

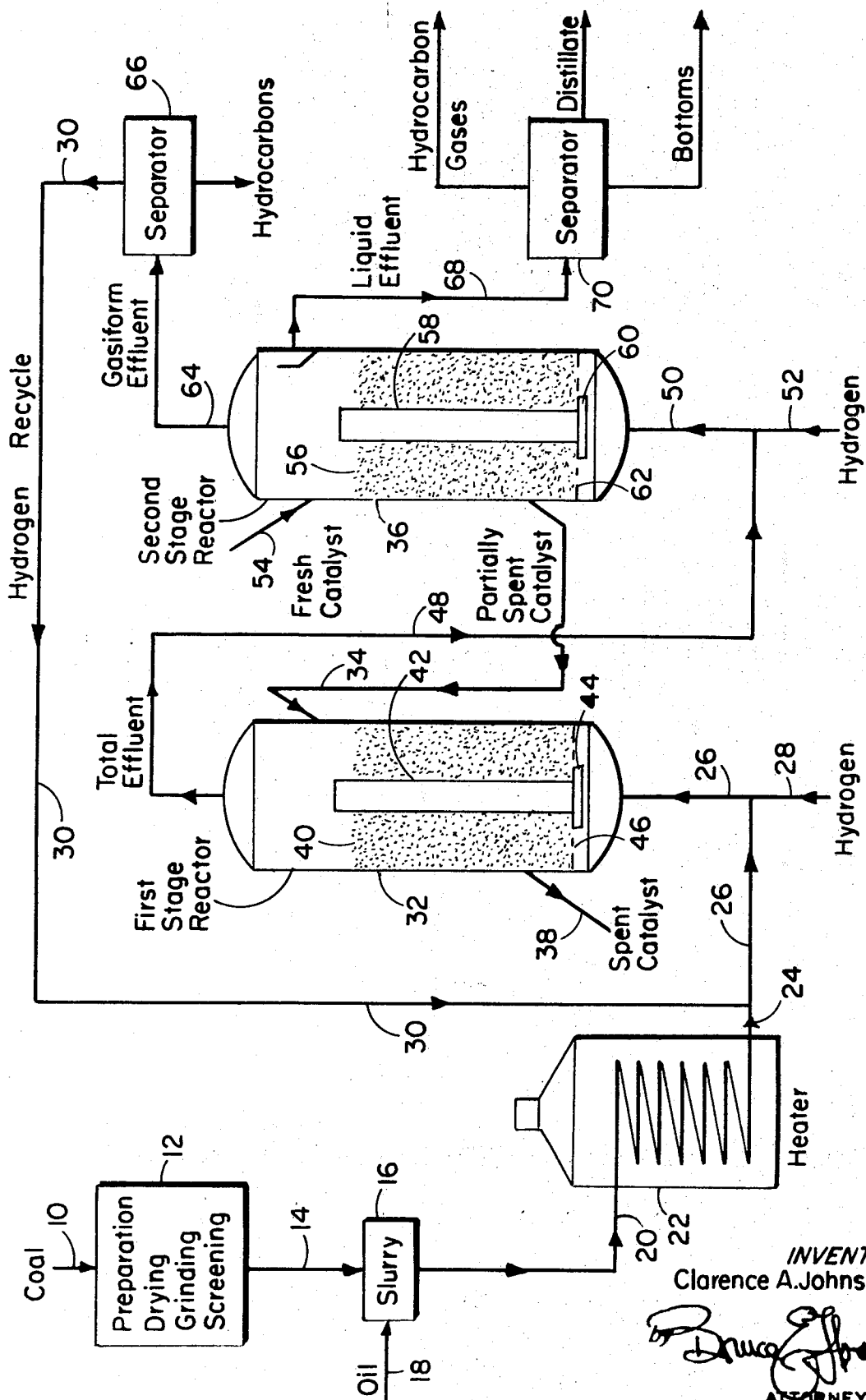
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TWO STAGE COUNTER-CURRENT HYDROGENATION OF COAL

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TWO STAGE COUNTER-CURRENT HYDROGENATION OF COAL

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5 Claims

ABSTRACT OF THE DISCLOSURE

In the ebullated bed catalytic hydrogenation of coal into hydrocarbonaceous products either greater coal throughput per pound of catalyst can be achieved or, alternatively, less catalyst per ton of coal can be employed by conducting the hydrogenation of the coal in first and second stage ebullated bed reaction zones and by using the partially spent catalyst from the second stage as the catalyst in the first stage.

BACKGROUND OF THE INVENTION

The hydrogenation of coal to valuable gaseous and liquid hydrocarbonaceous products by means of an ebullated bed hydrogenation zone has been described heretofore in U.S. Reissue Pat. No. 25,770 and in U.S. Pat. No. 3,519,555. Although these processes have proved quite satisfactory for the hydrogenation of a wide variety of coal, they could be improved upon either by being able to achieve greater coal throughput per pound of catalyst or, alternatively, by being able to employ less catalyst per ton of coal.

SUMMARY OF THE INVENTION

Accordingly, it is the principal object of the present invention to provide a process for the hydrogenation of coal into hydrocarbonaceous products wherein either greater coal throughput per pound of catalyst is achieved or, alternatively, less catalyst per ton of coal is employed.

We have found that in the single stage ebullated bed catalytic hydrogenation of coal the catalyst becomes contaminated with the metallic impurities present in the coal, particularly with titanium in the form of titanium dioxide so that the catalyst rather rapidly becomes spent or deactivated. As a consequence, it is necessary periodically to replenish or replace the catalyst particles in the ebullated bed sooner or more frequently than would be desirable.

In accordance with the process of the present invention, the ebullated bed catalytic hydrogenation of coal into hydrocarbonaceous products is performed by conducting the hydrogenation of the coal in first and second stage ebullated bed reaction zones and by using the partially spent catalyst from the second stage as the catalyst in the first stage. Thus, the coal and catalyst are in counter-current flow to one another and the partially spent catalyst used in the first stage serves to protect or guard against the rapid contamination or deactivation of fresh catalyst fed into and used in the second stage.

More particularly, in the process of the present invention coal is prepared for hydrogenation by drying, grinding and screening the coal to form a coal feed which is thereafter slurried with a slurry oil liquid produced in the process. The slurry is partially hydrogenated in a first

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stage ebullated bed reaction zone with hydrogen in the presence of ebullated partially spent hydrogenation catalyst particles which are fed therein from a second stage ebullated bed reaction zone. The entire effluent stream containing partially unreacted coal and the resultant spent hydrogenation catalyst particles are separately withdrawn from the first stage zone. The partially unreacted coal-containing effluent stream is further hydrogenated in a second stage ebullated bed reaction zone with hydrogen in the presence of ebullated hydrogenation catalyst particles which are fed fresh or uncontaminated therein. A gasiform effluent stream, a solids-containing liquid effluent stream and resultant partially spent hydrogenation catalyst particles are separately withdrawn from the second stage zone. The partially spent hydrogenation catalyst particles from the second stage zone are fed into the first stage zone and fresh or uncontaminated hydrogenation catalyst particles are fed into the second stage zone. Hydrocarbonaceous products are recovered from the separate gasiform and liquid effluent streams of the second stage zone.

Further details and suitable operating parameters for the process of the invention are described hereinafter.

DESCRIPTION OF THE DRAWING

The drawing is a diagrammatic view, partially in section, of typical process equipment suitable for practicing the process of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As shown, a coal such as bituminous, semi-bituminous, sub-bituminous, brown coal or lignite, entering the system at 10 is first passed through a preparation unit generally indicated at 12. In such a unit it is desirable to dry the coal of all surface moisture and to grind the coal to a desired mesh and to screen it for uniformity. For our purposes, it is preferable that the coal has a particle size between about 20 to about 200 Tyler mesh, i.e., the coal particles all pass through a 20 mesh Tyler screen and substantially all (not less than 80%) of the coal particles are retained on a 200 mesh Tyler screen. However, it will be observed that the preciseness of size may vary between different types of coal.

The coal particles discharge at 14 into the slurry tank 16 where the coal is blended with a carrying or slurring oil indicated at 18 which, as hereinafter pointed out, is conveniently made in the system. To establish an effective transportable slurry, it has been found that the ground coal should be mixed with at least about an equal weight of carrying oil and usually not more than 10 parts of oil per part of coal.

The coal-oil slurry is then passed via line 20 through the heater 22 to bring the slurry up to reaction temperature, such heated slurry then discharging at 24 into the first stage reaction zone feed line 26 wherein it is supplied with make-up hydrogen from line 28 as well as recycled hydrogen in line 30.

The entire mixture of hydrogen and coal-oil slurry then enters a first stage ebullated bed reaction zone 32 passing upwardly from the bottom at a rate and under pressure and at a temperature to accomplish partial hydrogenation. The first stage ebullated bed reaction zone 32 is charged with partially spent hydrogenation catalyst particles fed therein via line 34 from a second stage ebullated

bed reaction zone 36. The resultant spent hydrogenation catalyst particles are periodically withdrawn from the first stage ebullated bed reaction zone 32 via line 38. They can be regenerated by conventional technology and reused as the fresh catalyst in the second stage reaction zone 36.

By concurrently flowing streams of liquid and gasiform materials upwardly through a vessel containing a mass of solid particles of a contact material, which may be a specific hydrogenation catalyst, as further described herein-after, and expanding the mass of solid particles at least 10% over the volume of the stationary mass, the particles are placed in random motion within the vessel by the up-flowing streams. A mass of solid particles in the state of random motion in a liquid medium may be described as "ebullated." The characteristics of the ebullated mass at a prescribed degree of volume expansion can be such that a finer, lighter solid may pass upwardly through the mass so that the particles constituting the ebullated mass are retained in the first stage reaction zone and the finer, lighter material may pass from the first stage reaction zone.

The contact material (herein hydrogenation catalyst) is preferably in the form of beads, pellets, lumps, chips or like particles at least about $\frac{1}{32}$ inch or more frequently in the range of $\frac{1}{16}$ to $\frac{1}{4}$ inch (i.e., between about 3 and 14 mesh screens of the Tyler scale). The size and shape of the particles used in any specific process will depend on the particular conditions of that process, e.g., the density, velocity, and viscosity of the liquid involved in that process.

It is a relatively simple matter to determine for any ebullated process the range of throughput rates of up-flowing liquid which will cause the mass of solid contact or catalyst particles to become expanded and at the same time placed in random motion. The gross volume of the mass of contact or catalyst particles expands when ebullated without, however, any substantial quantity of the particles being carried away by the up-flowing liquid and, therefore, a fairly well defined upper level of randomly moving particles establishes itself in the upflowing liquid. The upper level 40 above which few, if any, particles ascend will herein after be called the upper level of ebullation.

In contrast to process in which fluid streams flow downwardly or upwardly through a fixed mass of particles, the spaces between the particles of an ebullated mass are thus large with the result that the pressure drop of the liquid flowing through the ebullated mass is small and remains substantially constant so the fluid throughput rate is increased. Thus, a considerably smaller consumption of power is required for a given throughput rate. Moreover, the ebullated mass of particles promotes much better contact between the coal fines and gasiform streams than with any fixed bed process. Under these conditions, a significantly greater fluid throughput rate carrying the coal fines may be used without impairing the desired degree of contact than if conventional downflow or upflow through a fixed bed of contact particles is used.

Moreover, solid material will pass through an ebullated bed where it would otherwise plug a fixed bed. Additionally, the random motion of particles in an ebullated mass causes these contact particles to rub against each other and against the walls of the vessel so that the formation of deposits thereon is impeded or minimized. The scouring action helps to prevent agglomeration of the contact or catalyst particles and plugging up of the vessel. This effect is particularly important where catalyst particles are employed and maximum contact between coal fines, hydrogen and the catalytic surfaces is desired, since the contact surfaces are exposed to reactants for a greater period of time before becoming fouled or deactivated by foreign deposits.

The process of the invention may be carried out under a wide variety of conditions. To obtain the advantages of this invention it is only necessary that the liquid, coal

fines, and gasiform materials flow upwardly through a mass of solid particles of a contact material at a rate causing the mass to reach an ebullated state. In each ebullated system, variables which may be adjusted to attain the desired ebullation include the flow rate, density and viscosity of the liquid and gasiform material, and the size, shape and density of the particulate material. However, it is a relatively simple matter to operate any particular process so as to cause the mass of contact material employed to become ebullated and to calculate the percent expansion of the ebullated mass after observing its upper level of ebullation through a glass window in the vessel, or by radiation or acoustic permeability, or by other means such as liquid samples drawn from the vessel at various levels. In general, the gross density of the stationary mass of contact material will be between about 25 to about 200 pounds per cubic foot, the flow rate of the liquid between about 5 and about 120 gallons per minute per square foot of horizontal cross-section of the ebullated mass, and the expanded volume of the ebullated mass usually not more than about double the volume of the settled mass.

Liquid may be recycled internally within the reaction zone 32; in such case, a standpipe 42 with a top open and above the upper level of ebullation 40 may be used to pass liquid from the top of the reaction zone 32 to pump 44 disposed below distributor 46 in the bottom of the reaction zone 32, the liquid discharged by the submerged pump thence flowing upwardly again through the mass of ebullated solids. In lieu of distributor 46 which uniformly distributes the flow of liquid and gasiform material to the entire mass of ebullated solids in reaction zone 32, the bottom of the reactor may be tapered or funnel-shaped so that the admixed liquid and gasiform streams introduced into the bottom of the funnel will flow uniformly through the entire ebullated mass.

As a further alternative, the liquid may be recycled externally of the reaction zone 32. In such a case, the line 48 can be provided with a heat exchanger (not shown) for heat tempering the liquid effluent stream described hereinafter and line 48 can be connected to line 26 via a line and a pump (neither shown) to maintain the desired superficial liquid velocity in the reaction zone 32.

The operating conditions of temperature and pressure in the first stage reaction zone 32 are in the range of from about 750° F. to about 950° F., preferably from about 825° F. to about 925° F., and a pressure of from about 500 to about 3000 p.s.i.g.

In the first stage reaction 32, the coal-oil slurry is partially hydrogenated. The entire effluent stream containing partially unreacted coal (and slurry oil, unconsumed hydrogen and gaseous and liquid hydrocarbonaceous products and by-products of hydrogenation) is separately withdrawn from the top of reaction zone 32 via line 48 and fed to feed line 50 of the second stage ebullated bed reaction zone 36.

Hydrogen is fed into the second stage reaction zone 36 via line 52. A hydrogenation catalyst bed is provided in the second stage reaction zone 36 by feeding fresh or uncontaminated catalyst therein via line 54. Partially spent or partially contaminated catalyst is withdrawn from the reaction zone 36 via line 34 and thereby fed from the second stage zone 36 into the first stage zone 32. The upper level of ebullation in reaction zone 36 is indicated at 56.

The second stage reaction zone 36 can be operated under the same operating conditions of temperature, pressure and liquid feed rate as given above for the first stage reaction zone 32 and it can be provided with a standpipe 58, pump 60 and distributor 62 for internal recycle of liquid to maintain the desired superficial liquid velocity. External recycle liquid can also be employed.

The coal feed rate through the first stage reaction zone 32 and the second stage reaction zone 36 is from about 15 to about 100 pounds per hour per total cubic feet of the two reaction zones 32 and 36. The total hydrogen feed

rate to both the first and second stage reaction zones 32 and 36 is generally from about 20 to about 60 standard cubic feet per pound of coal and the separate hydrogen feed rate in each of said two zones is usually proportional to the zone volume or size thereof. The ratio of the volume or size of the first stage reaction zone 32 to the volume or size of the second stage reaction zone 36 generally is from about 1:3 to about 3:1 and preferably is about 2:1.

Thus, where the volume of the first stage reaction zone 32 is twice that of the second stage reaction zone 36 and where the total hydrogen feed rate through both of the two reaction zones 32 and 36 is about 30 standard cubic feet per pound of coal, the directly proportional separate hydrogen feed rate through the first stage reaction zone 32 is about 20 standard cubic feet per pound of coal and in the second stage reaction zone 36 is about 10 standard cubic feet per pound of coal. It will be appreciated, however, that the first and/or second stage reaction zones 32 and 36 can be constituted of a single ebullated bed reactor each or a plurality of ebullated bed reactors in parallel. For example, and for reasons of economy in equipment costs, the first stage reaction zone 32 can be two ebullated bed reactors arranged in parallel and the second stage reaction zone 36 can be a single ebullated bed reactor, with all three ebullated bed reactors being of equal size or volume. In such an arrangement, the ratio of volume or size of the first stage reaction zone to the volume or size of the second stage reaction zone would be 2:1 and where the total hydrogen feed rate to both the first and second stage reaction zones is about 30 standard cubic feet per pound of coal, the directly proportional separate hydrogen feed rate to each of the three equal volume reactors would be 10 standard cubic feet per pound of coal.

In the second stage reaction zone 36 the partially unreacted coal-containing entire effluent stream from the first stage reaction zone 32 fed to the second stage reaction zone 36 via lines 48 and 50 is further hydrogenated. A gasiform effluent stream is separately withdrawn from the top of the second stage reaction zone 36 via line 64 and passed therein to a separator 66 wherein hydrocarbonaceous vapors, any entrained solids or liquids, by-product gases and excess hydrogen gas can be separated from one another to the extent desired and the recovered hydrogen gas recycled to the first stage reaction zone 32 via line 30. If desired, recovered hydrogen gas can also be recycled to the second stage reaction zone.

A solids-containing liquid effluent stream is separately withdrawn from the second stage reaction zone 36 via line 68 and fed to a recovery unit 70 for recovery and separation of hydrocarbonaceous and other products, such as gasoline, fuel oil, residual oil, char, and the like. A fraction of the recovered oil product (distillate and bottoms), can be used as the slurry oil and fed to slurry tank 16 via line 18.

The fresh or uncontaminated catalyst which is fed via line 54 into the second stage reaction zone 36 would be from the class of cobalt, molybdenum, nickel, tin, iron and the like deposited on a base of the class of alumina, magnesia, silica, and the like. The catalyst, after it reaches a partially spent state, i.e., is contaminated with from about 0.4 % to about 0.5 % by weight of titanium dioxide, is withdrawn from the second stage reaction zone 36 and fed via line 34 to the first stage reaction zone 32. This partially spent catalyst is withdrawn from the first stage reaction zone 32 via line 38 for regeneration by conventional techniques after it has reached the state of being spent, i.e., is contaminated with from about 3.5 % to about 4.8 % by weight of titanium dioxide, or it may be discarded.

The process of the invention will be further illustrated by the following representative example thereof.

EXAMPLE 1

Illinois No. 6, Belleville area coal having the following analysis was treated in accordance with the above-described two-stage hydrogenation process of the invention:

TABLE I

	As received	Dry
Proximate analysis, percent:		
Moisture.....	11.04	-----
Ash.....	9.88	10.54
Volatile.....	37.99	42.70
Fixed carbon.....	41.59	46.76
Total.....	100.00	100.00
Ultimate analysis, percent:		
Moisture.....	11.04	-----
Carbon.....	62.10	69.81
Hydrogen.....	4.53	5.09
Nitrogen.....	1.02	1.15
Chlorine.....	0.02	0.02
Sulfur.....	3.17	3.56
Ash.....	9.88	10.54
Oxygen.....	8.74	9.80
Total.....	100.00	99.97

The exemplary operating parameters for the two stage hydrogenation process of the invention were as follows:

TABLE II

Coal feed.....	20-200 Tyler mesh particles.
Coal to slurry oil weight ratio.....	1:3.3.
Coal feed rate through first and second stage reaction zones.....	31.2 pounds per hour per total cubic feet of the two stage reaction zones.
Ratio of volume of the first stage reaction zone 32 to the volume of the second stage reaction zone 36.....	About 2:1, i.e., 0.7:0.3.
Temperature and pressure in both the first and second stage reaction zones.....	650° F., 2,250 p.s.i.g.
Liquid feed rate through each of the first and second stage reaction zones.....	20 gallons per minute per square foot of horizontal cross-section thereof.
Total hydrogen feed rate through both the first and second stage reaction zones.....	35 standard cubic feet per pound of coal.
Hydrogen feed rate through first stage reaction zone.....	23.4 standard cubic feet per pound of coal.
Hydrogen feed rate through second stage reaction zone.....	11.7 standard cubic feet per pound of coal.
Chemical nature and particle size of hydrogenation catalyst fed into second stage reaction zone 36 and thereafter fed in a partially spent state to the first stage reaction zone 32.....	Particles of cobalt molybdate on alumina of uniform cylindrical size about 0.06 inch in diameter and 1/8 inch in length.

Two runs (Run 1 and Run 2) were made using the two stage hydrogenation process of the invention. A comparative run (Run 3) was made on the same coal using only a single stage reaction zone having a volume or size equal to the total volume or size of both the first and second stage reaction zones 32 and 36 utilized in the above illustrative example (Run 1 and Run 2) of the two stage hydrogenation process of the invention. In this comparative run (Run 3) the operating parameters were otherwise the same as those given above in Table II with the additional exceptions that the hydrogen feed rate to the single stage reaction zone was 35 standard cubic feet per pound of coal and hence was equal to the total hydrogen feed rate through both the first and second stage reaction zones 32 and 36 used in the illustrative process of the invention and that fresh or uncontaminated hydrogenation catalyst particles were fed into the single stage reaction zone and spent hydrogenation catalyst particles withdrawn therefrom.

The results of the single stage comparative run (Run 3) and the two stage runs (Run 1 and Run 2) of the process of the invention are set forth in the following Table III:

TABLE III

Run number.....	1	2	3
Pounds of coal per pound of catalyst.....	2,000	2,700	2,000
Chemical analysis of catalyst (wt. percent):			
TiO ₂ content of fresh catalyst feed.....	0	0	0
TiO ₂ content of partially spent catalyst from the second stage.....	0.4	0.5	-----
TiO ₂ content of spent catalyst from the first stage or from the single stage.....	3.5	4.8	3.5
Average TiO ₂ content of catalyst from single stage process.....	-----	-----	3.5
Average TiO ₂ content of catalyst from the two stages of the two stage process.....	¹ 2.5	² 3.5	-----
Hydrocarbon liquids:			
Weight percent of dry coal.....	56	56	56
Barrels/ton of dry coal.....	3.5	3.5	3.5

¹ 0.3(0.4) + 0.7(3.5) = 2.5%.

² 0.3(0.5) + 0.7(4.8) = 3.5%.

From the above data it will be observed that in both the two stage counter-current Run 1 of the invention and in the single stage comparative Run 3, 2000 pounds of coal per pound of catalyst were used, i.e., equal amounts. However, in Run 1 of the invention the average TiO₂ contaminate content of the catalyst from the two stages of the two stage process reached a value of only 2.5%, whereas in the comparative single stage Run 3 the average TiO₂ contaminate content of the catalyst reached a much higher value of 3.5. Therefore, these two runs establish that by the two stage hydrogenation process of the invention it is possible to use less (e.g., 30% less) catalyst per ton of coal before the catalyst becomes as spent as in a single stage process.

In Run 2 of the invention and in comparative Run 3 the average TiO₂ contaminate content of the catalyst reached the same value of 3.5%. However, in the single stage comparative Run 3, only 2000 pounds of coal per pound of catalyst was processed, whereas in the two stage hydrogenation Run 2 of the invention a much greater amount of coal was processed per pound of catalyst before the catalyst became as spent, i.e., 2700 pounds of coal per pound of catalyst. Accordingly, the data for Run 2 versus comparative single stage Run 3 show that the two stage hydrogenation process of the invention makes possible the achievement of greater coal throughput (e.g., 35% greater) per pound of catalyst before equal contamination or deactivation thereof.

It will be further noted from the above data that the achievement of either greater coal throughput per pound of catalyst or, alternatively, less catalyst per ton of coal is made possible by the two stage hydrogenation process of the invention without sacrifice in the yield of hydrocarbonaceous products obtained.

It will be appreciated that various modifications and changes may be made in the process of the invention in addition to those described above by those skilled in the art without departing from the essence of the invention and that accordingly the invention is to be limited only within the scope of the appended claims.

What is claimed is:

1. A two stage process for the hydrogenation of coal into hydrocarbonaceous products which comprises:

- (a) drying, grinding and screening coal to form a coal feed,
- (b) slurring said coal feed with a slurry-oil liquid produced in the process,
- (c) partially hydrogenating the slurry in a first stage ebullated bed reaction zone with hydrogen in the presence of ebullated partially spent hydrogenation catalyst particles fed therein from a second stage ebullated bed reaction zone,
- (d) separately withdrawing the entire effluent stream containing partially unreacted coal and the resultant spent hydrogenation catalyst particles from said first stage zone,
- (e) further hydrogenating said effluent stream in a second stage ebullated bed reaction zone with hydrogen in the presence of ebullated hydrogenation catalyst particles fed fresh therein,
- (f) separately withdrawing a gasiform effluent stream, a solids-containing liquid effluent stream and resultant partially spent hydrogenation catalyst particles from said second stage zone,
- (g) feeding said partially spent hydrogenation catalyst particles from said second stage zone into said first stage zone,
- (h) feeding fresh hydrogenation catalyst particles into said second stage zone, and
- (i) recovering hydrocarbonaceous products from the separate gasiform and liquid effluent streams of said second stage zone.

2. The process as defined by claim 1 wherein the spent hydrogenation catalyst particles withdrawn from said first stage zone are regenerated into fresh hydrogenation catalyst particles and are thereafter fed into said second stage zone.

3. The process as defined by claim 1 wherein the partially spent hydrogenation catalyst particles withdrawn from said second stage zone and fed into said first stage zone are contaminated with from about 0.4% to about 0.5% by weight of titanium dioxide.

4. The process as defined by claim 1 wherein the spent hydrogenation catalyst particles withdrawn from said first stage zone are contaminated with from about 3.5% to about 4.8% by weight of titanium dioxide.

5. The process as defined by claim 1 wherein the fresh hydrogenation catalyst particles fed into said second stage zone are free of titanium dioxide contaminant.

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