

Feb. 12, 1946.

H. Z. MARTIN ET AL

2,394,928

CONVERSION PROCESSES AND APPARATUS THEREFOR

Filed Feb. 27, 1941

2 Sheets-Sheet 1

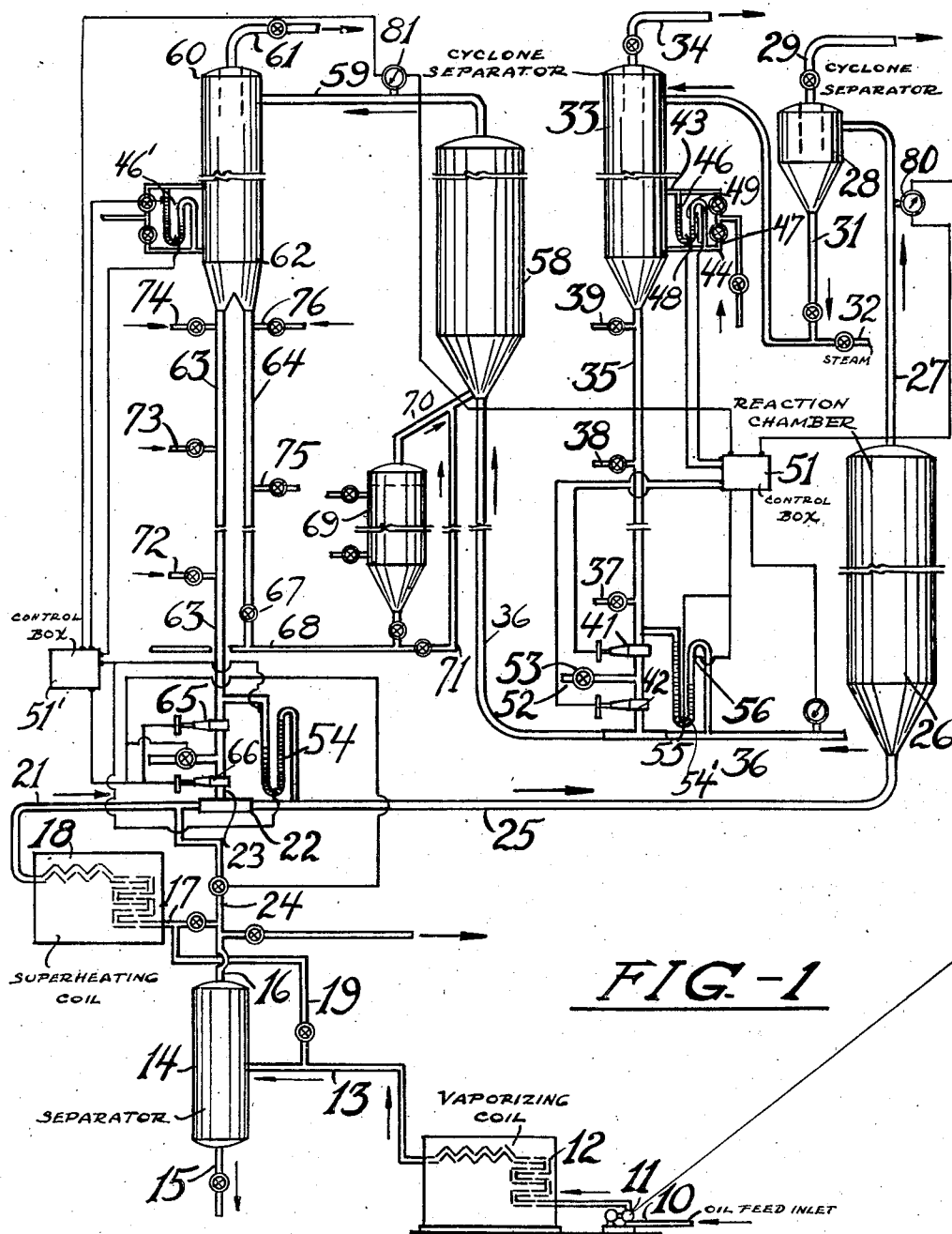


FIG-1

Homer Z. Martin
Eger V. Murphree
Edwin J. Coker
Inventors
By *John H. Graham* Attorney

H. Z. MARTIN ET AL

CONVERSION PROCESSES AND APPARATUS THEREFOR

Filed Feb. 27, 1941

2 Sheets-Sheet 2

Homer T. Martin
Eger V. Murphree
Edwin J. Cochr
John M. Graham Inventors
By P. A. Young Attorney

UNITED STATES PATENT OFFICE

2,394,928

CONVERSION PROCESS AND APPARATUS
THEREFOR

Homer Z. Martin, Elizabeth, and Eger V. Murphree and Edwin J. Gohr, Summit, and John M. Graham, Dunellen, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

Application February 27, 1941, Serial No. 380,888

12 Claims. (Cl. 196—52)

This invention relates to conversion processes wherein gases or vapors are treated with finely-divided material and pertains more particularly to processes wherein the finely-divided material is successively injected or intermixed with different types of gases which should not be intermingled.

In certain industrial processes wherein powdered material is successively contacted with different gaseous agents, it is of utmost importance to prevent the intermingling of such gases. One specific example of such an operation is the catalytic cracking of hydrocarbon oils wherein the catalyst in finely-divided form is injected into the stream of oil vapors to be cracked, the catalyst subsequently separated from the cracked products, and reinjected into a stream of oxidizing gas such as air for removing carbonaceous deposits from the catalyst mass. In such operation safety requires that the air or other oxidizing gas be prevented from intermingling with the oil vapors to be cracked in case abnormal operating conditions should arise.

The object of the present invention is to provide a method and apparatus for preventing the intermixing of the two gases.

The specific object of the invention is to provide an improved method and apparatus for preventing intermingling of regenerating gas and oil vapors in catalytic cracking operations wherein a powdered cracking catalyst is employed.

Other objects and advantages of the invention will be apparent from the detailed description hereinafter, in which reference will be made to the accompanying drawings.

In the drawings, Fig. 1 is a diagrammatic view of a catalytic cracking apparatus to which the invention may be applied; and

Fig. 2 is an enlarged detailed view partly diagrammatic of certain safety controls forming part of the present invention.

Referring to Fig. 1, the reference character 10 designates a charge line through which the oil to be treated is introduced into the system. This oil may comprise a clean condensate stock such as a gas oil or it may be a residual stock containing unvaporizable constituents under the conditions obtained within the cracking zone. The charging stock from line 10 is forced by means of pump 11 through a vaporizing coil 12 located in a heating furnace wherein the oil is heated to a temperature sufficient to effect substantial vaporization of the oil. The heated oil from the vaporizing coil 12 is transferred through line 13 to a separator 14 wherein vapors separate from unvaporized residue. The unvaporized residue is

withdrawn from the separator through line 15 and may be subjected to any further treatment desired outside of the purview of the present invention.

5 Vapors liberated in separator 14 pass overhead through lines 16 and 17 to a superheating coil 18 wherein the vapors may be further heated before passing to the cracking zone.

In cases where a clean condensate stock which is completely vaporizable is employed, the separator 14 may be omitted or the oil vapors from the initial coil 12 may by-pass through line 19 directly to the heating coil 18. Products from heating coil 18 may pass through line 21 to a dispersion chamber or chest 22 wherein they are intermixed with a powdered catalyst introduced through conduit 23. This catalyst may be any suitable cracking catalyst capable of effecting or accelerating the cracking of oils. Among such catalysts may be mentioned naturally active or activated clays, such as acid treated bentonite clays, and synthetic gels comprising silica and alumina or silica and magnesia or mixtures thereof.

25 In some cases, superheating coil 18 may be omitted and the oil vapors removed overhead from the separator 14 may be passed through line 24 and mixed directly with the catalyst.

30 The combined mixture of catalyst and oil vapors is transferred through line 25 to a reaction chamber 26 wherein the oil vapors are retained for a period sufficient to obtain the desired amount of cracking. The velocity of the oil vapors passing through reaction chamber 26 is preferably insufficient to carry the catalyst along at substantially the same velocity as the vapors. In other words, the velocity is such that the catalyst tends to separate out of the oil stream during its passage through the reaction chamber. By operating at this relatively low velocity, there is continuous churning or intermixing of the powdered catalyst within the reaction chamber and uniform conditions are maintained. As an example, the time of residence of the oil vapors within the cracking zone may be of the order of from 5 to 50 seconds more or less, whereas the resident time of catalyst within the reaction zone may be of the order of 2 minutes to an hour or more. The velocity of the oil vapors is preferably sufficiently high, however, to prevent catalyst from completely settling and packing within the reaction chamber. As a result, the oil vapors leaving the reaction chamber can be used as a carrier for removing the catalyst therefrom.

The cracked products containing catalyst entrained therein leave the reaction chamber 26 through line 27 and pass to a cyclone separator 28 or some equivalent device for separating finely-divided solids from gases. The oil vapors separated from the catalyst in the separator 28 are passed overhead through line 29 and may be passed to any suitable recovery system for segregating the desired motor fuel product. If desired, the overhead products from the first separator 28 may be passed to a further separating and purifying apparatus, such as additional cyclone separators, for further removal of residual powdered material from the oil vapors before passing to the fractionating tower or other recovery apparatus.

Catalyst separated in the initial separator 28 is removed from the bottom therefrom through conduit 31 and is discharged into a stream of inert gas, such as steam introduced through line 32 which may serve to remove volatile hydrocarbons from the catalyst mass. The mixture of inert gas and catalyst passes through line 32 to a second cyclone separator 33, wherein the catalyst is separated from the inert gas. The stripping gas is rejected from the second separator through line 34 and the catalyst separated is collected in the bottom section thereof which may serve as a hopper of sufficient capacity to provide a reserve supply of catalyst.

The stripping gas removed from separator 33 through line 34 may be passed to suitable fractionating or other recovery equipment for separating oil constituents therefrom.

The catalyst so separated from the cracked products may be returned to the cracking zone without any intermediate regenerating treatment. In most cases, however, it is desirable to subject the catalyst to a regenerative treatment to remove carbonaceous deposits before returning the same to the cracking zone. To this end the catalyst from the bottom section of the cyclone separator 33 discharges through a vertical conduit or standpipe 35 into a stream of air or other oxidizing gas introduced through line 36. The height of the standpipe or column 35 is preferably such as to develop a pressure at the bottom thereof sufficient to feed the catalyst into the stream of oxidizing gas which in turn must be under a pressure at least sufficient to overcome the resistance of the regenerating circuit to the flow of such a mixture of gas and powdered material. In order to transmit the static pressure through the length of the column or standpipe 35, catalyst contained therein must be maintained in a freely flowing condition or in a fluidized state. In many instances it is necessary to introduce a fluidizing gas at one or more spaced points along the length of the column through lines 37, 38 and 39 in order to maintain the catalyst in a freely flowing state.

The bottom portion of the column 35 is provided with a pair of valves 41 and 42, one of which may be controlled to regulate the amount of catalyst flowing into the stream of regenerating gas and the other of which may be operated automatically to close in case abnormal conditions should arise within the operating unit which would tend to cause a flow of the regenerating gas upwardly through the column 35 and into the stream of cracked vapors removed from cyclone separator 33.

Referring to Fig. 2, either or both valves 41 and 42 may be operated by a level controller in

the hopper located above the standpipe 35 to automatically close when the level in the hopper drops below a predetermined point which might permit air to pass upwardly through the standpipe into the hopper. Any suitable level controller may be employed for regulating the valves. In Fig. 2 the level controller is shown in the form of two tubes 43 and 44 connected to the hopper at spaced points through which an inert gas is supplied through line 45 under a pressure sufficient to feed the gas into the hopper. A U-tube 46 filled with mercury or other suitable conductor may be provided, having one end connected to the tube 43 and the opposite end connected through line 47 with tube 44. The difference in level of the mercury and the two legs of the U-tube indicates the difference in pressure between the two tubes 43 and 44. Consequently, if the level in the hopper should drop below the lower tube 44, the outlet pressure of the two tubes 43 and 44 would be substantially the same and consequently the level of mercury on both legs of the U-tube 46 would be substantially equal. By providing electrical contact points at the bottom of the U-tube such as at 48 and at an intermediate point 49 in the U-tube 46 when the mercury in both legs of the U-tubes tends to become equal, an electrical circuit may be closed operating suitable relay switches or other equivalent devices in a control box 51 which in turn may cause either one or both of the valves 41 and 42 to close. As illustrated, a steam line 52 is provided between the two valves. Upon closing of the valves 41 and 42, valve 53 in steam line 52 may be opened automatically by suitable relay switches in the control box 51 to introduce steam between the two valves under a pressure in excess of that existing in the oil line or in the standpipe. Consequently, if either of the two valves should leak, the steam or other inert gas introduced through line 52 would flow outwardly against the oil vapors and thus prevent their passage to the standpipe 35.

As a further precaution, a second U-tube 54 containing mercury or other pressure differential controller may be interposed between the air line 36 and the standpipe 35 immediately above valve 41 so that if the pressure in the air line should approach the pressure above the valve 41 an electrical circuit may be closed by suitable contact points 55 and 56 which in turn may operate suitable relay switches for the closing of valves 41 or 42, or both. When this happens, valve 53 in steam line 52 may also open automatically to introduce steam between the valves.

As a further precaution, the level controller 46 or the pressure differential controller 54 may be employed to automatically operate suitable valves in the oil vapor lines to cut off the supply of oil vapors to the system and to by-pass them to suitable recovery equipment (not shown).

While the level controller and the pressure differential controllers have been shown in the form of U-tubes containing mercury, it will be understood that any other suitable controller operating in a similar manner can be employed in their stead. Furthermore, while two separate valves have been shown, one of which is adapted to remain open during normal operations and to close automatically in case of abnormal operations, as hereinbefore described, whereas the other is adapted to be operated to regulate the flow of catalyst into the air line 36, it will be understood that a single valve may be provided to operate both as a control and as a shut-off

valve, if desired. However, as a matter of safety, it is preferred to provide a separate shut-off valve operating independently in case of abnormal conditions arising within the unit which might tend to cause the intermingling of the air with the oil vapors.

Returning again to Fig. 1, the catalyst recovered from the cracked products and collected in standpipe 35 is fed at a controlled rate through control valve 41 and safety valve 42 into the air line 36 through which it is transferred to a regenerating chamber 58.

Carbonaceous deposits formed during the cracking operation are removed from the catalyst particles by burning with air introduced through line 36. The regenerator may be of any desired construction. The flow of the regenerating stream through the reactor 58 is preferably controlled as described in connection with the reaction vessel 26 so that the velocity of the air or regenerating medium is insufficient to carry the catalyst undergoing regeneration at a velocity approaching that of the air. In other words, the velocity of the stream is regulated in proportion to the size and density of the catalyst particles so that the particles move through the regenerating zone at a much slower rate than the air stream. Consequently, there is continuous intermingling of the catalyst particles with the air stream resulting in the maintenance of a uniform temperature within the regenerator. This is of particular importance since in many cases the activity of the catalyst is seriously impaired if the temperature is allowed to exceed a predetermined maximum. For example, when regenerating activated clays, the temperature in general should be maintained below 1200° F. On the other hand, to effect rapid regeneration of the catalyst, it is desirable to carry out the regeneration at the maximum temperature which will not impair the activity of the catalyst. By regulating the flow of air or regenerating gas through the reactor as described, much closer temperature control may be maintained.

The regenerated catalyst and regenerating gas are withdrawn from the regenerator 58 through line 59 and may be passed to a cyclone separator 60 or other equivalent separating device for segregation of the regenerating gas from the regenerated catalyst. The regenerating gas is removed from the cyclone separator through line 61. This gas may, if desired, be passed to further recovery system for removal of the powdered material before being vented or exhausted to the atmosphere. Regenerated catalyst separated in the cyclone separator 60 collects in hopper section 62 located immediately below from which it passes into either or both of two standpipes 63 and 64. Catalyst collected in standpipe 63 discharges into the dispersion zone or chamber 22 through which the oil vapors pass from line 21.

The bottom of the standpipe 63 is also provided with two valves 65 and 66, one of which is adapted to be controlled to regulate the flow of catalyst into the oil vapors and the other of which is adapted to function as a shut-off valve in case abnormal operating conditions tend to arise which might cause transfer of oil vapors upwardly through the standpipe 63. The shut-off valve and the control valves 65 and 66 may be operated in the same manner as valves 41 and 42 located in the standpipe 35. In view of this, corresponding parts of the control mechanism have been shown in the drawings by prime numbers. The shut-off valve which it be assumed to be valve 66

may be operated automatically when the level of the hopper 62 drops below a certain point or when the pressure of the oil vapors in the dispersion chamber 22 tends to exceed or approach the pressure on the opposite side of valve 66.

In order to control the temperature within the regenerator 58, a portion of the regenerated catalyst may be recirculated after having been cooled to the desired point. To this end the portion of the catalyst collected in the standpipe 64 is passed through valve 67 into a gas stream passing through line 68. The gas stream passing through line 68 may be air or it may be an inert gas serving as a carrier for the catalyst. The stream of regenerated catalyst and gas carrier passes through line 68 through a cooler 69 and then passes through line 70 into the regenerator 58 where it intermixes with the unregenerated catalyst introduced through line 36 and serves as a cooling agent therefor. In order to more closely regulate the catalyst within the chamber 58, a portion of the regenerated catalyst recycled through line 68 may by-pass around the cooler 69 through line 71.

In order to maintain the catalyst in the standpipe or vertical column 63 and 64 in a suitable freely flowing fluidized state, the fluidizing gas may be introduced at one or more spaced points through lines 72, 73, 74, 75 and 76.

The safety controls hereinbefore described are for the purpose of preventing intermingling of oil vapors and regenerating gas either by backing up of regenerating gas upwardly through standpipe 35 or by backing up of oil vapors through standpipe 63.

Conditions may also arise which might tend to force oil vapors downwardly through standpipe 35 into the air stream in line 36 or regenerating gas downwardly through standpipe 63 to the oil vapor stream in mixing jet 22.

To avoid these possibilities the transfer line 27 may be provided with an automatic pressure control valve 80 adapted to cut off the oil supply or to by-pass the oil to suitable run-down and recovery apparatus not shown. Such pressure controller may also function to close either or both of valves 41 and 42 and to open stream line 52.

Likewise, a pressure controller 81 may be placed in line 59 leading from regenerator 58. This controller may function to cut the air supply in line 36 and line 68 and may also function to close either or both valves 65 and 66 and to open a stream line therebetween.

While the invention has been described as applied to a particular type of catalytic cracking apparatus, it will be understood that the invention is directed to a method and apparatus for preventing intermixing of oil vapors and regenerating gas and may be applied to forms of apparatus other than that shown.

The term "abnormal pressure conditions" as herein employed means pressure conditions materially different than those existing during normal operation. Such abnormal pressure conditions may arise, for example, by building up of excessive pressures on the oil vapors due to coking or plugging of oil lines or from other causes, or a failure in pressure on the regenerating gas, or vice versa.

Having described the preferred embodiment of the invention, it will be understood that it embraces such other variations and modifications as come within the spirit and scope thereof.

What is desired to be protected by Letters Patent is:

1. In a process for contacting solids and gases wherein one stream of reactants passes through a reaction chamber containing a relatively dense mass of finely-divided contact material, a second stream of gases passes through a second chamber containing a mass of said finely-divided contact material, the contact material from one chamber being continuously passed to the other through a valved conduit in open communication with said chambers and wherein it is desired to prevent intermingling of gases from one chamber with the gases from the other; the improvement which comprises imposing a pressure on the contact material passing through said conduit substantially greater than the pressure on the gases passing to the chamber into which said contact material passes under normal operating pressure conditions, measuring the difference between the pressure on the contact material in said conduit and the pressure existing in said last-named chamber under normal conditions and closing the valve in response to a predetermined reduction in said pressure differential to prevent passage of gases from one chamber to the other.

2. In a process for the conversion of hydrocarbon oils wherein the oil to be converted is passed through a conversion chamber containing a relatively dense mass of finely-divided contact material, a regenerating gas is simultaneously passed through a second chamber containing a mass of said finely-divided contact material, the contact material from the conversion chamber being continuously transferred to the regenerating chamber through a valved conduit in open communication with said chambers; the improvement which comprises imposing a pressure on the finely-divided contact material passing through said conduit substantially greater than the pressure on the gases passing through the regenerating chamber, measuring the difference between the pressure on the contact material in said conduit and the pressure on the regenerating gases passing through said regenerating chamber and closing the valve in response to a predetermined reduction in said pressure differential to prevent intermingling of the regenerating gas with the oil vapors.

3. In a process defined by claim 1, the further improvement which comprises injecting an inert gas into said conduit when said pressure difference drops below a predetermined value.

4. In the process defined by claim 2, the further improvement which comprises discontinuing the supply of oil into said conversion chamber when the pressure difference drops below a predetermined value.

5. In an apparatus comprising a reaction chamber adapted to contain a mass of finely-divided contact material, means for passing a stream of gases to be reacted through said reaction chamber in direct contact with said finely-divided material, a second chamber, means for passing a second stream of gases through said last-named chamber, a conduit having one end in open communication with said first-named stream of gases and the opposite end in open communication with said last-named stream of gases, said conduit being adapted for transferring finely-divided contact material from one of said streams of gases to the other, means for imposing a pressure on the contact material passing through said conduit substantially greater than the pressure on the stream of gases into which said contact ma-

terial is transferred, and means responsive to a predetermined change in the differential between the pressure imposed on the contact material passing through the conduit and the pressure on said last-named gas stream to close said conduit.

6. In an apparatus for carrying out chemical reactions in the presence of finely-divided contact material comprising a reaction chamber adapted to contain a mass of said finely-divided contact material, means for passing a stream of gases through said reaction chamber in direct contact with said finely-divided material, a regeneration chamber for regenerating said contact material, means for passing a stream of regenerating gas through said regenerating chamber, a conduit having one end in open communication with said stream of reaction gases and the opposite end in open communication with said stream of regeneration gases, said conduit being adapted to transfer finely-divided contact material from one of said gas streams to the other, means for imposing a pressure on the contact material passing through said conduit substantially greater than the pressure on the stream of gases into which said contact material is transferred, and means responsive to a predetermined change in the differential between the pressure imposed on the contact material passing through said conduit and the pressure on said last-named stream of gases to close said conduit.

7. In an apparatus for carrying out the conversion of hydrocarbon oils in the presence of a finely-divided conversion catalyst which requires frequent regenerations comprising a conversion chamber, means for passing a stream of hydrocarbon vapors to be reacted through said conversion chamber, means for introducing finely-divided conversion catalyst into said stream of hydrocarbon vapors, a regeneration chamber, means for passing a stream of regeneration gases through said regeneration chamber, a conduit having one end in open communication with the hydrocarbon vapors and the opposite end in open communication with said stream of hydrocarbon gases, said conduit being adapted to transfer finely-divided conversion catalyst from one of said streams of gases to the other, means for imposing a pressure on the finely-divided conversion catalyst passing through said conduit substantially greater than the pressure on the stream of gases into which said conversion catalyst is transferred, and means responsive to a predetermined change in the differential between the pressure imposed on the conversion catalyst passing through said conduit and the pressure on the last-named gas stream to close said conduit.

8. In the apparatus defined by claim 7, the further improvement which comprises means responsive to said pressure differential for injecting an inert gas into said conduit.

9. In the apparatus defined by claim 7, the further improvement which comprises means responsive to said pressure differential for discontinuing the flow of hydrocarbon vapors.

10. In the apparatus defined by claim 7, the further improvement which comprises means responsive to said pressure differential for stopping the flow of said regeneration gas.

11. In an apparatus comprising a reaction chamber, means for passing a confined stream of reaction gases through said reaction chamber, means for introducing finely-divided contact material into said stream of gases, a regeneration chamber for said contact material, means for passing a confined stream of regeneration gases

through said regeneration chamber, a vertically disposed conduit having one end in open communication with said stream of reaction gases and the opposite end in open communication with said stream of regeneration gases, means for transferring finely-divided contact material from one of said gas streams into the upper end of said conduit, means for discharging the contact material at the bottom of said conduit into said other stream, means for controlling the rate of discharge of said contact material into said last-named stream, said last-named means being normally controlled to maintain a predetermined level of finely-divided contact material within said conduit, means adapted to maintain a fluidizing gas in admixture with said finely-divided material within said conduit to keep said contact material in a freely flowing, fluidized state to develop thereby a hydrostatic pressure at the base thereof, the level of said contact material within said conduit being normally controlled to develop a hydrostatic pressure at the base of said conduit substantially greater than the pressure on the gas stream in open communication therewith, and means responsive to a predetermined reduction of said level to close said conduit.

12. An apparatus for the conversion of hydrocarbon oils wherein the oils are converted in the presence of a finely-divided conversion catalyst comprising a conversion chamber, means for passing a confined stream of hydrocarbon vapors to be converted through said reaction chamber, means for introducing finely-divided contact material into said stream of gases, a regeneration chamber, means for passing a confined stream of regeneration gases capable of burning carbonaceous deposits from said contact material through said regeneration chamber, a vertical conduit having one end in open communication with said hydrocarbon vapors and the opposite end in open communication with said stream of regeneration gases, means for introducing contact material from one of said streams into the upper end of said conduit, means for discharging contact material from the bottom of said conduit into the other stream of gases, means for controlling the rate of discharge of said contact material into said last-named stream, said control means being normally regulated to maintain a predetermined level of finely-divided material within said conduit, means adapted to maintain a fluidizing gas in admixture with said finely-divided material within said conduit to keep said contact material in a freely flowing, fluidized state and thereby develop a hydrostatic pressure at the base thereof, the level of said contact material within said conduit being normally controlled to develop a hydrostatic pressure at the base of said conduit substantially greater than the pressure on the gas stream into which said contact material discharges, means responsive to a predetermined change in the differential between the pressure on the contact material at the base of said conduit and the pressure on the gases into which said contact material discharges to close said conduit, and further means responsive to a predetermined reduction in the level of said contact material in said conduit to close said conduit.

HOMER Z. MARTIN.
EGER V. MURPHREE.
EDWIN J. GOHR.
JOHN M. GRAHAM.