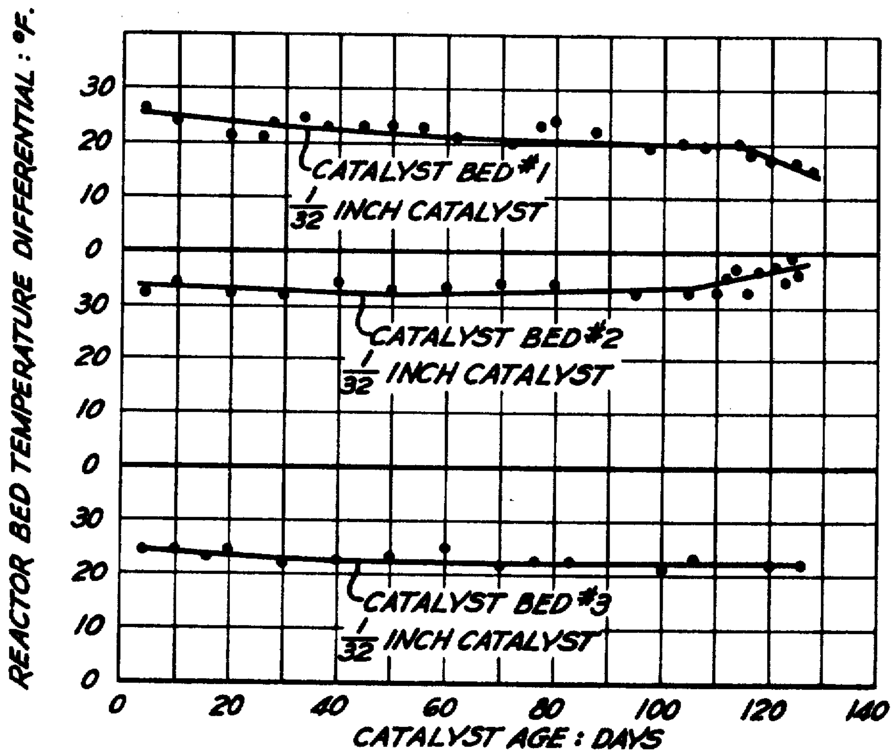

Fig. 6

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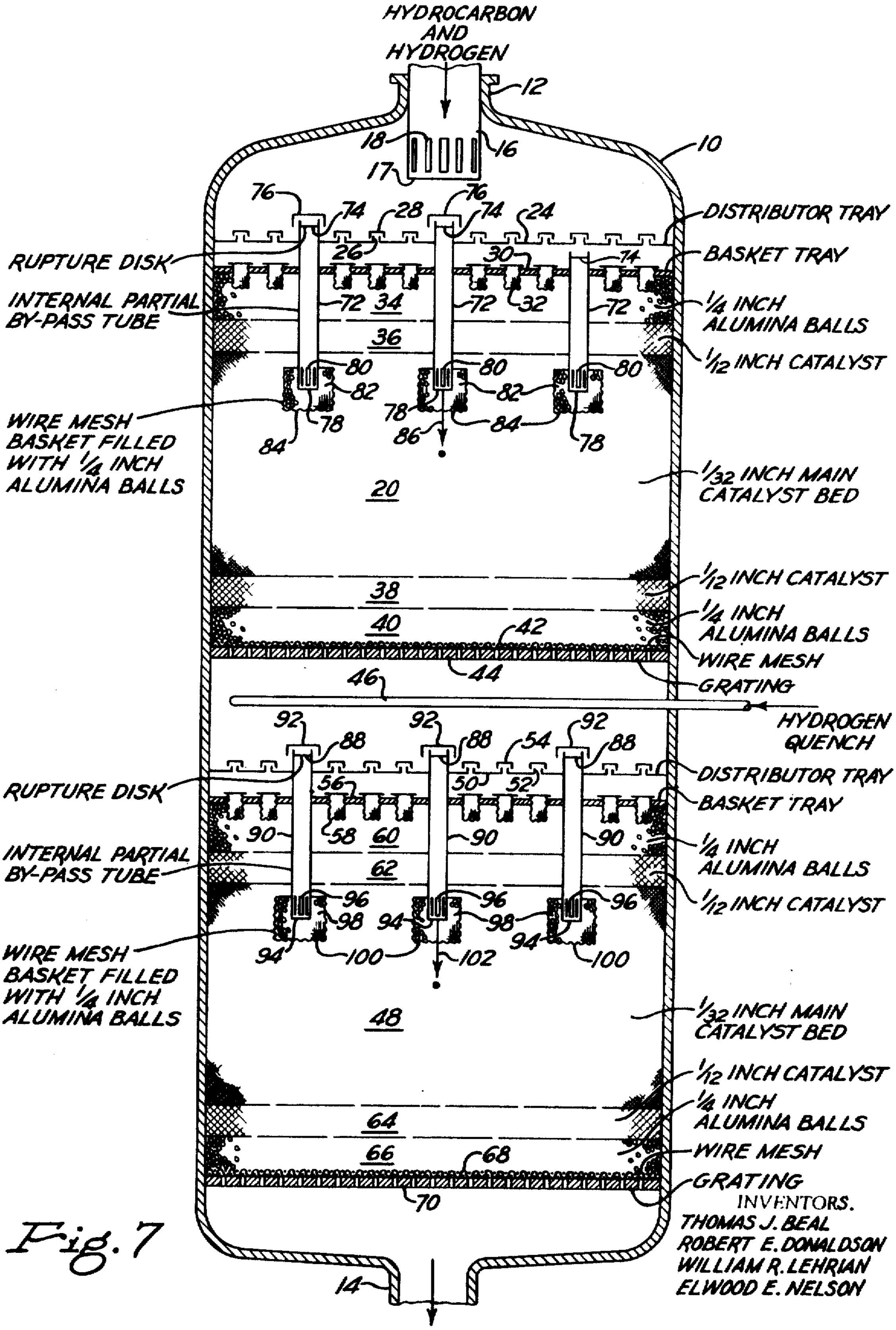

Fig. 7

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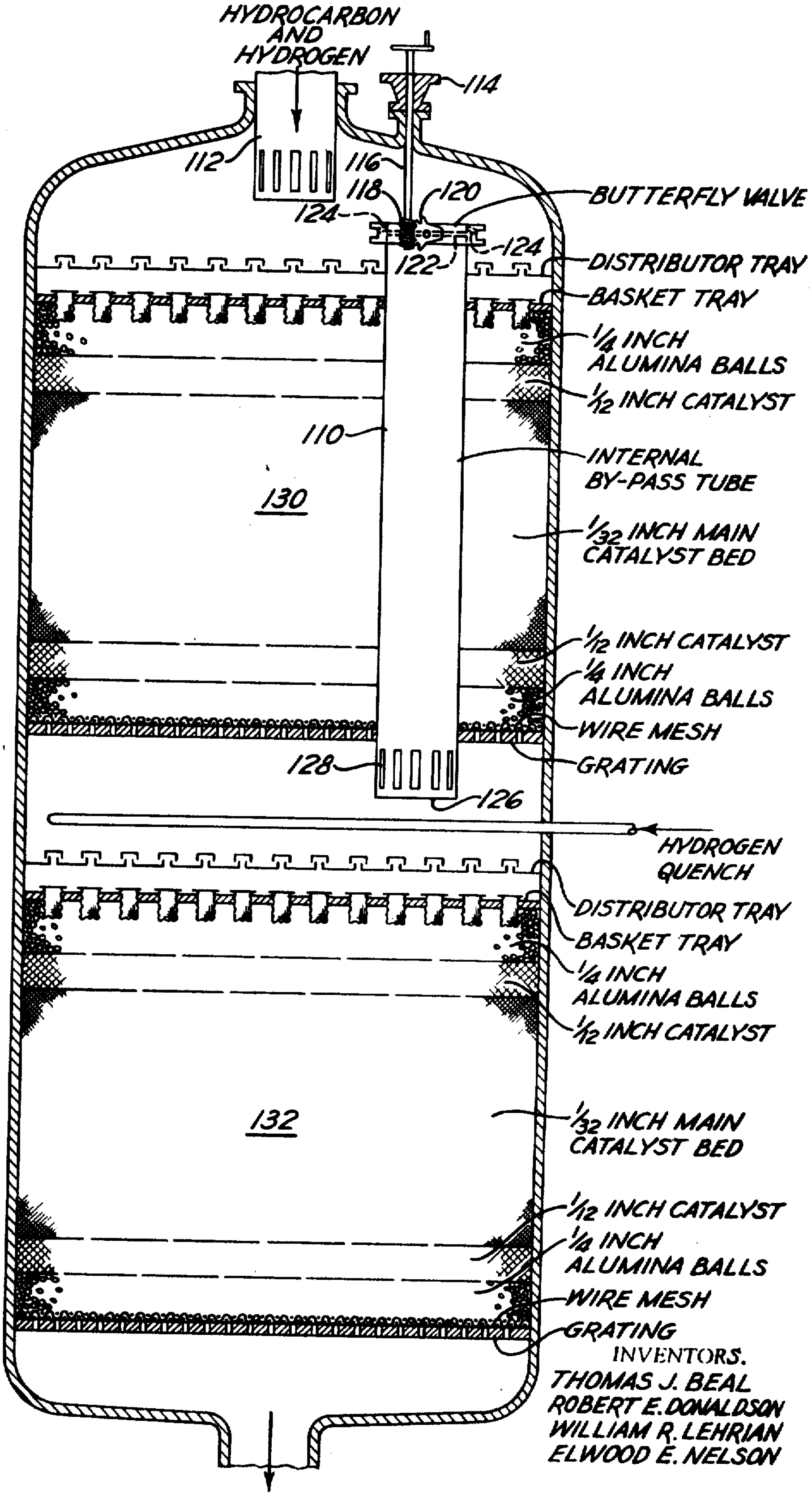

Fig. 8

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INTERNAL BYPASS FOR A CHEMICAL REACTOR

Many processes involve the passage of hydrocarbon vapors and hydrogen through a fixed nonfluid bed of catalyst. Such processes include hydrodesulfurization of oils containing the asphaltene fraction, hydrocracking of crude and other oils and hydrofining processes for the production of lubricating oils. In such processes the hydrocarbon oil charge often contains contaminative solids which are removed generally in about the top three to 10 percent of the catalyst bed, forming a crust or coke deposit layer and imparting a considerable pressure drop increase in the region of said deposit. An increase in pressure drop caused by fouling in the top of a catalyst bed limits run length or cycle time within which a unit must be shut down to remove the deposited layer.

It has not been considered desirable to alleviate the increase in pressure drop due to crust formation by utilizing a conventional external bypass arrangement because by diverting the flow of hydrocarbon and hydrogen externally around all or a portion of a catalyst bed the directional change of flow might itself impart a considerable pressure drop, in addition to greatly increasing the cost of the reactor in which it is employed and weakening the ability of the reactor to withstand high pressures. In accordance with the present invention a substantially vertical and straight normally closed standpipe or conduit means is provided which extends completely internally in a reactor vessel having a fixed catalyst bed from a position outside said bed on the inlet side thereof to a position in the interior of said bed or completely through the bed on the discharge side thereof which permits a high pressure drop bed to be partially or wholly bypassed by all or a portion of the reactants without changing the direction of flow of the reactants and without channeling the reactants outside of the reactor proper. Bypass of an entire catalyst bed can be practiced in a reactor wherein a plurality of separate catalyst beds are disposed in series within the whether The present invention can also provide bypass of only the uppermost portion of a catalyst bed so that reactants substantially without catalyst flow directly from a position on the inlet side of the bed no matter whether the inlet side is above or below the bed to a position in the interior of the bed to reduce the pressure drop across the bed. The straight-through internal bypass circuit of this invention is normally closed and can be opened manually or automatically upon occurrence of a predetermined pressure drop along a given length of reactor to permit passage of reactants substantially free of catalyst. Either a single or a plurality of parallel internal bypass circuits can be provided through a given bed. A plurality of parallel internal bypass circuits can terminate at the same or at differing positions along the length of a bed and some or all can extend entirely through the bed. Internal bypass circuits can be used in more than one bed in the same reactor.

The present invention has a particular and a very high utility in the hydrodesulfurization of a crude oil or a reduced crude oil containing the asphaltene fraction proceeds at unexpectedly low temperatures by utilizing a catalyst comprising a Group VI and Group VIII metal on alumina where the catalyst particles are very small and have a diameter between about 1/20 and 1/40 inches. It is shown below that the small size of the catalyst particles permits the use of a surprisingly low temperature to accomplish a given degree of desulfurization but at the same time the small size of the catalyst particles creates a large pressure drop. The present invention thereby has high utility in the hydrodesulfurization process as described below since it can overcome any excessive additional pressure drop increase due to deposit formation upon the small size hydrodesulfurization catalyst particles.

In its preferred embodiment the present invention relates to the use of an internal bypass method and apparatus as described in a process for the hydrodesulfurization of a crude oil or a reduced crude oil in the presence of a supported Group VI and Group VIII metal hydrodesulfurization catalyst having an exceptionally small particles size such that substantially all or a large proportion of the catalyst particles have a diameter of between about 1/20 and 1/40 inches.

Although nickel-cobalt-molybdenum is the preferred active metals combination for the hydrodesulfurization catalyst, other combinations can be utilized such as cobalt-molybdenum, nickel-tungsten and nickel-molybdenum. Alumina is the preferred supporting material but other noncracking supports can also be used as silica alumina and silica magnesia.

Hydrodesulfurization catalysts comprising supported Group VI and Group VIII metals, such as nickel-cobalt-molybdenum on alumina, having a particle size as small as the catalyst particles of the preferred embodiment of the present invention were not considered advantageous for use in a large or commercial scale because a bed comprising particles of the small size of the preferred embodiment of the present invention induces an extremely high pressure drop, which is highly deleterious to a hydrodesulfurization process which has a limited inlet pressure because the temperature required by a catalyst to accomplish a given degree desulfurization increases with loss of hydrogen pressure.

The accompanying drawings indicate graphically in:

FIGS. 1–6 various reaction conditions that are affected by the catalyst particle size.

FIGS. 7 and 8 are directed to the internal bypass apparatus of the invention for diverting the reactant stream through a catalyst reactor.

The preferred embodiment of the present invention relates to a hydrodesulfurization process in which the small particle size catalyst is utilized in a manner which manifests an unexpectedly high activity so that hydrodesulfurization of crude oil charge to any desired sulfur level, such as 1 percent sulfur level, proceeds at an unexpectedly low temperature. Although extrapolation of the initial temperature required to produce a liquid product having 1 percent sulfur content with ⅛ inch diameter and 1/6 inch diameter NiCoMo catalyst particles, which are above the size of the preferred embodiment of the invention, indicates that the temperature requirement would be lower with the small catalyst particles of the preferred embodiment of this invention it was found that the small size NiCoMo catalyst particles permit the use of a hydrodesulfurization temperature which is considerably lower than the temperature which would be expected by extrapolation of the temperature data obtained with larger size catalyst particles. Moreover, the very discovery that hydrodesulfurization with the catalyst of the preferred embodiment of the present invention could be carried out at an unexpectedly low temperature had been obscured by the extremely high pressure drop through a bed of the small size catalyst particles of the preferred embodiment of the present invention. The reason is that in a hydrodesulfurization process pressure drop itself increases the temperature requirement to achieve a given degree of desulfurization usually by an extent which equals or exceeds the temperature advantage due to the small particle size of the preferred embodiment of this invention.

It is seen that there are two unexpected features surrounding the preferred embodiment of the present invention. The first is that there is an unexpectedly great temperature advantage achievable in a hydrodesulfurization process by employing a bed of catalyst having a particle size of the preferred embodiment of the present invention. FIG. 1 (all figures are discussed in detail herein below) shows that the hydrodesulfurization temperature required to produce a residual product having 1 percent sulfur with 1/32 inch catalyst is much lower than what would be expected by extrapolation of the line connecting the data obtained with ⅛ and 1/16 inch catalyst particles even though the surface area defined by the pores of all three catalysts is about the same. The second feature is that the unexpected temperature advantage is completely disguised by the ordinary approach to its determination, i.e. by making a test in a reactor with relatively large size catalyst particles as a blank and then making a test in the same reactor under the same conditions except that the catalyst particle size is within the range of the preferred embodiment of the present invention (particle size being the only variable changed in the two tests). In this regard, the vertical dashed line in FIG. 2

shows that if a 1/16 inch catalyst, which is larger than a catalyst of the preferred embodiment of this invention, is tested in a 9.5 foot diameter reactor and then a 1/32 inch catalyst is tested in the same reactor under unchanged conditions, including an unchanged space velocity, the pressure drop in the 1/32 inch catalyst bed in the same reactor is so much greater than that for the 1/16 inch catalyst that the pressure drop increase itself would easily nullify the temperature advantage achievable because of particle size and therefore the advantage of the present invention would be completely masked. The horizontal dashed line of FIG. 2 shows that if the 1/16 inch catalyst is tested in a 9.5 foot diameter reactor a comparably pressure drop can only be achieved if the 1/32 inch catalyst is tested in an 11 foot diameter reactor, when both tests are performed at a liquid hourly space velocity of one. Therefore, it is only by making the tests in two different reactors, to equalize pressure drop, that the temperature advantage of the 1/32 inch catalyst becomes apparent. It is clear that not merely one but rather two variables must be changed to reveal the advantage of the preferred embodiment of the present invention.

The great effect of pressure drop upon temperature requirements to produce a hydrocarbon product having a 1 percent sulfur content is demonstrated by reference to FIG. 3. In FIG. 3 the solid line represents a hydrodesulfurization process having a constant hydrogen partial pressure of 1,830–1,850 p.s.i.a. The dashed line represents a decreasing hydrogen partial pressure starting with the 1,830–1,850 p.s.i.a. range and decreasing to a range of 1,720–1,740 p.s.i.a. which reduction is caused by the recycle hydrogen stream becoming progressively diluted with other gases. FIG. 3 shows that as the hydrogen partial pressure progressively decreases the temperature required to produce a 1 percent sulfur product progressively increases, so that it is considerably above the temperature required with constant hydrogen partial pressure. Since pressure drop due to flow across a catalyst bed similarly reduces partial hydrogen pressure, FIG. 3 illustrates the detrimental effect upon reaction temperature of pressure drop through a catalyst bed of the preferred embodiment of this invention.

The charge to the process of the preferred embodiment of this invention can be a full crude or a reduced crude containing substantially all of the residual asphaltenes of the full crude. The residual asphaltenes are deficient in hydrogen and comprise only about 10 percent of the charge oil but contain substantially all of the metallic components present in the crude, such as nickel and vanadium. Since the desulfurization catalyst has a greater activity for demetalization than for desulfurization, it removes nickel and vanadium for a charge stock more rapidly than it removes sulfur. These metals deposit most heavily on the outermost regions of the catalyst cross section and tend to reduce the desulfurization activity of the catalyst. Nickel and vanadium removal constitutes substantially the entire deactivation of the catalyst while sulfur and nitrogen removal contributes very little to catalyst deactivation. Furthermore, the asphaltenes comprise the highest boiling fraction of the full crude and contain the largest molecules in the crude. These large molecules are the ones least able to penetrate catalyst pores and most likely to plug these pores. The preferred embodiment of the present invention is directed towards the hydrodesulfurization of a full crude or a residual oil containing substantially the entire asphaltene fraction of the crude from which it is derived and which therefore contains 95 to 99 weight percent or more of the nickel and vanadium content of the full crude. The nickel, vanadium and sulfur content of the liquid charge can vary over a wide range. For example, a nickel and vanadium can comprise 0.002 to 0.03 weight percent (20 to 300 parts per million) or more of the charge oil while sulfur can comprise about 2 to 6 weight percent or more of the charge oil. If an oil containing smaller quantities of nickel, vanadium and sulfur is processed, such as a furnace oil, considerably lower temperature conditions, pressures as low as 1,000 pounds per square inch, lower gas circulation rates and hydrogen of lower purity than required by the preferred embodiment of this invention, will suffice to produce a liquid product containing 1 percent sulfur, and therefore the process of the preferred embodiment of the present invention will not be essential.

As the hydrodesulfurization reaction proceeds, nickel and vanadium removal from the charge tends to occur preferentially over sulfur removal. However, deposition of nickel and vanadium upon the catalyst results in a greater degree of catalyst deactivation than does sulfur removal because the removed metals deposit upon the catalyst whereas sulfur removed from the charge escapes as hydrogen sulfide gas. Low hydrodesulfurization temperatures tend to inhibit metal removal from the charge and thereby reduce catalyst deactivation. Since the hydrodesulfurization reaction is exothermic, it is important to quench the reactor to maintain a reaction temperature as low as the small catalyst size of the preferred embodiment of this invention permits to obtain the desired degree of desulfurization in order to inhibit catalyst deactivation. Unnecessarily high temperatures by encouraging catalyst deactivation will result in loss of the initial temperature advantage of the catalyst. Quenching is advantageously accomplished by dividing the total catalyst bed into a plurality of relatively small beds in series and injecting relatively cool hydrogen between the beds, as demonstrated below. It is seen that there is a high degree of interdependence between the use of a high metals content asphaltene charge, the small size catalyst particles, and the use of a quench to insure that the reactor remains at a temperature as low as the catalyst size permits.

The hydrodesulfurization process of the preferred embodiment of this invention employs conventional reaction conditions such as, for example, a hydrogen partial pressure of 1,000 to 5,000 pounds per square inch, generally, 1,000 to 3,000 pounds per square inch, preferably, and 1,500 to 2,500 pounds per square inch most preferably. Reactor design limitations usually restrict inlet pressures under the conditions of the preferred embodiment of the present invention to not more than 2,000, 2,500, or 3,000 p.s.i.g. It is the partial pressure of hydrogen rather than total reactor pressure which determines hydrodesulfurization activity. Therefore, the hydrogen stream should be as free of other gases as possible. Furthermore, since reactor design limitations restrict hydrogen inlet pressures, hydrogen pressure drop in the reactor should be held as low as possible.

The gas circulation rate can be between about 2,000 and 20,000 standard cubic feet per barrel, generally, or preferably about 3,000 to 10,000 standard cubic feet per barrel of gas preferably containing 85 percent or more of hydrogen. The mol ratio of hydrogen to oil can be between about 8:1 and 80:1. Reactor temperatures can range between about 650 and 900° F., generally, and between about 680 and 800° F., preferably. The temperature should be low enough so that not more than about 10, 15 or 20 percent of the charge will be cracked to furnace oil or lighter. At temperatures approaching 800° F. the steel of the reactor walls rapidly loses strength and unless reactor wall thickness of 7 to 10 inches or more are utilized reactor a temperature of about 800° F. constitutes a metallurgical limitation. The liquid hourly space velocity in each reactor can be between about 0.2 and 10, generally, between about 0.3 and 1 or 1.25, preferably, or between about 0.5 and 0.6 most preferably.

The catalyst employed in the hydrodesulfurization process is conventional and comprises sulfided Group VI and Group VIII metals on a support such as nickel-cobalt-molybdenum or cobalt-molybdenum on alumina. Suitable hydrodesulfurization catalyst compositions are described in U.S. Pat. No. 2,880,171 and also in U.S. Pat. No. 3,383,301. However, an essential feature of the catalyst particles is that the smallest diameter of these particles is considerably smaller than the diameter particles. The smallest diameter particles of the catalyst particles of the preferred embodiment of the present invention is broadly between about 1/20 and 1/40 inches, preferentially between 1/25 and 1/36 inches, and most preferably between about 1/29 and 1/34 inches. Lower particle sizes would induce a pressure drop which is too great to make them practical. The catalyst can be prepared so that nearly all or at least about 92 or 96 percent of the particles are within the stated range. The catalyst can be in any suitable configuration in which the smallest particle diameter is within the stated range such as roughly cubical, needle-shaped or round granules, spheres, cylindrically shaped extrudates, etc. By smallest particle diameter we mean the smallest surface to surface dimension through the center or axis of the catalyst particle, regardless of the shape of the particle. The cylindrical extrudate from having a length between about 1/10 and ¼ inches is highly suitable.

Since the asphaltene molecules which are hydrodesulfurized in accordance with the preferred embodiment of the present invention are large molecules and must enter and leave the pores of the catalyst without plugging the pores, in order to obtain good aging properties most of the pore volume of the catalyst should be in pores above 50 A. in size. Advantageously 60 to 75 percent or more of the pore volume should be in pores of 50 A. or more. Most preferably, 80 to 85 percent or more of the pore volume should be in pores above 50 A. in size. Catalyst having smaller size pores have good initial activity but poor aging characteristics due to gradual plugging of the pores by the asphaltene molecules. For example, catalyst A below exhibited good activity for about one month while catalyst B below exhibited good activity for about three months.

	Percent of pore volume			
Pore size, A.	Catalyst A		Catalyst B	
200-300	1.2	21.7	2.3	87.3
100-200	4.3		41.7	
50-100	16.2		43.3	
40-50	16.4		6.4	
30-40	22.6		5.6	
20-30	26.6		1.0	
7-20	12.5		0.0	

As indicated above, as the diameter of conventional hydrodesulfurization catalyst particles progressively decreases within a range which is above the range of the preferred embodiment of the present invention, hydrodesulfurization of a crude oil to a one percent sulfur level proceeds at progressively lower temperatures. However, the following tests show that the diminishing of catalyst diameter size to a level within the range of the preferred embodiment of the present invention results in an unexpectedly great reduction in hydrodesulfurization temperature which is much greater than indicated by the particle diameter-temperature relationship exhibited by larger size particles. However, counteracting this temperature advantage is the fact that the small catalyst particle diameters result in a large pressure drop through a catalyst bed comprising them, and this pressure drop tends to nullify the temperature advantage achievable with the catalyst of the preferred embodiment of the present invention because hydrodesulfurization temperature requirements increase as hydrogen partial pressures decrease.

Although it is expected that reduction in catalyst particle size will increase pressure drop occasioned by using a bed of catalyst particles of the size of the preferred embodiment of this invention as compared to a bed of catalyst particles only slightly larger is great within reactors having moderate diameters. As shown in FIG. 2 the increase in pressure drop occasioned by utilizing the catalyst size of the preferred embodiment of the present invention as compared to slightly higher catalyst sizes can be greatly moderated by utilizing a reactor having a very high diameter such as 10 or 11 feet or more. However, high pressure reactors having large diameters require extremely thick walls, especially under the elevated temperature conditions of the present process.

As indicated above, in the temperature vicinity of 800° F. which is required for hydrodesulfurization of crude oil or reduced crude oil a considerably metallurgical weakening occurs in the steel reactor walls. In order to guard against reactor failures to the 2,000 or 2,500+ pounds per square inch operating pressures of the process extremely thick steel walls are required, for example, a thickness of 8, 10 or 12 inches. At the reaction temperature of the preferred embodiment of this invention the required reactor wall thickness increases appreciably with relatively small increases in reactor inlet pressure. Furthermore, at any temperature or pressure of the preferred embodiment of this invention the wall thickness required also increases with reactor diameter. Therefore the excessive increase in reactor wall thickness which is required upon any increase in reactor diameter or reactor temperature exerts a practical design limitation upon maximum allowable pressure in a reactor.

The existence of a maximum pressure limitation tends to be prohibitive to the use of a hydrodesulfurization catalyst having a small diameter because a bed comprising such a small catalyst induces a very high pressure drop, diminishing still further the average pressure within the reactor, and the magnitude of this pressure drop is closely related to reactor diameter. For example, FIG. 2 shows that the pressure drop curves for 1/12 inch, 1/16 inch and 1/32 inch catalyst beds are roughly parallel at reactor diameters of 11 feet or greater. However, the pressure drop curve for the 1/32 inch catalyst is much steeper at reactor diameters less than 11 feet than the pressure drop curves for the 1/12 inch and 1/16 inch catalyst. Therefore, for a catalyst of the preferred embodiment of the present invention the diameter of the reactor within the range of conventional reactor sizes has an important effect upon pressure drop.

Since there is a practical limit on reactor inlet pressure, as explained above, due to reactor wall thickness requirements, it is important to hold pressure drop in the reactor as low as possible. In effect there is a pressure squeeze in the system in that inlet hydrogen pressure should be held down whole reactor outlet pressure should be as high as possible. Therefore, in reactors having an inlet pressure limitation of about 2,000 or 2,500 or 3,000 p.s.i.g., the diameter to depth ratio of the catalyst bed should be high enough to reduce pressure drop so that the reactor outlet pressure is not more than about 150, 250 or 350 p.s.g. lower than the inlet pressure. Control of reactor pressure differential with a high diameter to depth ratio catalyst bed is especially important in single reactor systems capable of accepting only relatively low inlet pressures. The diameter to depth ratio becomes less important in reactors which can accept relatively high inlet pressures or in parallel reactor systems wherein pressure drop can be reduced by diverting a portion of reactant flow to another reactor.

There is an additional problem relating to pressure drop arising when utilizing the very small catalyst particles that is alleviated considerably by utilizing a large diameter reactor or parallel reactors. When catalyst particles having the very small size within the range of the preferred embodiments of this invention, reactant flow through them causes them to shift and scrape against each other in a process of compaction. Scraping of particles against one another result in production of fines which further increases pressure drop. Since a catalyst bed may be in continuous operation for long periods of time, production of fines can be considerable. The use of a large diameter reactor of a parallel reactor system by permitting a greater catalyst cross section per volume of reactor flow, inhibits fines formation and thereby inhibits an increasing pressure drop across the catalyst field due to this cause.

In accordance with the preferred embodiment of the present invention a hydrodesulfurization catalyst whose diameter is between 1/20 and 1/40 inches which provides an unexpected and substantial temperature advantage due to its size but whose size also induces a large pressure drop in reactors of common or standard size which pressure drop tends to nullify said temperature advantage is arranged in a bed having a sufficiently large diameter to depth ratio to preserve the temperature advantage due to catalyst size. The catalyst can be advantageously divided into separate beds arranged in series containing a greater quantity of catalyst than its preceding bed. The total liquid charge stream comprising crude oil or reduced crude oil together with a portion of total hydrogen requirements is charged to the reactor inlet. An effluent stream comprising desulfurized liquid together with gases is withdrawn from the reactor and cooled. Liquid and gases are separated from each other in the cooled effluent stream. Impurities are removed from said effluent gases to provide a recycle hydrogen stream having an increased proportion of hydrogen. The recycle hydrogen is recycled to a plurality of positions in series in the reactor between the separate catalyst beds therein.

The diameter of the catalyst bed should be adequate to reduce the pressure drop across the catalyst bed sufficiently to permit the reaction to occur near the low temperature level permitted by the small catalyst size. The apportioning of the recycle hydrogen to separate positions in the reactor train rather than total recycle of the hydrogen to the beginning of the reactor serves to minimize overall hydrogen pressure drop in the system. Finally, the apportioning of the recycle hydrogen so that is is injected between the separate catalyst beds permits it to serve as a quench to cool the flowing stream as it passes between catalyst beds, thereby permitting reaction temperature to remain near the low temperature level permitted by the small catalyst size. In the absence of a hydrogen quench as described the temperature increase of reactants across each bed would become cumulative so that neither deep beds nor a number of beds in series could be used. Furthermore, temperatures even slightly higher than necessary are detrimental because, as shown in FIG. 4, moderate temperature elevations considerably enhance thermal cracking of liquid producing among other products light hydrocarbons gases which dilute the hydrogen stream and reduce the partial pressure of hydrogen therein.

The hydrogen quench by reducing the actual temperature also reduces the required temperature and therefore cooperates interdependently with the small catalyst particles of this invention. By lowering the temperature, the hydrogen quench reduces cracking which would consume hydrogen and produce light hydrocarbon gases leading to a lower hydrogen concentration, which in turn would reduce the hydrogen concentration, partial pressure and increase the required reaction temperature.

It is seen that the feature of catalyst beds having a high diameter to length ratio arranged as a plurality of separate catalyst beds in series and the feature recycle hydrogen injection between the separate catalyst beds function highly interdependently with respect to each other and with respect to the use of the small catalyst particle size of this invention. The small catalyst particle size permits hydrodesulfurization to occur at an unexpectedly low temperature level but imposes a high pressure drop which tends to nullify the temperature advantage. The use of a catalyst bed having a large diameter reduces the pressure drop in the liquid flow stream while the use of separated catalyst beds in series with injection of recycle hydrogen between the beds serves not only to reduce the pressure drop of the hydrogen flowing through the system but also serves to quench reactant temperature along the length of the reactor. As stated above, the quenching effect inhibits thermal cracking and thereby avoids hydrogen consumption for cracking and excessive dilution of the hydrogen stream with light hydrocarbon gases which would reduce the partial pressure of the hydrogen stream, thereby also tending to nullify the advantageous temperatures effects of the small particle size catalyst.

As shown in FIG. 2, at reactor diameters below about 11 feet, the pressure drop through the 1/32 inch catalyst bed of the present invention increases extremely rapidly with reduction in reaction diameter at the indicated space velocity. However, in the diameter range shown the pressure drops through 1/16 inch catalyst bed and 1/12 inch catalyst bed, which are both above the range of the preferred embodiment of this invention, are not nearly as sensitive to reduction in reactor diameters below 11 feet. FIG. 2 also shows that at reactor diameters above 11 feet the pressure drop through a 1/32 inch catalyst bed is not significantly more sensitive to changes in reactor diameter than are the pressure drops through the 1/12 inch catalyst beds. Therefore, there is a much more sensitive pressure drop relationship between a 1/32 inch catalyst bed of this invention at the reactor diameters shown in FIG. 2 than there is with beds of larger size catalysts particles. However, at the high temperature and pressure conditions of the hydrodesulfurization process of the preferred embodiment of this invention metallurgical requirements require reactor walls of great thickness at reactor diameters of 11 feet or more, reactor wall thickness requirements increasing with increasing reactor diameter, so that economic considerations prohibit reactor diameters much larger than 11 feet in the process of this invention. Therefore, with a 1/32 inch catalyst bed in order to accommodate charge rates which would require a reactor diameter much greater than 11 feet, it is necessary to utilize a parallel reactor system. FIG. 2 clearly indicates that at the indicated space velocity and with the reactor diameters shown a critically regarding pressure drop sensitivity arises when employing a 1/32 inch catalyst bed which is far greater than in the case of the 1/12 inch and a 1/16 inch catalyst bed.

All of the tests indicate in FIG. 2 for the various catalyst sizes were made at the same liquid hourly space velocity. Therefore, in the tests within a reactor of relatively large diameter, the catalyst bed depth was relatively shallow. In the tests within a reactor of relatively small diameter, the catalyst bed was deeper. FIG. 2 shows that in utilizing a 1/32 inch catalyst rather than a larger size catalyst, the catalyst bed configuration must provide a diameter which is sufficiently great that the pressure drop is held at a level low enough to retain the advantage of the lower hydrodesulfurization temperature possible with said catalyst. Therefore, when utilizing a bed of small size catalyst particles of the preferred embodiment of the present invention the configuration of the bed is important and the ratio of diameter to depth of the bed must be sufficient high to retain the temperature advantage of the catalyst bed.

EXAMPLE 1

A series of tests were conducted to illustrate the temperature advantage of a small particle size catalyst. These tests were conducted by employing NiCoMo on alumina catalyst of various sizes for hydrodesulfurizing at 36 percent Kuwait reduced crude from which furnace oil having an 800° F. TBP had been removed at 2000 p.s.i.a. partial pressure of hydrogen and a space velocity of 3.0 liquid volumes per hour per volume of catalyst. The charge was 78 percent desulfurized to a 1.0 percent product sulfur content. The arrangement of the reactor was such that there was no significant or readily detectable pressure drop in any of the tests. FIG. 1 shows the effect of catalyst size upon the initial temperature required to produce a product containing 1 percent sulfur. The solid line based upon initial temperature determined in tests with ⅛ inch and 1/16 inch diameter extrudate catalyst whose particles size is above the range of this invention. The dashed extrapolation of the solid line indicates that a 1/32 inch diameter extrudate catalyst would be expected to require an initial temperature of only 775° F. However, FIG. 1 surprisingly shows that 1/32 inch diameter extrudate catalyst requires an initial temperature of 750° F. It is noted that the surface area defined by the pores of all three catalyst tested is about the same. The position of the data point for the 1/32 inch catalyst is highly surprising because if the dashed line in FIG. 1 were curved downwardly towards the 1/32 inch catalyst data point the resulting curve would tend to indicate that as catalyst particle size becomes very small the activity of the catalyst becomes unlimited, which is obviously unreasonable. Therefore, the straight configuration of the dashed extension of the curve in

FIG 1 is a reasonable extrapolation of the solid line and the position of the 1/32 inch data point is highly unexpected

EXAMPLE 2

When the catalysts similar to the 1/32 inch catalyst of Example 1 except that the particle size is smaller within the range of this invention, such as 1/34 or 1/40 inches, or except that the particles size is larger within the range of this invention, such as 1/29 or 1/20 inches, are utilized under the conditions of example 1, the initial temperature in each instance to achieve hydrodesulfurization to one percent sulfur is at about the same level as that shown in FIG 1 for the 1/32 inch catalyst.

EXAMPLE 3

When the catalyst compositions other than NiCoMo on alumina, such as NiCoMo on silica alumina, CoMo on alumina, NiW on alumina, NiW on silica alumina, NiW on silica magnesia of NiMo on alumina having a particle size within the range of the preferred embodiment of this invention are utilized under the conditions of Example 1 to achieve hydrodesulfurization to 1 percent sulfur, a similar unexpected temperature advantage is realized as compared to the extrapolated temperature based on larger size particles of the same composition.

EXAMPLE 4

Tests were made which demonstrate that a 1/32 inch nickel-cobalt-molybdenum on alumina extrudate is not only capable of hydrodesulfurizing a reduced crude oil to a one percent sulfur level at a considerably lower initial temperature than a similar catalyst in the form of a 1/16 inch extrudate but also is capable of maintaining a lower hydrodesulfurization temperature with age. The tests with the 1/32 inch catalyst were based on a 0 55 liquid hourly space velocity and a hydrogen partial pressure of 1,830 pounds per square inch The reactor pressure drop was about 50 pounds per square inch The charge was 50 percent Kuwait reduced crude The reaction was preformed in a single reactor having three separate beds and recycle hydrogen gas was used as a quench after each bed. There was no separate guard chamber before the reactor The first second and third beds contained 13 3 percent, 41 6 per cent and 45 1 percent of the total catalyst respectively Typical data for the test utilizing the 1/32 inch catalyst are shown below and the general data is illustrated in FIGS 5 and 6 FIG 5 shows the aging characteristics for the entire 1/32 inch catalyst reactor as compared with a comparable aging run with a 1/16 inch catalyst reactor FIG. 6 shows the aging characteristics for the individual beds within the 1/32 inch reactor and shows that when the first bed becomes deactivated the second bed assumes a greater desulfurization load

The test utilizing the 1/16 inch nickel-cobalt-molybdenum on alumina catalyst was performed at a 1 1 liquid hourly space velocity but is illustrated in FIG 5 on a basis comparable to the 0 55 space velocity of the test made with the 1/32 inch catalyst The total pressure for the 1/16 inch catalyst teat was 2,500 pounds per square inch gauge 5,000 SCF/bbl. of gas was charged to the reactor The reactor contained four catalyst beds and recycle gas was used as a quench after each bed The average reactor temperature was increased throughout the test to maintain a 1.0 percent by weight sulfur level in the **660°** F = residual product Typical data for both the 1/32 inch and the 1/16 inch catalyst tests are shown below

	1/32 inch Catalyst	1/16 inch Catalyst
Oil Charge	Kuwait 50 per cent reduced crude	Kuwait 50 per cent reduced crude
Catalyst	1/32 inch diameter NiCoMo on alumina extrudates having 0.5 wt % nickel 1.0 wt % cobalt and 8.0 wt % molybdenum a surface area of 200 m.²/g. and a pore volume of 0.5 cc./g.	1/16 inch diameter NiCoMo on alumina extrudates
Volume, cc.	2,294	2,254
Weight, gram	1,543.0	1,768.0
Age, days this measurement	97.6	87.6
Total Throughput, Volume Oil Per Volume Catalyst	1,293	2,323
Operating Conditions		
Reactor Bed Temp (°F)(Inlet, Outlet)	694,716	
Reactor Pressure	2,050	2,519
Avg. Reactor Temp °F.	**703**	784
Space Velocity		
Vol.Hr.Vol.	0.54	1.11
Wt./Hr./Wt.	0.78	1.36
Reactor Gas Charge,		
SCF/Bbl.	4,385	4,969
Percent H_2	91	81
Makeup Gas,		
SCF/Bbl.	890	735
Percent H_2	93	95
Recycle Gas		
SCF/Bbl.	3,495	4,233
Percent H_2	89	80
Product Yields, Wt %		
Bottoms (660° F +)	91.1	84.7
Furnace Oil (380 660° F)	4.9	9.4
Naphtha (IBP 380° F)	0.8	2.2
Gas	5.4	5.4
Chemical Hydrogen Consumption		
SCF/Bbl.	476	617
Hydrogen Sulfide		
SCF/Bbl	139	127

The charge and product inspections for the test employing the 1/32 inch catalyst are as follows

	Charge	Product Bottoms
Gravity, °API	14.6	20.4
Sulfur % by wt	4.07	1.03
Nitrogen: % by wt	0.22	0.17
Carbon Residue % by wt	8.59	4.97
Nickel: p.p.m	16	5.1
Vanadium p.p.m.	55	9.3
Heat of Comb B.T.U./lb.	18,360	19,094
Distillation, Vacuum		
10% at °F	715	716
30	809	807
50		918
60		983
	CR at 995	

The 660° F + residual oil product inspections for the 1/16 inch catalyst test are as follows.

Gravity, °API	21.4
Sulfur: %	1.08
Nitrogen: %	0.17
Pour Point, D97: °F	65
Viscosity Kin. D445: CS 122° F	104.9

Table—Continued

210° F	16.36
Carbon Residue Rams D524 % by wt	4.86
Vanadium, p p m	14
Nickel, p p m	6.8
Flash Point, D93 °F	390
Distillation Vacuum D1160	
10% at °F	719
30	788
50	874
70	1,010
90	

EXAMPLE 5

Tests were made to show the effect of temperature upon liquid yield in a hydrodesulfurization process. The tests were made in a pilot plant equipped with a four-bed 2,254 cc. adiabatic reactor. Reactor charge gas was used as quench between the catalyst beds for temperature control. The charge stock passed through a cotton fiber cartridge filter before it was preheated and charged to the reactor. The filter which was at steam tracing temperature takes outmost of any solid contaminants in the feed, but does very little in removing any small or organically combined metals present in the charge stock.

The reactor effluent flowed into a high pressure separator where hydrogen-rich gas was separated from the hydrocarbon liquid. The hydrogen-rich gas was scrubbed with 3 percent to 5 percent diethanolamine and water and recycled to the reactor. After high pressure separation of high pressure hydrogen-containing gas, the liquid product flowed to distillation towers where gases, naphtha, furnace oil, and residual were removed from the unit.

The charge to the unit was a 50 percent Kuwait reduced crude. The operation was designed to produce a 660° F. + product having a 1.0 percent sulfur level. The catalyst was 1/16 inch extruded NiCoMo on alumina. The operating conditions were 2,500 pounds per square inch gauge total pressure, 1.1 liquid hourly space velocity and 5,000 SCF/Bbl of 80 percent hydrogen with recycle gas quench as required for temperature control. The results of the tests are illustrated in FIG. 4 and in the following data.

Catalyst	NiCoMo on alumina having 0.97 wt. % cobalt, 8.6 wt. % molybdenum and 0.59 wt. % nickel
Age Days at this measurement	45.9
Bbl./lb.	4.43
Space Velocity LHSV	1.1
Average Reactor Temp. °F	760
Reactor Gas	
Inlet SCF/Bbl	5,008
% H_2	82
Quench SCF/Bbl	2,920
% H_2	82
Reactor Pressure p.s.i.g.	2,500
Hydrogen Consumption, SCF/Bbl	623

Product Yields	Percent by weight
H_2S	3.4
C_1	0.2
C_2	0.1
C_3	0.2
C_4	0.2
C_5-380° F	1.5
380-460° F	1.4
460°-600° F	2.8
600°-660° F	2.5
660° F +	88.6

EXAMPLE 6

Tests were conducted to illustrate the effect of a change in hydrogen partial pressure upon the temperature required to hydrodesulfurize a reduced crude to 1 percent sulfur in the residual product. The comparative tests were performed by in one case, not recycling hydrogen containing light hydrocarbons which build up in the hydrogen stream and reduce the partial pressure of the hydrogen in the stream but instead charging to the hydrodesulfurizer only fresh hydrogen charge having a uniform hydrogen purity. In the other case, a recycle hydrogen stream which was not subjected to naphtha scrubbing to remove light hydrocarbons so that the hydrogen partial pressure therein continually decreased throughout the test was recycled to the hydrodesulfurizer. The reactor system catalyst and operating conditions for both tests are generally the same as that described in the tests of Example 4. The results are illustrated in FIG. 3. The solid line in FIG. 3 represents the test utilizing only fresh hydrogen at 1,830–1,850 pounds per square inch of hydrogen pressure. The broken line in FIG. 3 represents the test wherein non-napthta scrubbed recycle gas is recycled causing hydrogen partial pressure to continually decrease so that at the last data point shown the hydrogen partial pressure was 1,720–1,740 pounds per square inch. The following data are representative of the test represented by the broken line.

Oil charge	50 percent Kuwait reduced crude
Catalyst	1/32 inch NiCoMo on alumina
Volume, cc	2,296
Weight, gram	1,771
Age, days at time of this measurement	7 2
Throughput, Vol. Oil Per Vol. Cat	96
Reactor Bed Temp °F Inlet, Outlet)	668,690
Operating Conditions	
Reactor Pressure, p.s.i.g.	2,058
Avg. Reactor Temp. °F	676
Space Velocity	
Vol/Hr/Vol	Wt./hr./Wt.
Wt/hr/Wt	0.66
Reactor Gas Charge	
SCF/Bbl.	
4,462	
% H_2	88
Makeup Gas	
SCF/Bbl.	587
% H_2	94
Recycle Gas	
SCF/Bbl	3,874
% H_2	85
Product Yields, Wt. %	
Stripper Bottoms	92.5
Furnace Oil	4.[illegible]
Naphtha	0.6
Gas	3.7
Net Hydrogen Sulfide	
SCF/Bbl	108

	Charge Oil	Product Stripper Bottoms
Gravity: °API	15.7	20.6
Viscosity,		
SUS D2161		
100°F 4,906		2,181
210°F.	171.8	114.8
Carbon, Wt. %	84.52	85.52
Hydrogen, Wt. %	11.43	11.68
Nitrogen, Wt. %	0.20	0.17
Sulfur, Wt. %	4.06	1.11
Carbon Residue, Wt. %	8.16	5.12
Nickel, p.p.m	16	4.7
Vanadium, p.p.m	54	6.1
Heat of Combustion, B.t.u./lb.	18,423	19,908
Distillation,		

Table – Continued

	Charge Oil	Product Stripper Bottoms
Vacuum, % at °F		
5	608	654
10	674	682
20	762	750
30	829	807
40	Cr at 888	866
50		925
60		992
		Cr at 1,011

EXAMPLE 7

Simulation experiments were conducted to show the effect of catalyst particle size on pressure drop in hydrodesulfurization processes in reactors of various diameters. All tests were made with the same liquid hourly space velocity in a single bed reactor, charging a 75 percent reduced Kuwait crude, using recycle hydrogen and maintaining a hydrogen purity of 77 percent, using reactor inlet and outlet temperatures of 780 and 815° F., respectively, a reactor inlet pressure of 2,500 p.s.i.g., and a 1.0 liquid hourly space velocity. Three series of tests were made utilizing reactors of various diameters with 1/12 inch, 1/16 inch and 1/32 inch NiCoMo on alumina catalyst particles. The results are illustrated in FIG. 2.

FIGS. 7 and 8 illustrate in detail the internal bypass arrangement in a hydrodesulfurization reactor for the above-described process. FIG. 7 illustrates the use of a partial bypass arrangement employing a plurality of bypass tubes each equipped with a rupture disk. Each tube extends from above the inlet end of a catalyst bed to a position in the interior of the catalyst bed slightly below the top of the main bed portion in order to bypass the top 3 to 5 volume percent of the main catalyst bed portion wherein most of the deposit formation occurs. When the pressure drop across the deposit formation exceeds the pressure rating of the rupture disk the disk will break permitting reactants to enter directly into the interior of the catalyst bed thereby bypassing the upper layer of said bed.

FIG. 8 shows an arrangement wherein a bed is entirely bypassed by manual manipulation from the outside of the reactor of a butterfly valve which is within the reactor. The butterfly valve opens the standpipe which is shown to provide an internal bypass for reactants extending completely through an upstream catalyst bed permitting the reactants to bypass the upstream bed and directly approach a downstream bed within the same reactor. Although FIG. 8 shows the internal bypass extending completely through the upper catalyst bed it is apparent that the internal bypass of FIG. 8 can extend only partially through the upper catalyst bed and terminate in the interior of said bed as indicated in FIG. 7.

FIGS. 7 and 8 both show that the internal bypass apparatus of the present invention is capable of diverting all or a portion of a reactant stream partially or completely through a catalyst bed in a straight-through path without changing the direction of flow of the reactants and without directing the reactants outside of the reactor or in a circuitous route around any portion of the catalyst bed. Since the bypass apparatus of the present invention does not change the flow direction of the reactant stream, the bypassing portion of reactants and any nonbypassing reactant portion both travel in the same direction, that is, both have a straight-through flow pattern.

FIG. 7 shows an elongated reaction chamber **10** having an upper inlet port **12** and a lower discharge port **14**. A pipe **16** extends through inlet port **12** and is provided with elongated terminal slots **18** which provide a larger discharge area than would be provided by an open ended pipe and provide improved feed distribution, permitting the terminus of pipe **16** to be closed by plate **17**.

The reaction chambers of FIGS. 7 and 8 are provided with two separate catalyst beds comprising NiCoMo on alumina particles, although three or more beds could be employed. Where no numerical designations are shown in FIG. 8, the numerical designations of FIG. 7 can be applied to corresponding parts. FIG. 7 shows an upper main catalyst bed **20** of 1/32 inch particles and a lower main catalyst bed **48** of 1/32 inch with particles. Incoming hydrogen and hydrocarbon vapors are dispersed laterally in all directions through slots **18**, and passed through a distributor tray **24** containing a plurality of chimneys **26** each having a cover or baffle plate **28** disposed above and separated from its associated chimney to prevent liquid from dropping into the chimney but permit the passage of vapor therethrough. The distributor tray is employed to prevent channeling of incoming reactants through the catalyst bed and allow an even distribution of reactants along the entire cross section of the catalyst bed. The chimneys are provided on the distributor tray to provide surrounding low areas in which any hydrocarbon material in the liquid state can accumulate so that only gaseous material is likely to travel between the top of each chimney and its associated cover plate. Once beyond distributor tray **24**, incoming reactants will encounter basket tray **30** into which is inserted a plurality of wire mesh baskets **32** which are immersed in a bed **34** of ¼ inch alumina balls. The wire mesh baskets **32** are provided to remove any solids which might cause plugging of the main catalyst bed **20**. Bed **34** of ¼ inch alumina balls rests upon bed **36** of 1/12 inch catalyst. Beds **34** and **36** are each adapted to remove any material which might cause plugging of the main catalyst bed **20** and also to provide porous regions of relatively small pressure drop in advance of the main catalyst bed. Beds **34** and **36** also provide weight upon main catalyst bed **20** to prevent shifting of particles in the main bed which could lead to abrasion of particles in the main bed and fines formation therein, thereby increasing the pressure drop. Main catalyst bed **20** is followed by bed **38** of 1/12 inch catalyst which in turn is followed by a bed **40** of ¼ inch alumina balls which rests upon a wire mesh **42** which in turn is supported by a grating **44**.

Reactants and reaction products leave the upper catalyst bed in a heated condition due to the exothermic nature of the hydrodesulfurization reaction and are quenched by hydrogen charged through a sparger tube **46** and then continued their transit towards lower or downstream main catalyst bed **48**. The arrangement of the lower catalyst bed is substantially identical to that of the upper catalyst bed. The lower catalyst bed is provided with a distributor tray **50** and a plurality of chimneys **52** each equipped with a cover plate **54**. Beneath the distributor tray is a basket tray **56** which supports a plurality of wire mesh baskets **58**. The baskets are embedded within a bed **60** of ¼ inch alumina balls which overlies a bed **62** of 1/12 inch catalyst followed by a bed **66** of ¼ inch alumina balls which in turn rests upon a wire mesh **68** supported by a grating **70**.

The upper main catalyst bed **20** is provided with one or more vertical internal partial bypass standpipe tubes **72** each having a rupture disk **74** near the top thereof and each having a cover plate **76** above and separated therefrom, except if a rupture disk **74** is disposed below distributor tray **24**, as indicated by the right-hand standpipe in FIG. 7, no cover plate **76** is required. The bottom of each internal bypass tube **72** is enclosed by plate **78** and opens through a plurality of elongated slots **80** which provide about a 200 percent larger discharge area than the cross section of the tube and also provide better distribution of reactants in the catalyst bed. Slots **80** reduce vapor velocity without increasing pressure drop excessively in order to prevent erosion of alumina balls and catalyst. Discharge slots **80** are surrounded by a bed **82** of ¼ inch alumina balls contained in a wire mesh basket **84**.

Rupture disk **74** can be constructed to blow or rupture at any desired pressure drop between its upper surface and the lower region of the discharge of tube **72**. Also, each rupture disk can be constructed to blow at a predetermined pressure drop across the main bed such as about 50–75 p.s.i.g. Each rupture disk **74** can be constructed to break at the same pressure differential or the various rupture disks in the same catalyst bed can be constructed to break at different pressure differentials. After a disk blows, incoming vapors will flow through its associated standpipe since it constitutes a path of least resistance into the catalyst bed. If desired the bottom terminus of the various bypass standpipes can extend to the same depth in the catalyst bed **20** or to differing depths in the bed **20**. For example, the middle internal bypass tube shown in bed **20** can extend to the depth in the catalyst bed shown or it can extend to the deeper depth indicated by arrow **86**. It can also extend entirely through the bed. Generally it will only be necessary for internal bypass tubes **72** to extend about a few inches below the surface of main catalyst bed **20**, in order to avoid most of the pressure drop due to the deposit formation. The depth to which the bypass tube extends into the main catalyst bed will generally be sufficient to bypass about the top 1 to 10 percent of the bed, generally, or 2 to 5 percent of the bed, preferably, since this is the region at which most fouling is likely to occur.

If desired only the upper catalyst bed can be provided with internal bypass tubes. However, it s possible for the lower catalyst bed also to be provided with internal bypass tubes adapted so that the rupture disks therein will blow at a later time in reactor operation when and if fouling of the second bed should occur due to extensive bypassing of reactants through the first bed. Therefore, rupture disks **88** can blow when excessive deposit formation occurs at the upper region of lower main catalyst bed **48**. Lower bypass tubes **90** are generally similar to the upper internal bypass tubes **72**. Each lower bypass tube **90** is provided with a rupture disk **88** and an overhead cover **92**. The lower end of each tube **90** is enclosed by a plate **94** but is provided with elongated slot openings **96** surrounded by a bed **98** of ¼ inch alumina balls contained within a wire mesh basket **100**. The lower portion of internal bypass tubes **90** can terminate at the same depth within main catalyst bed **48** or one or more tubes can terminate at another depth, as indicated by arrow **102**. Also, all of the lower bed rupture disks **88** can be constructed to fail at the same pressure drip or they can be constructed to fail at differing pressure drops in order to stagger the extent of the internal bypass with changes in pressure drop.

Although not shown, the reactors of FIGS. 7 and 8 can be provided with pressure sensing means to determine the pressure differential between the upper portion of any catalyst bed and any point along the depth of the bed or the discharge end of the bed to determine the time at which failure of the various rupture disks an be expected to occur.

FIG 8 shows a reactor system substantially identical to that indicated in FIG. 7 except for the construction of the internal bypass apparatus. Instead of the rupture disk type of internal bypass shown in FIG. 7, FIG. 8 shows a manually operated internal bypass system which can be operated in response to the occurrence of an excessive pressure drop through the upper catalyst bed as indicated by pressure sensing or differential pressure sensing apparatus, not shown. If the pressure drop through the upstream catalyst bed increases to an excessive level, internal bypass tube **110** extending from above the catalyst bed to a position below the catalyst bed can be opened. Bypass tube **110** can provide the same cross section and velocity as feed inlet tube **112**. Internal bypass tube **110** is shown as extending entirely through the upper catalyst bed but it could extend only partially through the catalyst bed in the manner of the internal bypass tubes of FIG. 7. Internal bypass tube **110** is operated by external manual valve **114** connected to a stem **116** provided with a worm gear **118** which operates a rotating gear **120** having a common shaft with a butterfly valve **122**. Drain holes **124** are provided to drain off any liquid material falling on the upper surface of the butterfly valve. The bottom of internal bypass tube **110** is closed by means of a plate **126** but a plurality of elongated slots **128** is provided which greatly enlarges the area of discharge as compared to the cross section of the tube. Whereas the rupture disk type of control used in FIG 7 provides on-off control the manual operation of the apparatus of FIG. **8** provides either on-off or proportioning control. Although only one internal bypass tube assembly is shown in FIG. **8**, a plurality of such assemblies through the same catalyst bed could be provided to bypass reactants either partially through upstream bed **130** or completely through upstream bed **130** directly to downstream bed **132**.

We claim:

1. In a reactor containing means to retain a fixed catalyst bed therein a catalyst bed in said reactor having an upstream end and a downstream end on said means, inlet means in said reactor for admitting reactants to the upstream end of said bed for passage of said reactants through said bed, the improvement comprising an apparatus for distributing reactants within said catalyst bed said apparatus comprising conduit means, supported in said reactor and having its upper end located at a level above said upstream end of said bed and said lower end terminating in the interior off said bed, said conduit means having an upstream opening at its upper end and a downstream opening at its lower end said conduit means having closure means therein adapted to open upon an increase in pressure drop through said bed to pass fluid from said upstream end of the catalyst bed to the interior of said bed.

2. The reactor of claim **1** wherein said downstream opening comprises a bottom closure plate and lateral slots in said conduit means.

3. The reactor of claim **1** including porous means of relatively small pressure drop in the interior of said catalyst bed surrounding said downstream opening.

4. The reactor of claim **1** wherein said closure means is a rupture disk.

5. The reactor of claim **1** wherein said closure means is a valve.

6. The reactor of claim **1** including a plurality of said conduit means extending from the upstream end of the catalyst bed and terminating in the interior of the bed.

7. The reactor of claim **6** wherein the individual conduit means terminate at differing positions along the depth of the bed.

8. In a process wherein reactants are passed through a reactor containing means to retain a fixed catalyst bed therein, a catalyst bed having an upstream end which tends to acquire deposits which increase the pressure drop through said bed and a downstream end on said means, the improvement for distributing reactants within the catalyst bed which comprises actuating bypass conduit means upon an increase in pressure drop through said bed, said conduit means being supported in said reactor and extending from above the upstream end of said bed to the interior of said bed to bypass at least a portion of said reactants directly from the upstream of the catalyst bed through said conduit means to the interior of said catalyst bed.

9. The process of claim **8** wherein bypassed reactants discharge from said conduit means in a lateral direction within said bed.

10. The process of claim **8** wherein said bypass means is actuated by failure of a rupture disk in said conduit means.

11. The process of claim **8** wherein said bypass means if actuated by means of a valve in said conduit means.

12. The process of claim **8** wherein separate portions of reactants are bypassed through a plurality of conduit means each extending to the interior of said bed.

13. The process of claim **12** wherein said plurality of conduit means extend to differing depths in said bed.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,607,000 **Dated** September 21, 1971

Inventor(s) Thomas J. Beal, Robert E. Donaldson, William R. Lehrian and Elwood E. Nelson

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 36, delete "whether" and insert --reactor-- .

line 54, after "hydrodesulfurization" insert --process described below wherein hydrodesulfurization-- .

Column 2, line 34, delete "1/6" and insert --1/16-- .

Column 4, line 73, after first "diameter" insert --of conventional hydrodesulfurization catalyst -- .

line 73, after second "diameter" delete "particles" .

Column 5, line 64, after "drop" insert -- , under desulfurization conditions the increase in pressure drop -- .

Column 6, line 45, delete "p.s.g." and insert --p.s.i.g.-- .

Column 7, line 4, after "ries" insert --to form a reactor train with each succeeding bed in series/-- .

line 65, after "cracking" insert -- of liquid -- .

Column 9, line 64, delete "=" and insert --+-- .

Column 14, line 52, after "catalyst" insert -- . Below the main catalyst bed 48 is a bed 64 of 1/2 inch catalyst-- .

Column 15, line 49, delete "an" and insert --can-- .

Signed and sealed this 13th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents