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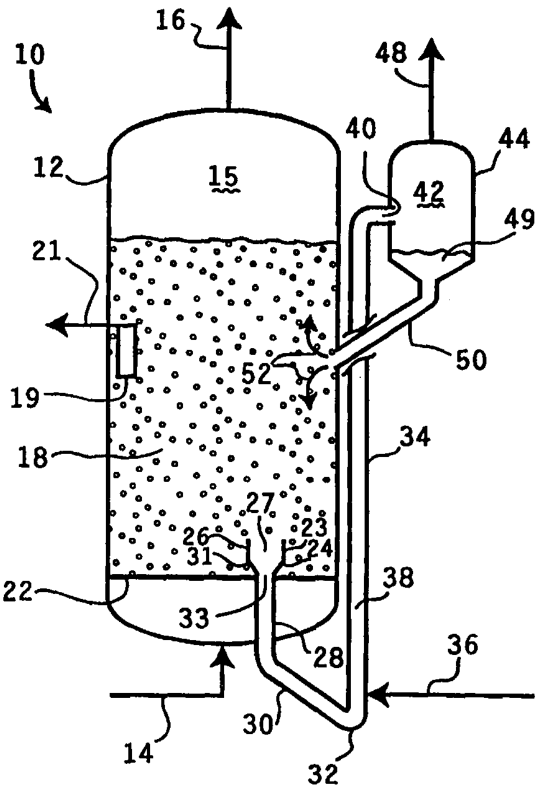
(54) Title: SLURRY HYDROCARBON SYNTHESIS PROCESS WITH CATALYST REJUVENATION IN EXTERNAL LIFT PIPE

(57) Abstract

A reversibly deactivated hydrocarbon synthesis catalyst in a hydrocarbon synthesis slurry is rejuvenated by passing the slurry into a lift pipe external of the reactor in which it contacts a hydrogen containing rejuvenating gas. The hydrogen rejuvenates the catalyst particles in the slurry and forms a mixture of a rejuvenation offgas which may contain catalyst deactivating species and a rejuvenated catalyst slurry. This mixture is passed into a gas separating and removal vessel in which the offgas is separated and removed from the slurry, which is then returned back into the reactor or elsewhere. The rejuvenating gas also acts as a lift gas to create slurry circulation up through the lift pipe and into the gas removal vessel.



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SLURRY HYDROCARBON SYNTHESIS PROCESS WITH CATALYST REJUVENATION IN EXTERNAL LIFT PIPE

BACKGROUND OF THE DISCLOSURE

Field of the Invention

The invention relates to a slurry hydrocarbon synthesis process with catalyst rejuvenation external of the reaction zone. More particularly, the invention relates to a process for rejuvenating solid catalyst particles in-situ in a three phase, Fischer-Tropsch type hydrocarbon synthesis slurry in a lift pipe external of the synthesis reactor, where the slurry comprises the catalyst particles, gas bubbles and a hydrocarbon slurry liquid.

Background of the Invention

Slurry hydrocarbon synthesis (HCS) processes are known. In a slurry HCS process a synthesis gas (syngas) comprising a mixture of H_2 and CO is bubbled up as a third phase through a slurry in a reactor in which the slurry liquid comprises hydrocarbon products of the synthesis reaction and the dispersed, suspended solids comprise a suitable Fischer-Tropsch type hydrocarbon synthesis catalyst. Reactors which contain such a three phase slurry are sometimes referred to as "bubble columns", as is disclosed in U.S. Patent 5,348,982. Irrespective of whether the slurry reactor is operated as a dispersed or slumped bed, the mixing conditions in the slurry will typically be somewhere between the two theoretical conditions of plug flow and back mixed. Syngas made from hydrocarbon feedstocks which contain nitrogen (i.e., natural gas) or nitrogen containing compounds (i.e., resids, coal, shale, coke, tar sands, etc.) invariably contains HCN and NH_3 which contaminate the reactive slurry and rapidly, but reversibly, deactivate the catalyst. Certain oxygenates and carbonaceous compounds which are formed in the slurry as by-products of the HCS reaction are also believed to cause rapid deactivation. Deactivation of such catalysts by these species is reversible and catalytic activity is restored (the catalyst rejuvenated) by contacting the deactivated catalyst with a hydrogen rejuvenating gas. The activity of the HCS catalyst in the reactive slurry may be intermittently or continuously rejuvenated by contacting the slurry with hydrogen or a hydrogen containing gas to form a catalyst rejuvenated slurry as is disclosed, for example, in U.S. Patents 5,260,239 and 5,268,344. In the process of the '239 patent rejuvenation takes place in a vessel external to the slurry reactor in which the rejuvenating gas is bubbled up through the slurry.

It has been found that the catalyst rejuvenation process produces a rejuvenation offgas as a by-product, which contains species that are catalyst deactivating. In the prior art processes, the rejuvenating offgas mixes with the slurry in the reactor or in the external vessel. Permitting the offgas to contact and mix with the slurry recontaminates it with catalyst deactivating species, thereby limiting the overall efficiency of the catalyst rejuvenation process. Therefore, it would be an improvement in the art if the catalyst could be rejuvenated in the slurry without recontaminating it with catalyst deactivating species present in the rejuvenation offgas.

SUMMARY OF THE INVENTION

The invention relates to a process for rejuvenating reversibly deactivated solid catalyst particles in-situ in a three phase hydrocarbon synthesis (HCS) slurry external of the synthesis reaction zone, with reduced contamination or recontamination of the slurry with catalyst deactivating species in the offgas produced by the catalyst rejuvenation. The process of the invention comprises passing slurry from the HCS reactor into a rejuvenation zone external of the reactor, in which it contacts a rejuvenation gas which at least partially rejuvenates the catalyst in the slurry to form a mixture of a rejuvenated catalyst slurry and a gas product (offgas) of the rejuvenation. The offgas contains species which reversibly deactivate the catalyst. This mixture is passed into a gas disengaging and separating zone to separate and remove the offgas from the slurry. The rejuvenated slurry may then be returned to the reactor. The rejuvenation zone is an external, hollow lift pipe or conduit in internal fluid communication with the slurry in the reactor. Catalyst rejuvenating gas is injected into the lift pipe in which it mixes with the slurry and at least partially rejuvenates the catalyst particles. The rejuvenating gas also serves as a lift gas to lift the gas and slurry up through and out of the lift pipe and into the gas disengaging and separating zone. The gas disengaging and separating zone is a separate vessel, also external of the HCS reactor. The disengaged and separated offgas is removed from the upper portion of the vessel and sent to further processing or disposal, while the rejuvenated catalyst slurry, reduced in offgas content, is removed from the lower portion of the vessel and returned to the reactor via a slurry conduit. Reactive slurry from the HCS reactor is passed into the lift pipe or external rejuvenating zone by means of a gas disengaging downcomer, as is disclosed in the prior art, to remove at least a portion of the CO containing gas bubbles from the slurry before it enters the rejuvenation zone. Unlike the prior art external rejuvenation process, the use of an external lift pipe enables the downcomer slurry entrance to be located further down in the reactive slurry where the catalyst concentration is typically greater, since slurry circulation through the lift pipe occurs as a result of the lifting action of the gas and not solely by gravity. It is beneficial to remove as much unreacted CO containing synthesis gas as possible from the reactive slurry before it contacts the rejuvenating gas, as it has been found that the presence of CO in the slurry hinders catalyst rejuvenation until the CO has been consumed. In the context of the invention, the expressions “rejuvenated slurry” and “rejuvenated catalyst slurry” are used interchangeably and mean an HCS slurry in which the catalyst particles have been at least partially rejuvenated. By rejuvenated is meant the restoration of at least a portion of the catalytic activity for forming hydrocarbons from a synthesis gas (syngas) feed comprising a mixture of H_2 and CO.

In an embodiment with specific regard to a slurry HCS process, the process of the invention comprises the steps of:

(a) contacting a syngas comprising a mixture of H_2 and CO in the presence of catalyst deactivating species with a solid particulate hydrocarbon synthesis catalyst in a slurry body comprising said catalyst, hydrocarbon slurry liquid and gas bubbles, under reaction conditions effective to form hydrocarbons from said syngas, at least a portion of which are liquid at said reaction conditions, wherein said species present in said syngas reversibly deactivate said catalyst in said slurry;

(b) passing a portion of said slurry from said slurry body through a gas disengaging zone to remove CO containing gas bubbles from said slurry and form a gas reduced slurry;

(c) passing said gas reduced slurry into a catalyst rejuvenation zone external of said slurry body;

(d) passing a gas comprising a catalyst rejuvenation gas into said catalyst rejuvenation zone in which said gas contacts said slurry to at least partially rejuvenate said catalyst therein to form (i) a rejuvenated catalyst slurry and (ii) a rejuvenating offgas which contains species which will deactivate said catalyst and wherein said gas also acts as a lift gas in said zone;

(e) passing said rejuvenated catalyst slurry and offgas into a gas separating and removal zone external of said slurry body in which said offgas is disengaged and separated from said slurry to form an offgas lean rejuvenated catalyst slurry, and

(f) passing said offgas lean rejuvenated catalyst slurry back into said slurry body.

As mentioned above, the rejuvenation zone comprises a vertical lift pipe which passes the slurry and offgas into a gas separation and removal vessel passes the rejuvenated slurry back into the HCS reactor or other vessel. The slurry reactor may be operating during rejuvenation or it may be taken off-line and batch rejuvenated. The rejuvenation may be conducted either continuously or on an intermittent basis. When rejuvenation occurs while the HCS reactor is on-line and producing hydrocarbon liquids, a portion of these liquids are either continuously or periodically withdrawn from the reactor. These liquids are further processed into useful products.

The process of the invention avoids contaminating or recontaminating either or both the rejuvenated catalyst slurry and the slurry in the reactor with the deactivating offgas species formed by the catalyst rejuvenation, and provides more efficient offgas disengagement and removal than the prior art processes. It also enables better control of the rejuvenating temperature, because the rejuvenation zone is not immersed in the slurry or in the HCS reactor. In the context of the invention, the term "catalyst deactivating species" is meant to include species which reversibly deactivate the catalyst and wherein the catalyst activity is restored (the catalyst rejuvenated) by contact with a rejuvenating gas in-situ in the slurry liquid. Hydrogen or a hydrogen containing gas is useful for such rejuvenation, as has been demonstrated in the prior art. Finally, while HCN, NH_3 and certain types of oxygenates and carbonaceous materials will deactivate the catalyst , the invention is not intended to be limited to use only with these species, but is useful with any species which reversibly deactivate the catalyst and wherein the catalyst activity can be restored with an appropriate rejuvenating gas. Yet another advantage of the invention resides in the ability to achieve slurry circulation between the reactor, lift pipe, offgas disengaging and separating vessel and back into the reactor as a result of the lifting action of the rejuvenating gas in the lift pipe and by gravity. In this embodiment no slurry pumps are used or required. Finally, it will be appreciated that while the practice of the invention finds particular use with rejuvenating an HCS catalyst in-situ in a hydrocarbon slurry liquid, it is not intended to be limited to this particular embodiment.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic cross section of an HCS slurry reactor with an external lift pipe gas rejuvenator and gas separating zone useful for practicing the process of the invention.

Figure 2 schematically represents an outboard rejuvenation process of the prior art in which the catalyst is rejuvenated in an outboard vessel.

DETAILED DESCRIPTION

In a Fischer-Tropsch slurry HCS process, a syngas comprising a mixture of H_2 and CO is bubbled up into a reactive slurry in which it is catalytically converted into hydrocarbons and preferably liquid hydrocarbons. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but which is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5. The stoichiometric mole ratio for a Fischer-Tropsch HCS reaction is 2.0, but there are many reasons for using other than a stoichiometric ratio as those skilled in the art know and a discussion of which is beyond the scope of the present invention. In a slurry HCS process the mole ratio of the H_2 to CO is typically about 2.1/1. The syngas may be formed by various means, including contacting a hot carbonaceous material such as coke or coal, with steam, or from a feed comprising methane. A feed comprising methane is preferred for convenience, cleanliness and because it doesn't leave large quantities of ash to be handled and disposed of. The methane containing gas feed is fed into a syngas generator and is obtained from natural gas or by burning coal, tar, liquid hydrocarbons and the like. The production of syngas from methane by either partial oxidation, steam reforming or a combination thereof is well known as is disclosed, for example, in U.S. patent 4,888,131. In many cases it is preferred to catalytically partially oxidize and steam reform the methane in a fluid bed syngas generating unit (FBSG) as is disclosed, for example, in U.S. Patents 4,888,131 and 5,160,456. Irrespective of the source of the methane, nitrogen or nitrogen containing compounds are typically present in the methane containing gas fed into the syngas generator, some of which are converted into NH_3 and HCN during the syngas formation. These will deactivate a Fischer-Tropsch HCS catalyst, particularly those comprising Co as the catalytic metal, and it is difficult and expensive to remove them to the extent that they are not present in amounts that will not result in catalyst deactivation over reasonable periods of time. It has been found that deactivation by these species is reversible and the catalyst can be rejuvenated by contacting it with hydrogen. This restoration of the catalytic activity of a reversibly deactivated catalyst is referred to as catalyst rejuvenation. However, while preferred and possible, complete restoration of the catalytic activity for all of the catalyst particles in the slurry passing through the rejuvenation tube may not always be achieved in the process of the invention. It's for this reason the expression "at least partially rejuvenates the catalyst" and the like, are used herein. It has been found that the rejuvenation process produces a rejuvenation product gas, which has been referred to herein as a rejuvenation offgas, and that this offgas contains some of the same catalyst deactivating species present in the syngas which resulted in the catalyst deactivation in the first place (e.g., NH_3 and HCN). Therefore it is important to remove the offgas from the rejuvenated slurry before it is passed back into the main slurry body in the HCS reactor to avoid recontaminating the reactive slurry with the catalyst deactivating species. The net effect can be that very little benefit is gained by the rejuvenation process and, consequently, a way had to be found to remove the offgas from the rejuvenated slurry in a manner which did not result in recontamination of the reactive HCS slurry with the catalyst deactivating species. The present invention is a solution to this problem.

The presence of CO in the rejuvenation zone hinders catalyst rejuvenation until the CO is consumed. Thus, removing at least a portion of the gas bubbles which contain unreacted syngas from the slurry before it is passed into the rejuvenation zone, substantially reduces the amount of CO present in the rejuvenation zone. This reduces the amount of hydrogen needed for the rejuvenation and results in a greater degree of rejuvenation. Further, due to the injection of the hydrogen or hydrogen containing rejuvenation-lift gas into the rejuvenation zone, the H_2 to CO ratio in the rejuvenation zone is substantially greater than the stoichiometric 2.1/1 and may be higher than 10/1. This means that instead of being converted to more desirable liquid hydrocarbon products, the CO in the rejuvenation zone is converted primarily to methane, thereby wasting valuable syngas and some of the added hydrogen rejuvenating gas. These gas bubbles also contain gas reaction products of the HCS reaction, of which 50 % or more may be water vapor, which interferes with the catalyst rejuvenation by acting as a diluent for the rejuvenation gas. Reacting CO with H_2 is exothermic. Reacting out the CO with H_2 in the rejuvenation zone, instead of at least partially removing the gas bubbles from the slurry before it passes into the rejuvenation and contacts the hydrogen or hydrogen containing rejuvenation gas, increases the slurry temperature. This also favors methane production from the CO and tends to promote hydrogenolysis and cracking of the hydrocarbon liquid to lighter products, such as methane. For these reasons it is beneficial to remove as much of the gas bubbles as is possible from the slurry before it is rejuvenated.

One embodiment of the invention is illustrated in schematic cross section in Figure 1 in which a slurry type HCS reactor 10, comprising a cylindrical steel vessel 12 containing a three phase slurry 18 within, a gas feed line 14 for feeding the syngas feed into the bottom of the reactor, and a gas product line 16 at the top for removing gas products of the Fischer-Tropsch type HCS reaction and unreacted syngas which rise up out of the slurry and collect in gas space 15. The slurry comprises hydrocarbon liquid in which is dispersed and suspended a particulate HCS catalyst and gas bubbles. The slurry liquid comprises HCS reaction products which are liquid at the slurry reaction conditions and the gas bubbles comprise the uprising syngas, along with gas products of the HCS reaction, a significant amount of which comprises steam or water vapor. The syngas is bubbled up into the bottom of slurry 18 through suitable gas distribution means located across the surface of an otherwise gas and liquid impermeable tray 22, located near the bottom of the reactor. A hydrocarbon liquid product withdrawal means 19, such as a filter, is located within the main slurry body 18 for withdrawing liquid hydrocarbon products from the reactor, via line 21. A gas disengaging downcomer 24 includes a substantially vertical, hollow conduit 28 which opens at its top into a vertically extending and upward opening gas disengaging means 26, for disengaging gas bubbles from the slurry. Means 26 also concentrates catalyst particles in the slurry liquid flowing down and out opening 33 into vertical, hollow downcomer conduit 28. Conduit 28 exits the reactor and extends laterally over as an angled transverse portion 30, which turns upward at its bottom 32 into lift pipe 34 and is in fluid communication with the interior catalyst rejuvenating zone 38 of the lift pipe. The gas disengaging and catalyst concentrating means 26 comprises an upwardly opening hollow cup having a cylindrical, vertical outer wall 23 and a sloping bottom 31 which define an interior gas disengaging and catalyst concentrating zone, indicated as 27. However, it could have a rectilinear, curvilinear or polygonal outer wall. The essential features of means or cup 26 include the upwardly opening gas disengaging and (optionally) catalyst concentrating zone 27, surrounded by peripheral wall 23, sloping bottom 31 and bottom orifice or slurry exit 33. The angle of the sloping bottom is greater than the angle of internal friction of the catalyst particles, so that catalyst particles disengaged from the slurry don't build up on the bottom. The cup must be open at the top to permit slurry to enter and, at the same time, permit disengaged gas to exit. Wall 23 and bottom 31 prevent the upwardly rising gas bubbles, indicated by small circles, from entering up into the slurry in the cup to permit gas disengagement and, if desired, concentrate the catalyst. It is also sized so as to provide enough residence time for the slurry flowing therethrough to achieve a more quiescent, preferably laminar downward flow, to permit maximum coalescence and release of the gas bubbles in the slurry, before it flows down into the vertical downcomer 28. This permits the suspended catalyst particles to drop out and concentrate in the slurry liquid entering the downcomer through opening 33, which is smaller than the opening at the top of the cup which is both the slurry entrance and the disengaged gas exit. That is, the horizontal cross section of the gas disengaging cup is significantly larger than that of the orifice in the bottom of the cup, to achieve a greater net concentration of catalyst in the downcomer than in the main slurry body 18. The increased catalyst concentration is due in part to the release of the gas bubbles which results in a denser slurry having a net greater catalyst content than in the main slurry body 18. Further, while there is considerable turbulence in the slurry bed 18, slurry just above zone 27, but not in the cup, will also drop catalyst, due to a decreased amount of uprising gas bubbles present immediately above the zone which serve to keep the catalyst particles in suspension. As shown in the Figure, the bottom of downcomer 28 exits the slurry and the reactor and bends laterally over as transverse portion 30 which turns upward at its bottom 32 into hollow lift pipe 34, the interior 38 of which is the catalyst rejuvenating zone. Thus, reactive slurry from the slurry body 18 in the reactor 10 flows down into the gas disengaging and catalyst concentrating zone 27 of the downcomer 24, in which the slurry disengages gas bubbles to form a gas reduced slurry and, at the same time concentrates the catalyst if desired, so that the slurry flowing down and out of the cup or zone 27 via orifice 31 and into downcomer conduits 28 and 30, is both gas reduced and catalyst concentrated, compared to the slurry in the main slurry body 18 from which the slurry is withdrawn. Although concentrating the catalyst in the gas depleted slurry fed into the lift pipe may be optional in some embodiments, it is a preferred embodiment in the practice of the invention when used with a three phase HCS slurry. The gas reduced and catalyst concentrated slurry then passes down the downcomer conduit, out of the reactor, over and up into the interior, catalyst rejuvenating zone 38, of lift pipe 34. Rejuvenating gas comprising hydrogen is passed, via line 36, into the interior 38 of lift pipe 34 near the bottom thereof, in which it contacts the catalyst in the gas reduced slurry liquid to at least partially rejuvenate it and form a rejuvenated catalyst slurry and rejuvenating offgas. The rejuvenating gas also acts as a lift gas to lift the slurry containing the rejuvenated catalyst up, over and out of the upper opening 40 and into gas disengaging and separating zone 42 in vessel 44. In gas separating zone 42, the offgas is separated from the slurry and removed via gas line 54. This offgas, rich in hydrogen, is consumed as fuel or sent to further processing to clean up the gas by removing the catalyst deactivating species and form a clean gas of which all, or a portion, may be used in other processing or recycled back into the bottom of the lift pipe as catalyst rejuvenating gas. The catalyst rejuvenated slurry from which the offgas has been removed, falls down into the bottom portion 48 of the outboard vessel 44 in which it is illustrated as 49, and from there it flows down through a hollow conduit or pipe 50, and back into the main slurry body 18 in reactor 10, in which it mixes with the reactor slurry body. While the outboard or external slurry catalyst rejuvenation means used to describe the process of the invention is shown as a hollow conduit or lift pipe, there are other embodiments in which the lift pipe may be vertically baffled into a plurality of vertically rising catalyst rejuvenation zones, into each of which is injected catalyst rejuvenating-lift gas.

Figure 2 represents an outboard slurry rejuvenation process of the prior art as disclosed in U.S. Patent 5,260,239, in which an HCS slurry reactor 60 comprising a cylindrical shell 62 contains a three phase slurry 61 within which comprises catalyst particles and gas bubbles dispersed and suspended in a slurry liquid. One or more gas disengaging downcomers for reducing catalyst maldistribution, of which only one (64) is shown for the sake of convenience, comprise an upper gas disengaging and catalyst concentrating cup from which depends a vertical downcomer pipe 68. This gas disengaging downcomer is of the type disclosed and claimed in U.S. Patent 5,382,748. Slurry liquid removal means 70, such as a filter, removes liquid products of the HCS reaction from the reactor via line 71. Feed gas line 72 feeds a syngas into the bottom of the reactor which is distributed up into the slurry via a plurality of gas distributing means arrayed across an otherwise gas and liquid impermeable tray 76. The top of the reactor comprises a gas collecting zone 80 from which gas is removed from the reactor via line 74. Another downcomer, 82, is shown also comprising a gas disengaging and catalyst concentrating cup 83 at the top of a hollow conduit which depends generally vertically downward from the cup, bends down and over out of the reactor and into catalyst rejuvenation vessel 84, into which it feeds a gas depleted and catalyst concentrated slurry from the slurry body 61 in the reactor. Catalyst rejuvenation vessel 84 comprises a cylindrical outer shell 86, one or more catalyst distributing downcomers, of only one is shown (88) for the sake of convenience, for maintaining a more even, vertical catalyst concentration in the vessel. It also contains a one or more downcomers, of which only one (90) is shown for the sake of convenience, which returns rejuvenated slurry back into reactor 60. Vessel 84 has an interior gas collecting zone 94 proximate the top of the vessel and gas is removed therefrom via gas line 96. One or more gas disengaging and catalyst concentrating downcomers 82 in HCS reactor 60 feed gas reduced and catalyst concentrated slurry, in which the catalyst is at least partially reversibly deactivated, from the reactor into catalyst rejuvenation vessel 84 via one or more orifices 98. In vessel 84 the gas reduced and catalyst concentrated slurry is contacted with a catalyst rejuvenating gas comprising hydrogen introduced into the bottom of the vessel via line 92, and bubbles up through the slurry 100 in the vessel, through suitable gas distribution means in an otherwise gas and liquid impermeable tray 87. The rejuvenating gas at least partially restores the activity of the catalyst particles in the slurry, a portion of which continuously passes into the gas disengaging zones of the one or more downcomers 90 which return the slurry back into the reactor. Rejuvenating offgas removed from the catalyst rejuvenated slurry contacts the slurry in the rejuvenation vessel.

The hydrogen or hydrogen containing catalyst rejuvenation gas injected into the rejuvenation zone comprises hydrogen which may contain other gasses such as nitrogen, CO_2, H_2O, CH_4, C_2-C_{4+} hydrocarbons, and also CO (as long as the mole ratio of the H_2 to CO) is sufficient to remove the CO and still rejuvenate at least a portion of the catalyst. In one embodiment referred to above, all or a portion of the hydrogen containing rejuvenating offgas may be recycled back into the rejuvenation zone, after it has been treated to remove catalyst poisons such as oxygenates and nitrogen compounds referred to above. This can be done physically in one or more solid adsorbent beds, by cooling and dissolving in water, etc.

As disclosed in U.S. Patent 5,288,673, the degree of catalyst rejuvenation can be controlled by independently controlling the slurry temperature in the rejuvenating zone irrespective of the temperature of the main body of slurry in the surrounding HCS reaction zone. This patent discloses that temperature control in the rejuvenation zone or tubes is achieved by one or more of either increasing or decreasing the slurry residence time in the zone, so as to utilize the exothermic nature of the rejuvenation reactions, by insulating the rejuvenation tubes, by introducing heat or a cooling medium into the zone, by preheating the rejuvenating gas, etc. The '673 patent teaches that the temperature in the rejuvenation zone should be high enough to remove CO and at least partially rejuvenate the catalyst and low enough to minimize methane formation and wax ($\sim C_{20+}$ alkanes) hydrogenolysis. These teachings apply to the present invention also.

In an HCS process, liquid and gaseous hydrocarbon products are formed by contacting a syngas comprising a mixture of H_2 and CO with a suitable Fischer-Tropsch type HCS catalyst, under shifting or non-shifting conditions and preferably under non-shifting conditions in which little or no water gas shift reaction occurs, particularly when the catalytic metal comprises Co, Ru or mixture thereof. Suitable Fischer-Tropsch reaction types of catalyst comprise, for example, one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru and Re. In one embodiment the catalyst comprises catalytically effective amounts of Co and one or more of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. Preferred supports for Co containing catalysts comprise titania, particularly when employing a slurry HCS process in which higher molecular weight, primarily paraffinic liquid hydrocarbon products are desired. Useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be found, for example, in U.S. Patents 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674.

The hydrocarbons produced by an HCS process according to the invention are typically upgraded to more valuable products, by subjecting all or a portion of the C_{5+} hydrocarbons to fractionation and/or conversion. By conversion is meant one or more operations in which the molecular structure of at least a portion of the hydrocarbon is changed and includes both noncatalytic processing (e.g., steam cracking), and catalytic processing (e.g., catalytic cracking) in which a fraction is contacted with a suitable catalyst. If hydrogen is present as a reactant, such process steps are typically referred to as hydroconversion and include, for example, hydroisomerization, hydrocracking, hydrodewaxing, hydrorefining and the more severe hydrorefining referred to as hydrotreating, all conducted at conditions well known in the literature for hydroconversion of hydrocarbon feeds, including hydrocarbon feeds rich in paraffins. Illustrative, but nonlimiting examples of more valuable products formed by conversion include one or more of a synthetic crude oil, liquid fuel, olefins, solvents, lubricating, industrial or medicinal oil, waxy hydrocarbons, nitrogen and oxygen containing compounds, and the like. Liquid fuel includes one or more of motor gasoline, diesel fuel, jet fuel, and kerosene, while lubricating oil includes, for example, automotive, jet, turbine and metal working oils. Industrial oil includes well drilling fluids, agricultural oils, heat transfer fluids and the like.

It is understood that various other embodiments and modifications in the practice of the invention will be apparent to, and can be readily made by, those skilled in the art without departing from the scope and spirit of the invention described above. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the exact description set forth above, but rather that the claims be construed as encompassing all of the features of patentable novelty which reside in the present invention, including all the features and embodiments which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

CLAIMS:

1. A slurry hydrocarbon synthesis process for forming hydrocarbons comprising:

(a) contacting a synthesis gas comprising a mixture of H_2 and CO in the presence of catalyst deactivating species with a solid particulate hydrocarbon synthesis catalyst in a slurry body comprising said catalyst and gas bubbles in a hydrocarbon slurry liquid, under reaction conditions effective to form hydrocarbons from said syngas, at least a portion of which are liquid at said reaction conditions, wherein said species present in said synthesis gas reversibly deactivate said catalyst in said slurry;

(b) passing a portion of said slurry from said slurry body through a gas disengaging zone to remove CO containing gas bubbles from said slurry and form a gas reduced slurry;

(c) passing said gas reduced slurry into a catalyst rejuvenation zone external of said slurry body;

(d) passing a gas comprising a catalyst rejuvenation gas into said catalyst rejuvenation zone in which said gas contacts said slurry to at least partially rejuvenate said catalyst therein to form (i) a rejuvenated catalyst slurry and (ii) a rejuvenating offgas which contains species which will deactivate said catalyst and wherein said gas also acts as a lift gas in said zone, and

(e) passing said rejuvenated catalyst slurry and offgas into a gas separating and removal zone external of said slurry body in which said offgas is disengaged and separated from said slurry to form an offgas lean rejuvenated catalyst slurry.

2. A process according to claim 1 wherein said offgas lean rejuvenated catalyst slurry is passed back into said slurry body.

3. A process according to claim 2 wherein said catalyst comprises at least one supported Group VIII metal.

4. A process according to claim 3 wherein said rejuvenation gas comprises hydrogen.

5. A process according to claim 4 wherein said metal comprises cobalt.

6. A process according to claim 5 wherein said gas disengaging zone is immersed in said slurry body.

7. A process according to claim 6 wherein a portion of said liquid hydrocarbons are withdrawn from said slurry body.

8. A process according to claim 7 wherein at least a portion of said hydrocarbons formed from said synthesis gas are upgraded by one or more conversion operations to at least one more valuable product.

9. A process according to claim 8 wherein said catalyst further includes titania.

10. A process according to claim 8 wherein said slurry body comprises a reactive slurry in a hydrocarbon synthesis reactor and wherein said rejuvenation zone is external of said reactor.

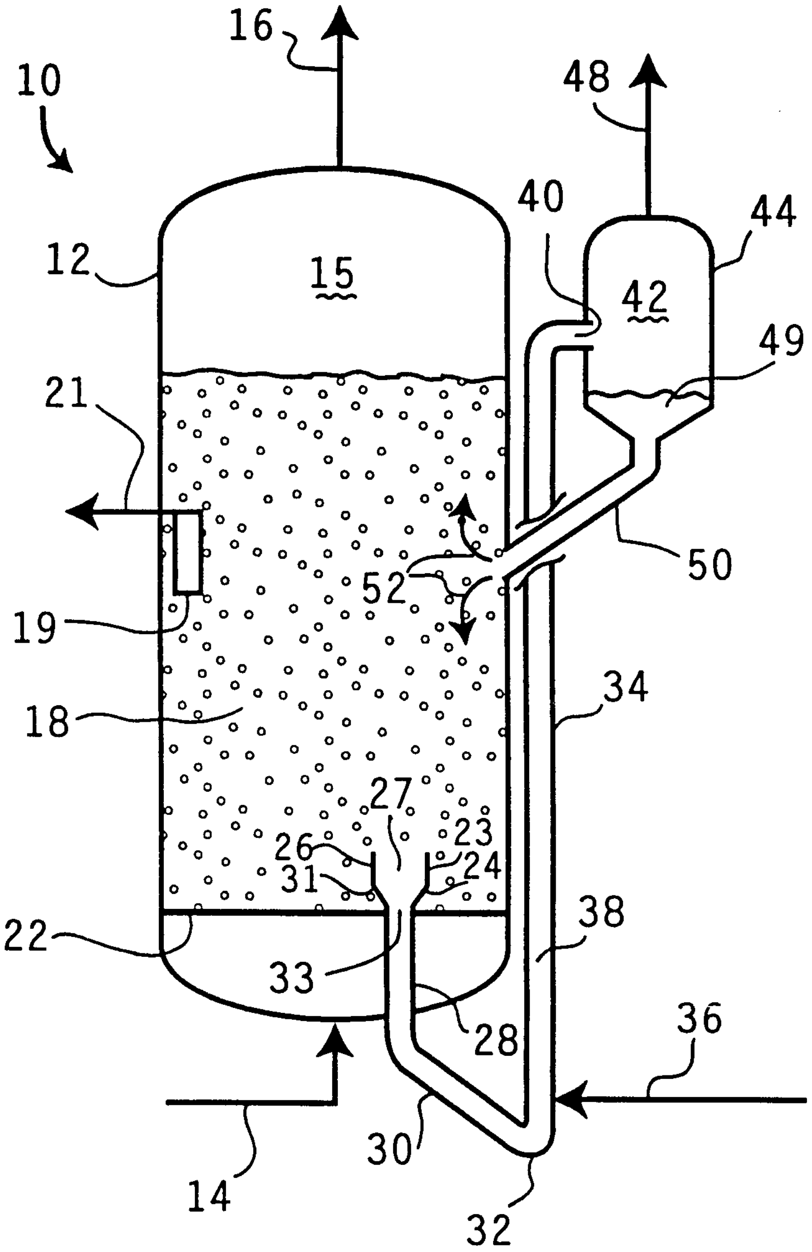
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FIG. 1

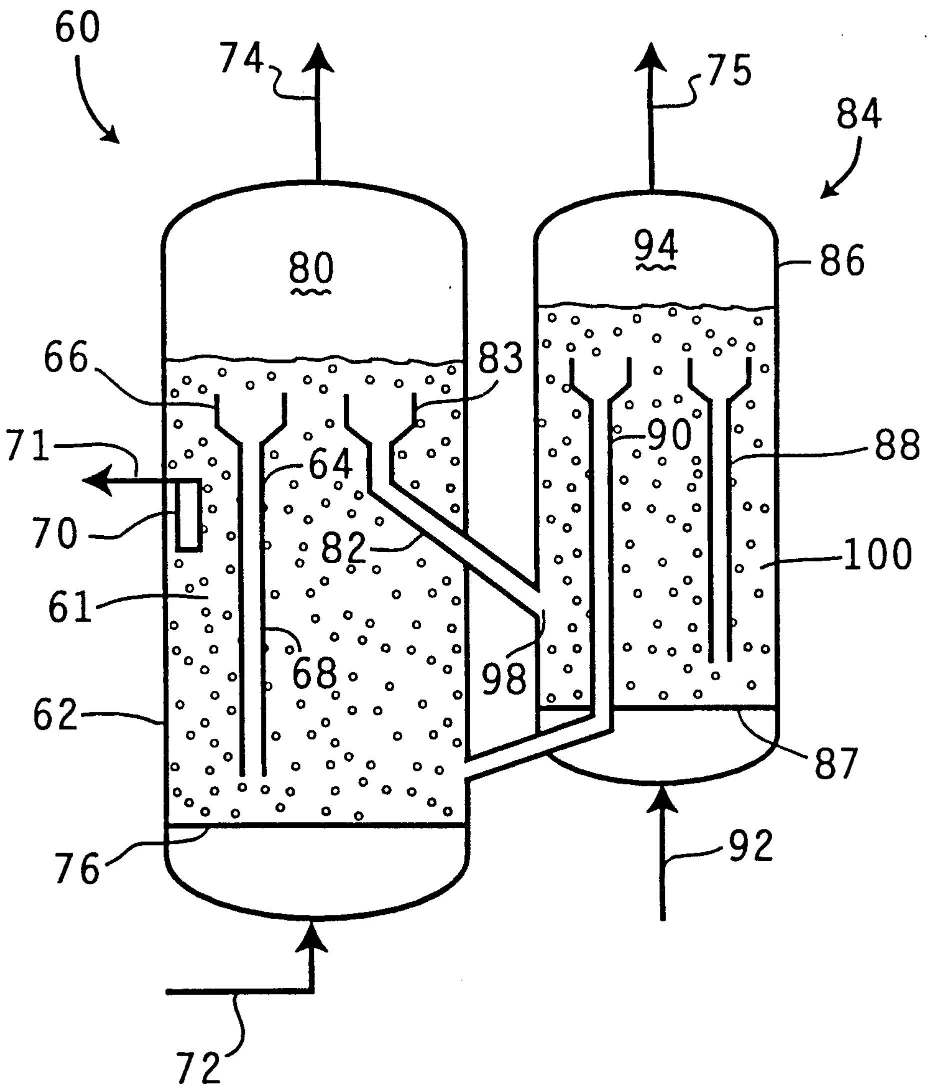

FIG. 2
(prior art)

INTERNATIONAL SEARCH REPORT

Internatio \pplication No
PCT/US 98/08789

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G2/00 B01J8/22

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C B01J C10G

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 260 239 A (HSIA STEPHEN J) 9 November 1993 cited in the application see claim 1 see column 6, line 50 see column 7, line 38 - line 45 -----	1-5,10

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

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search 22 September 1998	Date of mailing of the international search report 30/09/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer De Herdt, O

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INTERNATIONAL SEARCH REPORT

Info. ation on patent family members

International Application No
PCT/US 98/08789

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