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METHOD OF TREATING AND REMOVING FINELY-DIVIDED SOLID MATERIAL

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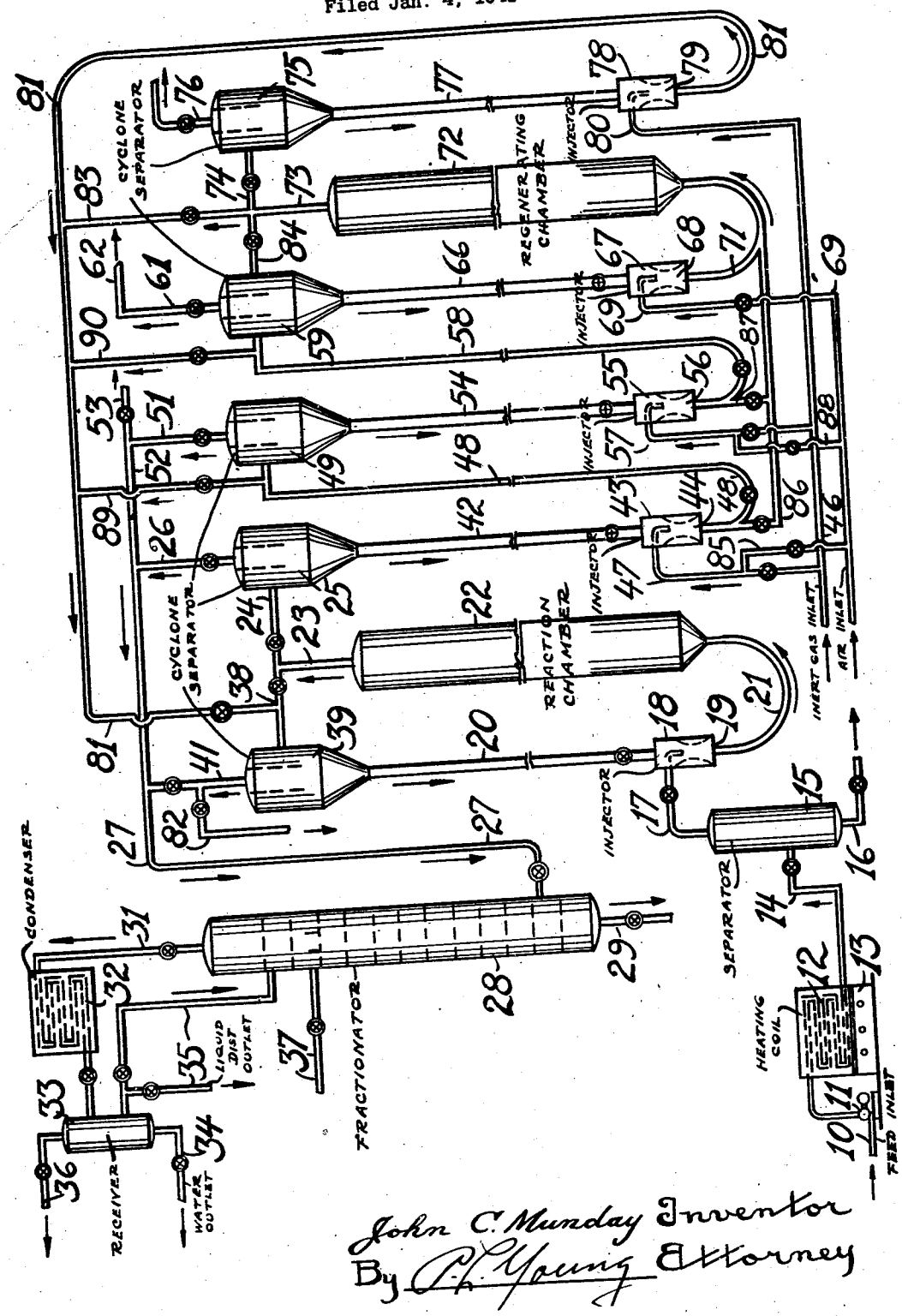

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METHOD OF TREATING AND REMOVING FINELY DIVIDED SOLID MATERIAL

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This invention relates to a process of and apparatus for carrying out catalytic reactions and pertains more particularly to processes and apparatus wherein the catalyst in finely-divided form is introduced into a stream of gases to be reacted and the resulting mixture passed through a reaction zone.

While the invention in its broader phases has a more general application, it is particularly suitable for the cracking of higher boiling hydrocarbon oils into lower boiling oils, such as motor fuels, diesel fuels, kerosenes, and the like.

It has heretofore been proposed to crack petroleum oils by first intermixing finely-divided catalyst with the oil vapors to be cracked and then passing the resulting mixture through a cracking zone maintained at the desired temperature for bringing about the cracking operation. Following the cracking operation, the catalyst is separated from the cracked products and the cracked products fractionated to segregate the motor fuel or other low boiling distillates from the insufficiently cracked higher boiling oil and the gaseous constituents formed during the cracking operation. The catalyst separated from the cracked products is normally subjected to a regenerative treatment to remove combustible deposits which accumulate during the cracking operation. Following the regenerative treatment, the catalyst is returned to the cracking zone for further use.

When operating according to this general type of procedure, difficulty has been encountered in introducing the catalyst into the stream of oil vapors. This difficulty is due in a large measure to the fact that the oil vapors must be under a substantial pressure at the time the catalyst is introduced therein. The pressure in the oil vapors must be, for example, at least sufficient to overcome the frictional resistance of the cracking apparatus and the adjoining fractionating and refining equipment to the flow of the oil vapors and the oil vapor-catalyst mixture therethrough. In commercial scale cracking equipment of this type, the pressure necessary to overcome such frictional resistance may be of the order of one atmosphere. Furthermore, in some cases it is desirable to operate the cracking process under superatmospheric pressure.

It is also desirable in many cases to operate the regenerative equipment under a substantial pressure in order to reduce the size of the equipment and for other reasons.

It has been a practice to build up the required pressure on the catalyst to introduce the same into the oil vapors or the regenerating gas by a compression screw. Such screws, however, are subject to certain inherent limitations. First, when constructed of abrasion-resistant alloys the cost of such screws is a serious factor in the economics of the process. Secondly, considerable power is required to operate the screw and compress the catalyst, which in turn increases the operating cost of the process. Thirdly, the life of the screw in many instances is relatively short even when constructed of abrasion-resistant alloys due to the abrasive characteristics of the catalytic material. Furthermore, in many cases the compression of the catalyst adversely affects the activity thereof. For example, it has been found that the action of the compression screw tends to agglomerate the particles into spheres and pellets having a lower catalyst activity.

One of the primary objects of the present invention is to provide an improved method of introducing the powdered catalyst into a stream of gases to be reacted which will not be subject to the inherent objections hereinbefore pointed out.

A further object of the invention is to provide an improved process of and apparatus for cracking hydrocarbon oils in the presence of finely-divided catalyst.

Other specific objects and advantages of the invention will be apparent from the detailed description hereinafter in which reference will be made to the accompanying drawing which is a diagrammatic illustration of an apparatus forming a part of the present invention and capable of carrying the process into effect.

For illustrative purposes the invention will be described as applied to the catalytic cracking of hydrocarbon oils, it being understood, as hereinbefore explained, that the invention in its broader phases has a more general application.

Referring to the drawing, the reference character 10 designates a charge line through which the oil to be cracked is forced by means of pump 11 into a heating coil 12 located in furnace 13. The oil, during its course through the heating coil 12, is heated to a temperature sufficient to vaporize at least a substantial portion of the oil. The products from the heating coil 12 are discharged through transfer line 14 into a separator 15 in which vapors formed during the heating thereof separate from unvaporized residue.

The oil employed in the process may consist of a clean condensate stock, such as a gas oil, or it may comprise a residual stock, such as a topped or reduced crude. In case a clean condensate

stock is employed, the separator 15 may be omitted or a by-pass line may be provided around the separator. Unvaporized oil separated in the separator 15 is withdrawn therefrom through line 16. Vapors liberated in the separator 15 pass overhead through line 17 to an injector 18 having a restricted Venturi nozzle 19. The catalyst is introduced into the injector 18 through a line 20. The catalyst from line 20 becomes intermixed with the oil vapors in the Venturi nozzle 19 of the injector 18. The pressure and velocity of the oil vapors introduced into the injector 18 should be sufficient to build up a substantial pressure on the resulting mixture of oil vapors and catalyst. The final pressure imposed on the oil vapor-catalyst mixture should be at least sufficient to overcome the frictional resistance of the cracking equipment and may be higher.

The catalyst introduced into the injector 18 may be of any suitable character capable of bringing about or accelerating the desired cracking of hydrocarbon oil. Such catalyst may consist, for example, of a naturally active or activated clay or synthetic gels of the same or different chemical composition. The relative amount of catalyst introduced into the oil vapors may be controlled by regulating a valve in the line 20. The relative amount of catalyst introduced into the oil vapors will depend upon the nature of the feed stock, characteristics of the catalyst, degree of conversion desired, temperature, and other factors. In most cases the concentration of catalyst is relatively high and may range from 0.5 part of catalyst per part of oil to 10 or more parts of catalyst per part of oil by weight. The oil vapors and catalyst mixture formed in the injector 18 is transferred through line 21 to a reaction chamber 22 in which the oil vapors are retained for a period sufficient to obtain the desired degree of cracking. For example, the amount of oil converted into gasoline during passage through the reaction chamber 22 may range from 20% to 60% or more of the fresh oil. The temperature maintained within the reaction chamber may be, for example, from 750° to 1000° F. This temperature may be maintained by the sensible heat resulting from passing the oil vapors through the preheating coil 12 or the oil vapors from separator 15 may be subjected to additional superheating by suitable heating elements (not shown) before being intermixed with the catalyst. Also a part of the heat may be supplied by the catalyst introduced into the oil stream.

The time of contact of the oil vapors within the reaction zone may be between 1 and 50 seconds. The velocity of the oil vapors passing through the reaction zone is preferably insufficient to carry the catalyst at substantially the same rate as the oil vapors. As a result, there is a general tendency for the catalyst to settle out of the oil vapors during its passage through the reaction zone. However, the velocity of the oil vapors should be sufficient to prevent complete settling of the catalyst. The velocity of the oil vapors may be, for example, between 1 and 10 feet per second. In such case the density of the oil vapor-catalyst mixture within the reactor will be materially higher than the density of the mixture passing into and out of the reactor. Furthermore, the time of passage of the catalyst through the reaction zone would normally be considerably longer than the time required for the passage of the oil vapors through the reaction zone. For example, the resident time of the catalyst within the reaction chamber 22 may range from a few minutes to an hour or more.

After passing through the reaction chamber 22, the mixture of cracked products and finely-divided catalyst is removed therefrom through line 23 and may pass through line 24 to a suitable separator, such as a cyclone separator 25, for the separation of the cracked products from the catalyst. The cracked products separated in the separator 25 are removed therefrom through line 26 and may pass through line 27 to a fractionating tower 28 wherein the products are fractionated to condense insufficiently cracked constituents therefrom. The higher boiling condensate boiling above the desired motor fuel fraction is withdrawn from the fractionating tower 28 through line 29. Vapors remaining uncondensed during passage through fractionating tower 28 are removed therefrom through line 31 and are passed to a condenser 32 wherein the desired motor fuel distillate is condensed. Products from the condenser 32 pass to a receiver 33 wherein liquid separates from uncondensed vapors.

In cases where substantial amounts of steam are employed during the cracking operation, for example, by adding steam to the oil passing through line 14 to separator 15, the water formed by condensation of the steam may be withdrawn from the receiver 33 through line 34 and the liquid distillate may be withdrawn through line 35. Gases separated in receiver 33 are removed therefrom through line 36 and may be rejected from the system or subjected to any further treatment for the recovery of gasoline constituents therefrom. If desired, a portion of the distillate separated in the receiver 33 may be returned to the top of the fractionating tower as reflux therefor. A kerosene fraction, Diesel oil fraction or heating oil fraction may be segregated in the fractionating tower 28 in a suitable trap-out tray and withdrawn therefrom through line 37.

Returning to the reaction chamber 22, it is sometimes desirable to recirculate a portion of the catalyst removed from the reaction chamber back to the inlet thereof. In other cases it may be desirable to recirculate all of the catalyst for a definite period of time. In such cases a part or all of the products removed from the reaction chamber 22 may be passed through line 38 to a suitable separator, such as a cyclone separator 39, for segregation of the cracked products from the catalyst mixture. The cracked products in the cyclone 39 are transferred through line 41 and line 27 to the fractionating tower 28 for fractionation as just described. The catalyst separated in the cyclone 39 discharges into the conduit or pipe 20 from which it is passed into the injector 18 for recycling to the cracking chamber.

For simplicity a single cyclone separator has been shown for separation of the catalyst from the oil vapors. However, it may be desirable to provide a plurality of such cyclones arranged in a series or to provide other suitable separating device in lieu of or addition to the cyclone separators.

As previously mentioned, a part of the catalyst may be continuously recycled to the reaction chamber through cyclone separator 39 and pipe 20 while the remainder is regenerated, or all of the catalyst may be recycled for a limited period, after which all of the catalyst will be passed to a regenerating circuit now to be described.

Referring again to the cyclone separator 25, catalyst separated therein discharges through line 42 into an injector 43 having a restricted

throat 44 into which an inert stripping gas is discharged through line 47 at a pressure and velocity sufficient to develop additional pressure on the outgoing mixture of gas and catalyst. The inert gas employed as a stripping and carrier medium for the catalyst may consist of steam, carbon dioxide, spent combustion gases, nitrogen, or the like. Such gas may be introduced into the system through line 46 and transferred to the injector 43 through lines 47.

The mixture of stripping gas and catalyst formed in the injector 43 is transferred through line 48 to a further cyclone separator 49 or other equivalent device for the separation of the catalyst from the stripping gas. This stripping gas separated in the separator 49 may contain small amounts of residual hydrocarbon vapors remaining on the catalyst after separation from the cracked vapors in the cyclone 25. In view of this, the stripped gas containing the hydrocarbon vapors may be passed through lines 51 and 52 to line 27 wherein stripping gas is intermixed with the cracked products. If desired, a part or all of the stripping gas may be rejected from the system through line 53 and, if desired, passed to other apparatus for the recovery of oil therefrom.

In some cases it is preferable to recycle catalyst to the reaction zone after it has been subjected to a stripping gas such as steam. To this end a line 89 leading from line 48 to line 81 is provided whereby the suspension of catalyst and stripping gas can be passed through lines 89, 81 and 38 to separator 39 and the stripped catalyst recycled to reaction zone 22 through line 20, injector 18 and line 21. If desired, the catalyst may be reheated prior to its return to the reaction zone.

Stripped catalyst separated in the separator 49 discharges through line 54 into another injector 55 having a restricted throat 56. Additional steam or other inert gas from line 46 may be introduced into the injector 55 through line 57 to effect additional stripping action on the catalyst. The resulting mixture of stripping gas and catalyst passes through line 58 into a further cyclone separator 59 wherein the stripped catalyst separates from the stripping gas. The stripping gas is withdrawn from the separator 59 through line 61 and may be rejected from the system through line 62.

Stripped catalyst separated in the cyclone separator 59 discharges through line 66 into an injector 67 having a restricted throat 68 into which an oxidizing gas, such as air or air diluted with other inert gases, is introduced through line 69. The amount and velocity of air introduced into the injector 67 is sufficient to build up additional pressure on the catalyst-air mixture so that at this stage the pressure is at least sufficient to overcome the frictional resistance of the regenerating system to the flow of the catalyst-gas mixture and may be sufficiently high to carry out the regenerative treatment under substantial superatmospheric pressure, such as from 2 to 10 or more atmospheres. The pressure employed in the regeneration zone may be considerably higher than the pressure employed in the cracking zone. The resulting mixture of regenerating gas and catalyst formed in the injector 67 is transferred through line 71 to a regenerating chamber 72 wherein the conditions are controlled to remove combustible deposits from the catalyst formed during the cracking operation. It is preferred to control the velocity of the regenerating gas so that the time of residence of the catalyst in the regenerating zone is substantially longer than the time required for the passage of the regenerating gas therethrough. By regulating the velocity of the regenerating gas passing through the regenerating zone, the length of time the catalyst is subjected to regeneration may be controlled over an extended range.

The suspension of regenerated gas and catalyst after passing through regenerator 72 is withdrawn through line 73 and may be passed through line 74 to a separator 75 adapted to separate the powdered regenerated catalyst from the regenerating gas. The regenerating gas separated in the separator 75 is removed therefrom through line 76 and may be rejected from the system or it may be passed to suitable heat exchangers for the recovery of energy therefrom. The regenerated catalyst separated in the separator 75 is transferred through pipe 77 to an injector 78 having a restricted throat 79 into which is injected a stream of inert stripping and conveying gas introduced through line 80. The amount and velocity of the stripping gas introduced into the injector are regulated to develop or build up additional pressure on the resulting mixture. The suspension of stripping gas and catalyst formed in the injector 78 is transferred through line 81, which in turn merges with line 38 leading to the separator 39. The regenerated catalyst is separated from the stripping or carrier gas in the separator 39 and the regenerated catalyst is discharged through line 20 into the injector 18 where it remixes with fresh oil vapors.

In carrying out a process of this sort wherein catalyst is transferred continuously from a reaction zone to a regeneration zone and from the regeneration zone to the reaction zone, it is generally necessary to keep the reactants separated from the regeneration medium. In the present example wherein hydrocarbons are the reactants and air is the regeneration medium, segregation is imperative. When the system is in normal operation, the level of catalyst in pipes 20, 42, 54, 66 and 77 leading to the injectors 18, 43, 55, 67 and 78, respectively, will maintain the desired seal between the cracking and regenerating sections of the equipment. Furthermore, the use of a stream of stripping gas in one or more stages between the two sections further assists in preventing intermingling of regenerating gas with hydrocarbon vapors and vice versa. However, since abnormal conditions may develop, more positive seals may be provided. For example, such seals may be mechanical devices responsive to abnormal conditions or a solid mass of deaerated catalyst may be interposed between the two parts of the quipment. In the present process, the use of mechanical moving parts is avoided by employing a head of catalyst powder as the seal.

It will be observed that the present process avoids the use of large storage hoppers, intermediate lock hoppers, and conveying systems and conduits in which catalyst is transferred in dense phase. Consequently, the amount of catalyst present in the system which is not actually in use in the reaction cycle or undergoing regeneration is reduced to a minimum.

In cases where none of the catalyst removed from the reaction zone is recirculated without intermediate regeneration and no stripping of regenerated catalyst is necessary, separator 75 may be by-passed, the suspension of regenerated catalyst withdrawn from the regenerator 72 being

passed through lines 73, 83, 81 and 38 directly to separator 39. In such case the regeneration gases are withdrawn from the separator 39 through lines 41 and 82, and the separated catalyst is returned to the reaction zone by way of line 20 and injector 18. Where a portion of the catalyst is recirculated directly through lines 23 and 38, the regeneration gases should be separated from the catalyst in separator 75 and the catalyst should be transferred to separator 39 by means of an inert gas injected through line 80 in order to avoid mixing of hydrocarbon vapors and regeneration gas in separator 39. On the other hand, a part of the twice-stripped catalyst from stripping conduit 58 may be returned to the cracking zone by passing it in suspension through lines 90, 81, cyclone separator 39 and line 20.

In some cases it is also desirable to recirculate a portion of the catalyst removed from the regenerator back into the regenerator rather than passing it to the cracking zone. When operating in this manner, a portion of the stream of regenerating gas and catalyst withdrawn from the regenerator 72 through line 73 may be passed through line 84 to separator 59 from which the catalyst is returned to the regenerator through line 66, injector 67, and line 71.

While the drawing shows two separate stripping steps for separating hydrocarbon oil vapors between the cracking and regenerating systems, it will be understood that only one step may be employed and in some cases the stripping step may be completely eliminated. In the latter case, the air or other oxidizing gas from line 69 may be passed through lines 85 and 47 to the injector 43 and the resulting suspension of air and catalyst may be passed from injector 43 through lines 86 and 87 to the regenerator 72.

In cases where one stripping stage is employed, the air or other oxidizing gas for regeneration may be passed from line 69 through lines 88 and 57 to injector 55 and the resulting suspension passed through lines 87 and 86 to the regenerating chamber 72. In either of the above cases the injector 67 may be used solely for recirculating catalyst to the regenerator 72. In such case the catalyst recirculated to the regenerator may be subjected to a cooling operation to control the temperature therein.

The temperature of the regenerator should be regulated to avoid permanently impairing the activity of the catalyst. In most cases it is desirable to maintain the temperature below about 1200° F.

Fresh catalyst may be introduced at any desired point in the system to make up for that lost in operating the process.

The present invention thus provides a continuous process for carrying out reactions in the presence of finely-divided solid and an apparatus therefor which is substantially free of moving parts. The invention also provides a process for increasing the pressure on powder by transferring it from a zone of lower pressure to a zone of higher pressure by means of injectors rather than by compression screws or other mechanical devices. Furthermore, it provides a process for the continuous circulation of a powdered material through a plurality of zones containing vapors which are incompatible with one another.

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 the catalytic conversion of hydrocarbon oils, wherein finely-divided catalyst is injected into a stream of oil vapors to be converted, the resulting mixture passed through a conversion zone, the catalyst thereafter separated from the conversion products, the catalyst so separated treated with an inert gas to remove volatile hydrocarbons retained thereon following the separation; the improvement in the method of removing said volatile constituents which comprises passing a stream of inert gas through a restricted throat under a substantial pressure and at a velocity sufficient to develop a low pressure area adjacent the entrance of said throat, introducing separated catalyst into said low pressure area to thereby subject said catalyst to low pressure treatment and to inject said catalyst into the stream of inert stripping gas passing through said throat and thereafter separating the stripped catalyst from said inert gas.

2. In the catalytic conversion of hydrocarbon oils wherein finely-divided catalyst is injected into a stream of oil vapors to be converted, the resulting mixture passed through a conversion zone, the conversion catalyst thereafter separated from the conversion products, the conversion catalyst so separated treated with an inert gas to remove volatile hydrocarbons retained thereon following said separation; the improvement in the method of removing volatile constituents retained on said catalyst which comprises passing a stream of inert stripping gas through a restricted throat under a substantial pressure and at a velocity sufficient to develop a low pressure area adjacent the entrance to said throat, introducing the separated catalyst into said low pressure area to thereby subject said catalyst to low pressure treatment and to inject said catalyst into the stream of inert stripping gas, thereafter separating the catalyst from said inert gas, passing a second stream of stripping gas through a second restricted throat under a pressure substantially greater than the pressure of the inert gases passing through said first-named restricted throat and at a velocity sufficient to develop a low pressure area adjacent the entrance of said last-named throat, introducing catalyst separated from said stripping gas into said last-named low pressure area to again subject said catalyst to low pressure treatment and to inject said catalyst into a second stream of stripping gas and thereafter separating the stripped catalyst from said second stream of stripping gas.

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