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SHOT HEATED FLUID CONVERSION SYSTEM

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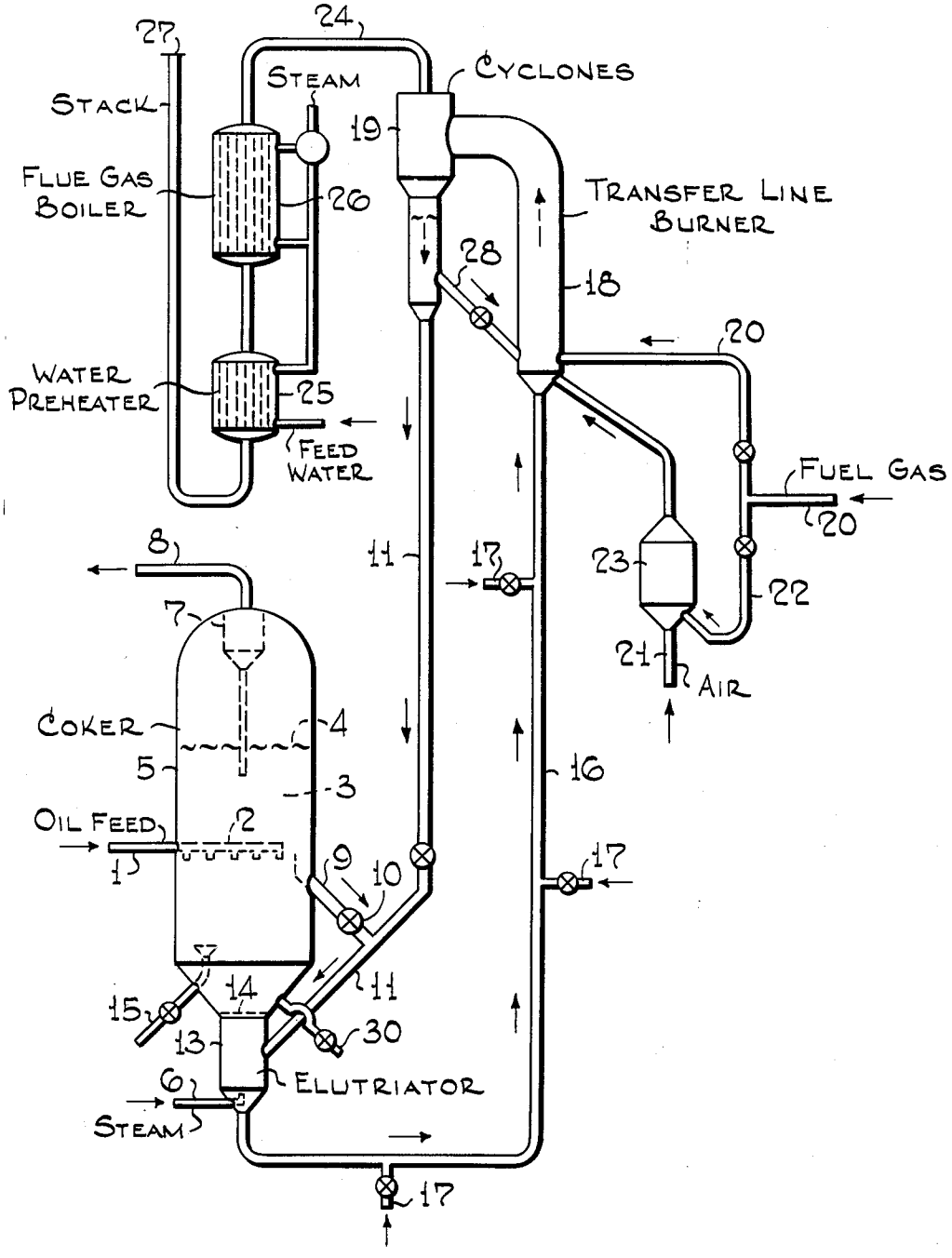

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SHOT HEATED FLUID CONVERSION SYSTEM

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This invention relates to the art of conducting chemical reactions and more particularly to a method for converting hydrocarbons at high pressure and temperature in the presence of a dense fluidized mass of solid contact particles.

When using the fluid solids technique, it is frequently desirable to circulate an extraneous solid as a carrier of heat. This may be the case, for example, when the catalyst used in the conversion zone would oxidize, reduce or otherwise deteriorate if exposed to conditions which may prevail in a heater or elsewhere outside of the conversion zone. Also, in certain adaptation of coking or hydroforming, heat must be added to a reactor operating at high pressure, and it is undesirable for one reason or another to use the contact solids as heat carrier, particularly since excessive standpipe heights would be required for pressuring the relatively low-density fluidized solids to pressures of 50 pounds per square inch or more.

It has been proposed to use high pressure combustion zones to reduce standpipe height, but such designs have tended to be unattractive in view of the extremely high investment and operating cost for the required air compressor. Alternatively, it has been proposed to use indirect heat exchange so as to permit operating the combustion zone at substantially atmospheric pressure, independent of conversion pressure and without exposing the conversion zone solids to undesirable chemical and physical conditions. However, when operating the conversion zone at high temperature and pressure, the severe operating conditions for the heat exchanger surface require very expensive construction.

It is among the objects of the present invention to provide an improved method for supplying heat to a reactor containing fluidized contact solids. A more specific object is to provide a method wherein the combustion zone necessary for supplying heat to the system can be operated at a pressure independent of the reactor pressure and wherein the contact solids need not be exposed to combustion conditions. Another object is to transfer heat from a low pressure combustion zone to a high pressure reactor by direct heat exchange of fluidizable reactor solids with an extraneous heavy sold heat carrier such as metal shot, and to avoid excessive standpipe heights. A further object involves the depressuring of the solid heat carrier without incurring undesirable erosion or attrition in orifices or valves. Still other objects and aspects of the invention will appear from the following detailed description and claims.

The accompanying drawing illustrates a typical system, shown in elevation, suitable for carrying out one preferred embodiment of the invention as applied specifically to coking of heavy hydrocarbon feed stocks.

Referring to the drawing, a residual petroleum stock such as a crude residuum having a gravity of about 5° API and an atmospheric boiling range essentially in excess of about 1100° F. may be preheated by conventional means (not shown) to about 700° F. and then injected through line 1 and spray head 2 into a coking

reactor 5 which is maintained at a temperature between about 800 to 1400° F. and a pressure between about 25 and 300, preferably at about 50 to 150 lbs./sq. in. gauge. Coke particles ranging in size between about 40 and 300 microns diameter are contained in the reactor 5 in an amount of about 0.1 to 10 pounds per pound per hour of feed.

Steam or other inert gas is admitted into the reactor 5 through line 6 and subsequently described elutriator 13, and also through line 30 if desired, at a rate sufficient to produce within the reactor, a total upward vapor velocity of about 1.5 to 3 feet per second. This maintains the coke particles in the form of a dense fluidized bed 3 having a density of about 20 to 40 pounds per cubic foot below its upper level 4, above which is a disperse phase which may have a density of only about 0.001 to 1 pound per cubic foot. At the indicated velocities the hydrocarbon vapors formed in the coking reactor 5 stay there for a period corresponding to a residence time of about 5 to 50 seconds before issuing overhead, preferably through a cyclone 7 or other suitable dust separating device. Separated solids may be returned from the separator to the coke bed through the usual dip leg while product vapors may be withdrawn through line 8 to product recovery or first subjected to further well-known processing steps such as catalytic cracking.

According to the essence of the present invention, heat of reaction is supplied to the reaction zone 5 by direct heat exchange of at least a portion of the coke particles with a hot extraneous heat carrier which can be circulated through a heating device. Specifically referring to the illustrative drawing, a portion of the coke is, preferably continuously, withdrawn from the fluidized bed 3 into the lower part of line 11 through line 9 and slide valve 10. In the lower part of line 11 the coke is heated by direct mixing with a solid heat carrier such as spheres of stainless steel (18–8 chrome-nickel) of about 100 micron diameter which descend through standpipe 11 after being heated to a temperature of 1000 to 2000° F. Since in this particular application it is desired to exclude the steel spheres from the coking zone proper in order to minimize coke deposition on the metal spheres, the mixture of coke and metal spheres is introduced from line 11, which acts as a standpipe, to an elutriator 13. The relatively light, reheated coke particles are stripped out by steam injected into the elutriator through line 6 as previously mentioned and are recycled under pressure to the coking reactor 5 through perforated distributor grid 14, thereby maintaining the temperature of the fluidized coke bed 3 at the desired value.

The presence of the heavy metal shot in line 11 increases the loading and pressure buildup therein, and facilitates circulation of the coke particles between coking bed 3 and elutriator 13. Of course, instead of passing the reheated solids to the reactor directly from the elutriator, the solids may first pass to an intervening zone wherefrom they may be lifted into the reactor in a manner well known, per se, in Fluid systems generally. Net coke product may be withdrawn from the reactor coke bed 3 through line 15. It will be seen that the described system avoids the difficulty of losing metal shot by withdrawal with the product char. Also, by keeping the shot out of the coking reactor, the oil feed is not exposed to the high temperature shot which could lead to less desirable products, both because of the excessive temperature of the shot and because of possibly undesirable catalytic effects of the latter. Moreover, coke deposited on the shot would carry over to the burner line, would reduce the heat transfer coefficient of the shot and also might tend to lower the effective standpipe density undesirably.

Conversely, it is apparent that the described system

avoids any recirculation of coke between reactor and burner. Consequently, such product coke as is withdrawn from the reactor is essentially unoxidized and possesses a relatively low content of ash and similar impurities. In contrast, in conventional systems substantially all coke is continuously circulated between reactor and burner. As a result all such product coke is considerably oxidized and also its non-volatile impurities become concentrated therein, all of which is highly objectionable if the coke is to be used for metallurgical purposes.

The relatively heavy metal spheres or shot, together with a small amount of relatively large coke particles if desired, are withdrawn downwardly from the elutriator and passed through riser 16 provided with air taps 17 to a transfer line heater 18 where the metal spheres are reheated to about 1000 to 2000° F. and recycled through cyclone 19 and previously mentioned standpipe 11 for transferring heat to further portions of reactor solids.

The metal spheres may acquire the necessary heat in burner 18 at substantially atmospheric pressure in part or wholly by burning the coke admixed with the withdrawn metal spheres or preferably by burning hydrocarbon fuel gas introduced through line 20 with an oxygen-containing gas such as air admitted through line 21. If desired, instead of burning the gas directly in heater 18, all or a portion of the fuel gas from line 20 may be passed through line 22 to an auxiliary burner 23 where the gas may be burned before admission into heater 18 where the metal spheres may then be brought to the desired temperature by contact with the hot combustion gases.

Some of the heated spheres may be recycled to the inlet of the burning zone 18 through line 28 after separation in cyclone 19. This affords a means of varying solids holdup or loading in the burning zone and in addition it facilitates combustion by raising burner inlet temperature to at least about 1300–1700° F., which may be especially important when the reactor is at a much lower temperature than the burner. After contact with and separation from the metallic heat carrier, residual heat may be recovered from the combustion gases withdrawn through line 24 by means of a flue gas boiler 26 and a water preheater 25 before venting the gases to a stack 27.

Since it is desirable to operate the combustion zone or heater 18 at substantially atmospheric pressure in order to avoid expensive air compression and pressure equipment, the shot or metal spheres which are at a high pressure in the heat exchange line 11 and elutriator 13 must be depressurized before entrance into heater 18. However, if the entire pressure drop, which may easily amount here to 100 lbs./sq. in or more, were taken across valves or orifices as in the case of finely divided catalysts introduced directly from a standpipe into the usual transfer line, the resulting erosion and attrition might well become prohibitive. Accordingly, an important feature of the present invention involves depressurizing the heat carrier and lifting it to the combustion zone 18 in a high density riser or reverse standpipe 16 wherein most of the pressure drop is inherently dissipated. Typically in such a reverse standpipe the superficial upward solids velocity may range between about 2 and 10 feet per second and the apparent density of the aerated shot may range between about 100 and 200 lbs./cu. ft. In the transfer line burner 18 the upward velocity may be between about 5 and 75 ft./sec. and the apparent density of the metal spheres suspended in gas may be from about ½ to 5 lbs./cu. ft. In the downleg or standpipe 11, the apparent density of the moving heat carrier solids having approximately the specific gravity of iron is about 100 to 250 lbs./cu. ft., requiring a standpipe having a vertical height of only about 70 feet when operating the reactor at 110 lbs./sq. in. gauge.

One advantage of the present system is that the coke from the reactor is passed through a higher temperature zone in the bottom part of standpipe 11. This releases additional valuable products from the coke and tends to dry it and reduce any tendency toward agglomeration. Also, product coke can be withdrawn from the upper part of high temperature zone 13, to assure having a dry coke of low volatile content. Such coke may then be raised to a still higher temperature by contacting with additional heated shot from line 11 in a separate zone (not shown).

Having described a specific embodiment of the invention in connection with coking, including the required equipment and operating method, it will be understood that this has been done largely for purposes of illustration rather than limitation. Consequently, the invention can be varied and modified in numerous ways which will occur to persons skilled in the art, without departing from the spirit of the present disclosure or the scope of the appended claims.

For instance, beyond the scope of the specific example given, the invention is applicable generally to the coking of heavy crude stocks such as residua as well as cycle stocks containing fractions which have an atmospheric boiling range above about 900 to 1150° F. and a gravity between about 0 and 20° API, but some advantage is obtained even with lighter petroleum stocks such as gas oils. The invention is of particular value with petroleum stocks having high coke forming tendencies, as indicated by Conradson carbon values between about 5 and 35 weight percent such as residua which can be obtained by atmospheric or vacuum distillation and which may represent about 2 to 25 volume percent of the whole crude distilled; or the invention may be applied to clarified oil from catalytic cracking, to various pitches, tars from visbreaking and so on.

Prior to being introduced into the coker, heavy feed stocks may be cut back with naphtha or other light products, and preferably preheated to temperatures ranging from 200 to 1000° F., or especially 600 to 800° F. Moreover, the hydrocarbon feed may also be diluted in the reaction zone with steam, recycle gas or other insert gas in amounts up to about 500 to 5000 cubic feet (at atmospheric conditions) per barrel, the presence of a diluent gas sometimes being desirable for the purpose of increasing the total vapor velocity in the reaction zone to facilitate fluidization of the solids contained in the reactor. Desirable fluidizing velocities may range from about 0.5 to 5 or 10 feet per second to establish apparent densities in the dense solids phase in the reactor of about 10 to 50 lbs. cu. ft. and about 0.001 to 5 lbs./cu. ft. in the disperse phase as is well known per se.

The contact solids used in the coker are preferably coke particles ranging in size up to about 200 or 500 microns. However, other inert solids such as sand, spent clays, pumice and the like may be used similarly, if a coke product of high ash content can be tolerated, as, for instance, when the coke-coated solids are used as fuel in the transfer line burner. Moreover, under some circumstances, some advantage may be obtained even when the metal shot itself is used to serve as the contact solids and is circulated directly between the burner and the coker. For example, this may sometimes be practical where the amount of coke laid down on the shot is such that it can be removed continuously by burning, or by other means. Similarly, hot circulating shot may be used to supply heat for other purposes. Thus it may provide heat for making steam when it is circulated through a zone containing water and is contacted directly with the latter, or the heat may be used for product recovery, etc. In one application of this, the heated shot is contacted with water in a countercurrent manner to generate superheated steam at high pressure for use in the process, etc. Contacting may be in a transfer line, and/or with staged fluid beds.

The shot used for heat transfer may be metal, metal oxide or other solid substances having a standpipe density

or apparent bulk density between about 30 and 200 lbs./cu. ft. Also, such shot should desirably have a heat capacity of at least 0.1 B. t. u./lb./°F., a good heat transfer coefficient or conductivity, and it should not deteriorate undersirably when exposed to the high temperature and oxidizing conditions prevailing in the burner. Moreover, the preferred heat carriers will not only reduce the necessary standpipe height as previously described, but because of their combustion catalyzing properties, they will usually also permit operation at a lower burner temperature. For example, the heat carrier particles may consist of iron, iron oxide, steel, copper copper oxide, chromium, nickel, various alloys, ceramic particles, dense silica, minerals such as corundum, etc., carborundum or other suitable substances preferably with high density and heat capacity. Moreover, the heat carrier may be purposely conditioned physically or chemically to promote combustion in the burner by using high surface area metals and/or by using a combustion catalyst comprising some chromium, copper or the like, which may, for example, be coated on a base material such as sponge iron, alumina, silica gel, etc.

In the preferred embodiment of the invention, wherein the heat carrier is not allowed to enter the reaction zone in substantial amounts and wherein another solid such as coke is used as the contact solid within the reaction zone size and/or density and/or other properties of the shot or heat carrier are selected to insure proper separation of the two solids in the elutriator or other separator. For example, stainless steel shot of 50 to 200 microns diameter is suitable when separation by elutriation of coke particles of about the same size is called for. Alternatively, separation of the two solids may be obtained by screening, selective cyclone or centrifugal action, or by magnetic forces, and so on.

In order to assure proper separation of two materials by elutriation, the following conditions must be met. First, the gas velocity must be high enough to carry up the more easily entrained material, but not so high as to entrain both materials. The methods of calculating the free fall velocity are well known, although it should be pointed out that small particles tend to agglomerate and then fall at a faster rate, particularly with particles smaller than about 20 microns. Another condition which must be met is that the velocity in the bed should be high enough to fluidize the bed and to agitate it sufficiently to prevent trapping of those particles which should be entrained upward. Methods have been published for calculating this, but it can easily be determined by experiment. The velocities determined as outlined above establish the upper and lower limits of allowable velocity in the elutriation zone.

From this discussion it will be seen that particle size and/or density of the materials must be selected so as to result in a reasonable operating range. Thus, two materials whose free fall velocities are in the ratio of 2:1 or less will be difficult to separate by elutriation and more favorable components should be selected in overcoming elutriation difficulties, although staging, etc., may be helpful. If desired, the velocities within the elutriation zone may be varied by changing cross-sectional area, or by adding more gas. One particularly useful improvement, is to provide a high velocity zone in the lower portion of the elutriation bed to strip out finer or lighter particles. The velocity in this zone can actually be higher than the free fall velocity of the heavier particles, since they can not escape through the upper zone where the velocity is lower than their free fall rate.

Reaction conditions may include coking temperatures of about 800 to 1400° F., preferably 1000–1200° F., and pressures between about 50 and 300 p. s. i. g., preferably 50 to 150 p. s. i. g. so as to reduce the amount of gas compression required in subsequent product recovery. Where high solids holdup in the reactor is required (within the range of about 0.1 to 10 lbs. oil fed/hr. per lb. of catalyst holdup), the coker itself may be a Fluid bed reactor (at 0.5 to 5 ft./sec. gas velocity), as illustrated in the accompanying drawing. However, where feed rates over 10 lbs. of feed per hour per pound of suspended contact zone solids can be tolerated, other types of reactors can be used, such as a transfer line reactor similar in design to burner **18**. These will frequently be operated at a higher linear velocity such as about 10 to 80 feet/second. The transfer line reactor is especially suited, for instance, when coking is carried out at high temperatures such as 1200 to 1400° F. Also, while the attached drawing shows the oil feed being sprayed directly into the dense coker bed, it is equally within the scope of this invention to inject or spray the feed into the coker bed from a point above its upper level. Also, fresh feed may be added to the mixing line **11** or into the elutriator **13** if coke deposition on the shot is not excessive, or it may be mixed with recycle coke in a separate zone for introduction into the reactor by way of a riser.

The conditions in the burner where the metal shot or other heat carrier is heated may include temperatures of about 1100 to 1800° F. and pressures of about 20 p. s. i. g. or less, since such low pressures substantially equal to the ambient or atmospheric pressure allow the most economic operation. The burner itself is preferably a transfer line burner as shown in the drawing since it is inexpensive, and the short contact time obtained in such burners leads to efficient operation by minimizing carbon monoxide formation in cases when excess carbon is present. In such a burner, the weight ratio of gases such as air fed per hour, to heat carrier or metal shot suspended therein is typically between about 10 and 90, the apparent density of the shot in vapor suspension being ½ to 5 lbs./ft. and the upward linear velocity of the vapors may range between about 10 and 80 ft./sec. However, instead of using a transfer line burner, a Fluid bed type combustion zone can be used likewise and may be especially advantageous where solid fuels such as coal, coke or coke-coated shot or other inert solids are used, and/or where relatively low temperatures such as 1000 to 1300° F. are used, and where efficient combustion consequently calls for longer contact times as is well known per se.

Furthermore, while the invention is most advantageous and has been described in connection with Fluid coking, some of its advantages can also be obtained by adapting it to other systems wherein heat is supplied to Fluid solids under pressure.

For example, in hydroforming, using a chromium type catalyst or the like, heat may be transferred from the regenerator to the reactor by means of the circulating catalyst. However, much of the heat available can not be so transferred, since the resulting high catalyst rate would lead to excessive oxidation-reduction, high carbon yields, etc. According to the present invention, extraneous particles such as metal shot are circulated to effect the desired heat transfer, independent of the normal catalyst circulation. The shot heated in the regenerator may be segregated by elutriation or the like, and added directly to the reactor, or it may be contacted in a separate zone with catalyst from the reactor in a manner similar to that illustrated in the attached drawing. One special adaptation to hydroforming is to preheat the recycle gas by heat exchange with the circulating hot shot. Catalyst, particularly regenerated catalyst, can then be contacted with the recycle gas in a "pretreat" zone below the reactor, and this may be at a temperature higher than that of the reactor.

Other Fluid processes to which the invention may be applied include thermal cracking, visbreaking, treating, various chemical processes such as sulfur recovery from natural and refinery gases by fluid char, and so on.

Moreover, the invention is also adaptable to processes

wherein heat is to be transferred to an operating zone containing liquids or gases under pressure, in which case the elutriation zone 13 of the system illustrated in the accompanying drawing can be replaced by a settling tank or thickener. The heavy solid heat carrier is allowed to settle out in such a thickener for recycling to the burner while the reheated reaction liquid or gas is returned to the reactor from the top of the thickener, either by means of the pressure imposed on the thickener by the standpipe effect of line 11 or by means of a pump. For instance, thus modified, the invention may be applied for supplying heat to pressure distillation columns, or to liquid phase coking systems, visbreaking, or to gaseous or liquid phase chemical reactions such as sulfuric acid concentration. Fluidizable solids, as well as liquids and gases, all are referred to in this specification and claims by the generic expression "fluid material."

Generally speaking, the invention is of value in systems or processes wherein thermal energy must be transferred from a low pressure zone to a high pressure zone, while avoiding use of expensive indirect heat exchange surfaces operating under severe conditions, or use of a high pressure heater system. The invention is particularly valuable where heat is to be transmitted from a low pressure combustion zone to a conversion zone operating at pressures above 50 p. s. i. g. Where operation conditions are such that the solid heat carrier may be fed to the reactor at 1000° F. or higher, further advantage may be possible by using a transfer line burner.

Among the main advantages of the present invention is its efficiency in transferring heat by means of fluidizable heat carrier of high density directly from a low pressure zone to a high pressure zone with a minimum of standpipe height and without requiring abrupt dissipation of pressure anywhere in the system. The elimination of heat exchange surfaces makes it possible to use lined carbon steel construction for vessels instead of expensive alloy, permitting operations with process conditions which would otherwise be impractical due to mechanical limitations. Thus, available alloys are not considered satisfactory to withstand sulfur corrosion under reducing conditions at temperatures above about 1600° F., as may be encountered in coal gasification. The difficult mechanical problems associated with this particular process are largely overcome by using ceramic-lined equipment, pipes, etc., and circulating ceramic particles or pellets to supply the necessary heat to the process.

Furthermore, the elimination of a gas compressor such as would be required, for instance, if the combustion zone of the previously described coking process were maintained at approximately the same high pressure as prevails in the coker, represents a very substantial saving. This can be judged from the fact that the air compressor alone for a high pressure heater on a high temperature coker feeding 23,000 bbl./day would cost almost as much as the total and all-inclusive coking section investment for the shot heated design of the present invention. Beyond the specific use discussed, the shot heater disclosed herein may also be more generally of importance in high pressure processes containing a low pressure zone other than a combustion zone.

Finally, as mentioned earlier herein, the invention offers a particularly attractive way of transferring heat from a low pressure heating zone to fluids in a high pressure operating zone employing solids such as chromium, molybdenum, and platinum type catalysts used in hydroforming, dehydrogenation, etc., which are of such character that they would be damaged if exposed directly to the temperature and/or oxidizing or other chemical conditions prevailing in the heating zone.

Having given a full illustrative description of the invention and of the manner and process of using it, its scope is particularly pointed and and distinctly claimed in the appended claims.

We claim:

1. An improved fluid coking process which comprises the steps of converting a feed stock in a coking zone containing a dense turbulent bed of fluidized coke particles under about 500 microns in size maintained at a coking temperature and a coking pressure above 50 p. s. i. g. to produce vapors and coke which is deposited on said particles, withdrawing said vapors as product, introducing coke particles from said coking zone into a mixing zone maintained substantially at said coking pressure, mixing with the coke particles in said mixing zone heavier high temperature particulate heat carrier in the absence of feed stock, the free fall velocity of said heat carrier being at least 2 times the free fall velocity of said coke particles, said heat carrier having a bulk density in the range of 30 to 200 lbs./cu. ft., flowing the resulting mixture to an elutriation zone also maintained substantially at said coking pressure, passing an inert aeration gas upwardly through the particles in said elutriation zone in the absence of feed stock at a velocity sufficient to entrain only heated coke particles, returning heated coke particles and aeration gas from said elutriation zone to said coking zone to maintain said coking temperature, passing heat carrier from the lower portion of said elutriation zone in the form of a dense upwardly flowing aerated column in a reverse standpipe to a heating zone maintained at a pressure below 20 p. s. i. g., said column being of sufficient height to dissipate the pressure originally on said heat carrier, heating said heat carrier in said heating zone to a high temperature above said coking temperature, and passing only high temperature heat carrier from said heating zone to said mixing zone as a descending aerated column in a standpipe, said column being of sufficient height to generate a hydrostatic pressure on said high temperature heat carrier at least equal to said coking pressure.

2. The process of claim 1 wherein said heating zone comprises a transfer line heating zone and said heat carrier is transported therethrough at a velocity in the range of 5 to 75 ft./sec. while in contact with a heating gas, and wherein a portion of said high temperature heat carrier is recycled to the inlet of said heating zone to raise the inlet temperature.

3. The process of claim 1 wherein said elutriation zone comprises a high velocity stage and an upper low velocity stage, and wherein said aeration gas is passed upwardly through said high velocity stage at a velocity higher than the free fall velocity of said heat carrier and through said low velocity stage at a velocity lower than the free fall velocity of said heat carrier.

4. A fluidized solids process for carrying out endothermic hydrocarbon conversion reactions which comprises the steps of converting a feed stock in a reaction zone containing a fluidized bed of finely divided contact solids maintained at a reaction pressure of at least 50 p. s. i. g. and at a reaction temperature, withdrawing resulting product gases from an upper portion of the reaction zone, withdrawing contact solids under reaction pressure from said fluidized bed, mixing the withdrawn solids in a mixing zone maintained substantially at said reaction pressure with finely divided heat carrier solids, said heat carrier solids being free from other solids and being withdrawn via a standpipe from a heating zone at a temperature above said reaction temperature and at about atmospheric pressure, said heat carrier solids having a bulk density in excess of 30 lbs./cu. ft. and a free fall velocity at least 2 times the free fall velocity of said contact solids, said standpipe having a height sufficient to creat a hydrostatic pressure on said heat carrier solids at least equal to said reaction pressure, passing an aeration gas upwardly through the resulting mixture in an elutriation zone also maintained substantially at said reaction pressure in the absence of fluid feed stock to strip out the finely divided heated contact solids from the mixture, returning stripped out contact solids and aeration

gas to said reaction zone to maintain said reaction pressure, and passing heat carrier solids from the lower portion of said elutriation zone to said heating zone as a dense upwardly flowing aerated column in a reverse standpipe of a height sufficient to dissipate the pressure difference between said reaction and heating zones.

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