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(12) Patent:

(54) PROCESSES FOR REGENERATION OF FLUID CATALYSTS

(54) PROCEDÉS DE RÉGÉNÉRATION DE CATALYSEURS FLUIDES

[View the full record](#)(72) Inventors (Country): PERCIVAL C. KEITH (Not Available)(73) Owner (Country): HYDROCARBON RESEARCH(71) Applicants (Country):(74) Agent:(45) Issued on: Aug. 28, 1951(22) Filed on:(43) Laid open on:(57) Canadian Class (CPC): 196/124(51) International Class (IPC): N/APatent Cooperation Treaty (PCT): No(30) Application priority data: NoneAvailable of licence: N/ALanguage of filing: Unknown

ABSTRACT:

CLAIMS: [Show all claims](#)

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The fluid catalyst process for the conversion of hydrocarbons, which comprises contacting hydrocarbon vapors with comminuted catalyst under fluidizing and conversion conditions, withdrawing simultaneously from the conversion zone converted hydrocarbon vapors and fouled catalyst, revivifying said fouled catalyst under fluidizing conditions with gas containing not less than 35% by volume of oxygen so that the carbonaceous deposit on said catalyst is reduced to less than about 0.1% by weight, and returning said revivified catalyst to the conversion zone for contacting with additional hydrocarbon vapors.

A 2. The fluid catalyst process for the conversion of hydrocarbons, which comprises contacting hydrocarbon vapors with comminuted catalyst under fluidizing and conversion conditions, withdrawing simultaneously from the conversion zone converted hydrocarbon vapors and fouled catalyst, revivifying said fouled catalyst under fluidizing conditions with gas containing not less than 95% by volume of oxygen so that the carbonaceous deposit on said catalyst is reduced to less than about 0.1% by weight, and returning said revivified catalyst to the conversion zone for contacting with additional hydrocarbon vapors.

3. The fluid catalyst process for the conversion of hydrocarbons, which comprises contacting hydrocarbon vapors with comminuted catalyst under fluidizing and conversion conditions, withdrawing simultaneously from the conversion zone converted hydrocarbon vapors and fouled catalyst, revivifying said fouled catalyst under fluidizing conditions with gas containing not less than 35% by volume of oxygen so that the carbonaceous deposit on said catalyst is reduced to less than about 0.05% by weight, and returning said revivified catalyst to the conversion zone for contacting with additional hydrocarbon vapors.

4. The fluid catalyst process for the conversion of hydrocarbons, which comprises contacting hydrocarbon vapors with comminuted catalyst under fluidizing and conversion conditions, withdrawing simultaneously from the conversion zone converted hydrocarbon vapors and fouled catalyst, revivifying said fouled catalyst under fluidizing conditions with gas containing not less than 95% by volume of oxygen so that the carbonaceous deposit on said catalyst is reduced to less than about 0.05% by weight, and returning said revivified catalyst to the conversion zone for contacting with additional hydrocarbon vapors.

5. In the fluid catalyst conversion of hydrocarbons wherein catalyst becomes fouled with carbonaceous matter during conversion of hydrocarbons in the reaction zone, resulting fouled catalyst is removed to a regeneration zone for regeneration and thereafter returned to the reaction zone, the method comprising introducing to the regeneration zone gas containing not less than about 35% by volume of oxygen, passing so introduced gas in contact therein with fouled catalyst at a temperature below the deactivation temperature of the catalyst but not below about 800°F. such that carbonaceous matter undergoes combustion, and circulating the catalyst through the conversion and regeneration zones at such rate that the carbonaceous matter on catalyst leaving the conversion zone is less than about 0.5% by weight and the residual carbonaceous matter on catalyst leaving the regeneration zone is in the range of 0.05% by weight and below.

6. In fluid catalyst processes for the conversion of hydrocarbons, the improvement which comprises regenerating spent catalyst by fluidization with gas containing not less than 95% by volume of oxygen, and circulating the catalyst through the conversion and regeneration zones at such rate that the carbonaceous matter on catalyst leaving the conversion zone is less than about 0.5% by weight and the residual carbonaceous matter on catalyst leaving the regeneration zone is less than about 0.05% by weight.

The invention pertains to an improved process for the re-generation of deactivated catalysts of the type which during use become fouled with a carbonaceous deposit and are revived when the carbonaceous deposit is removed by oxidation or combustion. More particularly, the invention relates to the oxidative regeneration of spent catalysts in accordance with the fluidization technique.

In recent years, the technique of conducting catalytic reactions by the passage of reactant gases or vapors through a bed of powdered catalyst at such velocities that the powder becomes suspended in the gas but exhibits what has been termed "hindered settling", has been developed rapidly and extensively for petroleum processing. This technique of fluidization, as it is commonly called, which keeps a mass of powdered material in a fluid, agitated state resembling a boiling liquid and which permits the establishment of a pseudo-liquid level between the fluidized mass and the gas space above it, is the basis of the "fluid catalyst" process that has attained prominence in the manufacture of aviation gasoline. Another view of fluidization may be stated as the technique by which reactant gases and solids are passed through a reactor under such conditions that the residence time of the solids in the reactor is longer than that of the gaseous reactant.

The fluid catalyst process has been widely publicized, e. g., in *Industrial and Engineering Chemistry*, Pages 768 to 773, July 1943. A fluid cracking plant comprises two major elements, a reactor and a regenerator. The remainder of the plant is composed of standpipes, cyclones, hoppers, pipes, blowers, etc., which are used to interconnect the reactor and the regenerator and to maintain circulatory flow of the fluid catalyst through these units.

In the evolution of large-scale commercial plants for the fluid catalyst cracking process, the productive capacity of such a plant has come to be set primarily in terms of the size of the regenerator. Unfortunately, some fixed concepts have largely influenced the design of

regenerators. A commonly accepted point of view is that the rate of introduction of air into a mass of spent catalyst must be carefully regulated if overheating and consequent deactivation of the catalyst is to be avoided; recent patents relating to the fluid catalyst process express such precautions and advise the admixture of flue gas, steam or other inert gas with the incoming air to bring its oxygen content down to 10% or less. At best, regenerators have been designed to take in air with its oxygen content substantially undiluted. Even under such circumstances, the complete revivification of spent catalyst, that is to say, the complete removal of the carbonaceous deposit on the catalyst is commercially unattainable because of the enormous equipment that would be required. In other words, complete removal of carbon is not practiced in industry because the regeneration time would be exceedingly long. A recent U. S. patent even purports that it is advantageous to leave not less than 0.5% by weight of carbonaceous material on the catalyst which is returned to the reactor from the regenerator. As a matter of fact, the best fluid catalyst plants have only been able to bring the carbon on revivified catalyst down to about 0.3% by weight.

Contrary to the teachings and fixed notions of the art, I have discovered that it is very significantly beneficial to remove the carbonaceous material on a catalyst completely or substantially completely.

A primary object of my invention is to provide a regeneration process by which the carbonaceous material on spent fluid catalyst can be eliminated completely or substantially completely in a commercially feasible manner.

Another principal object is to increase the productive capacity of existing fluid catalyst plants through improvements in catalyst regeneration.

A further object is to reduce in fluid catalyst plants the inventory of catalyst required for any chosen measure of hydrocarbon conversion.

Other objects of my invention will become apparent in the description which follows.

In accordance with my invention, I find it possible and highly desirable to effect complete or substantially complete removal of the carbonaceous material on spent, fluid catalysts by regenerating them with gases which are rich in oxygen, i. e., gases containing not less than about 35% by volume of oxygen, and preferably not less than 95% of oxygen. The regeneration with such oxygen-rich gases is conducted in accordance with the established fluidization technique, due attention being given to the provision of adequate heat exchange equipment to absorb the heat of combustion, i. e., regeneration, as rapidly as it is evolved so that the temperature of regeneration does not exceed the point at which thermal deactivation or injury of the catalyst begins. For the more commonly used catalysts, the deactivation temperature is in the vicinity of about 1100° F. In any case, however, the regeneration temperature should not be permitted to fall below about 800° F. With my oxygen-rich gases, I am able to burn the carbonaceous deposit on spent catalyst to a considerably greater extent than has been practiced heretofore, within the same order of magnitude of regeneration time and without injury of the catalyst; in fact, because of the resultant lower carbon content, the revived catalyst is markedly more active and productive in terms of the measure of hydrocarbon conversion which is attainable. Whereas under current practice, for reasonable hold-up times, fluid catalysts issue from the regenerators generally with not less than 0.3% by weight of carbon, and more frequently, with not less than 0.5%, the same catalysts when treated in accordance with my process may show only about 0.1% by weight of carbon and this may be reduced to about 0.05% or eliminated substantially completely. With such low carbon content in regenerated catalyst, I find it possible to keep the carbon content of fouled or spent catalyst below about 0.2% by weight and, preferably, below about 0.5%.

For a clearer and more detailed understanding of my invention, reference is made to the drawing attached to this specification.

The diagrammatic figure represents a typical fluid catalyst cracking plant in which the process of my invention for regenerating spent catalyst may be employed. Hydrocarbon vapors flowing through pipe 1 pick up regenerated catalyst admitted into pipe 1 by slide valve 2. The catalyst suspended in the vapor stream flows into reactor 3 wherein because of the decrease in gas velocity the catalyst exhibits "hindered settling" and forms a fluidized bed. By maintaining suitable reaction conditions, the vapors flowing through the fluid mass of catalyst in reactor 3 undergo the desired conversion. The reaction vapors and entrained spent catalyst flow up through pipe 4 and enter separator 5. Separator 5, which may be a cyclone, electrical precipitator or other suitable device, removes the spent catalyst from the vapor stream which flows out through pipe 6 to conventional fractionation and recovery equipment. The segregated spent catalyst drops into hopper 7 and flows down standpipe 8 which has slide valve 9. Valve 9 controls the admission of spent catalyst into pipe 10 through which the regeneration gas is flowing. The resultant suspension of spent catalyst in gas picks up additional catalyst admitted by control valve 11 and flows into heat exchanger 12. Exchanger 12 (shown partially in section) is provided with cooling tubes 13 around which water or other suitable coolant is circulated to remove the heat of regeneration. The fluidized mass of catalyst undergoing regeneration flows up through heat exchanger 12 into the main regenerating zone 14. To ensure a high rate of heat transfer and to maintain the temperature of regeneration below the point at which the catalyst would become deactivated, the catalyst is recycled from the main regenerator zone 14 to the heat exchanger 12 by way of standpipe 15. The flue gases carrying revived catalyst flow up through pipe 16 into a suitable separator 17 which segregates the catalyst and gases. The flue gases vent through pipe 18 while the revived catalyst drops

into hopper 19. Thence, the regenerated catalyst on flowing down through standpipe 20 and valve 2 enters pipe 1 where it is picked up by fresh feed vapors, thus starting its cyclic flow through the plant again. Above each of the slide valves 2, 9 and 11, a small stream of fluidizing gas is introduced to prevent clogging of the standpipe. These fluidizing streams are shown at 21, 22 and 23, respectively.

While steam is usually employed as the fluidizing gas in standpipe 8 and hopper 7 for the purpose of stripping absorbed hydrocarbons from spent catalyst as well as maintaining the catalyst mass therein in a fluid condition, I prefer to use oxygen-containing gas as disclosed in my copending Canadian application, Serial No. 530,206, and United States patent 2,456,707. In accordance with the invention of my copending application, gas containing not less than about 35% by volume of oxygen, and preferably not less than 95% oxygen, is used in controlled amount to remove absorbed hydrocarbons from spent catalyst. In the light of both of my inventions, it is therefore possible to utilize the same oxygen-rich gas in both the stripping and the regenerating zones of a fluid catalyst plant. As disclosed in my aforesaid copending application, my novel process of stripping hydrocarbons from spent catalyst may be carried to the point of effecting preliminary or partial regeneration of the catalyst. Such procedure obviously diminishes the regeneration load which must be handled by the regenerator. Accordingly, the stripping process of my copending application may be used to increase further the improvements in the operation and capacity of fluid catalyst plants as brought about by the utilization of oxygen-rich gas for catalyst regeneration in accordance with the process of my present invention.

As an example of specific operating conditions for the process represented in the diagrammatic figure, the following are cited. The catalyst is an activated clay of which the particle size range lies chiefly between 140 and 270 mesh. Gas oil is fed into the reactor with revived catalyst in the proportions of 1 part by weight of oil to 15

parts of catalyst. The reactor is maintained at a temperature of about 980° F. and at a pressure only slightly above atmospheric. As regeneration gas, I use oxygen of 98.5% purity to which recycled flue gases (predominantly the oxides of carbon) from the regenerator are added in such proportion that the oxygen content of the mixture is about 45% by volume. The removal of the carbonaceous deposit on spent catalyst by combustion in the regenerator is conducted at a temperature not exceeding about 1070° F. To prevent the temperature of regeneration from exceeding this limit, I permit the fluid mass to circulate at a very high rate through the heat exchanger which under the prevailing high turbulence of the fluid mass has an excellent heat transfer capacity. Under these conditions, the carbonaceous matter on spent catalyst is brought down from a value of about 0.4% by weight to about 0.05%. With such low residual carbon on the revived catalyst, I achieve a surprisingly high measure of hydrocarbon conversion per unit weight of catalyst with the result that my system may be operated with an appreciably smaller inventory of catalyst than has been found possible heretofore. From the reaction gases, I recover cracked hydrocarbons in the gasoline range which in both quality and quantity compare very favorably with the results obtained when the fluid process is operated in the conventional manner.

A noteworthy feature of my invention is that it can be used in existing fluid catalyst plants as well as incorporated in the design of new plants. Furthermore, my invention may be utilized to overcome various operational difficulties. For example, in several existing fluid catalyst plants, to maintain a commercially satisfactory rate of catalyst regeneration, a high gas velocity is necessitated with the result that the effluent gases carry a considerable quantity of the catalyst powder; in such cases, large and costly separators have to be installed and even so the loss of catalyst may be appreciable. Furthermore, high gas velocity accelerates erosion of both equipment and cata-

lyst and thus leads to higher operating costs. In regenerating fouled catalyst with gas containing not less than about 35% by volume of oxygen, the load on the separators and the loss of catalyst may be curtailed. Also, my oxygen-enriched regeneration gases may be employed to diminish the inventory of catalyst and the size of the regenerator for a given hydrocarbon conversion capacity, or to augment the conversion capacity of an existing plant by improvement of the regenerating step.

The significance of my finding that carbon begets carbon cannot be overemphasized. I shall state what I have learned in another way. If the regenerator of a fluid catalyst plant is built to burn about 16,000 pounds of carbon per hour with air and this equals the rate of carbon deposition in the cracking zone for a feed capacity of 15,000 barrels per day of a given oil, the daily overall capacity of the plant is then limited to 15,000 barrels of oil. On the other hand, through the regeneration of fouled catalyst with oxygen-enriched gases in accordance with my invention, the catalyst may be returned to the cracking zone with a markedly smaller content of residual carbon and this leads to a slower deposition of carbonaceous material during the hydrocarbon conversion. Accordingly, it is a reasonable expectation that the same oil will now yield 16,000 pounds of carbon per hour when it is flowed through the cracking zone at a daily rate of 25,000 barrels. It is, therefore, clear that the overall capacity of the plant may be about doubled by keeping the carbon on the catalyst at a low level through regeneration with oxygen-enriched gas. This example brings out clearly another important benefit of my invention, namely, curtailment of the loss of hydrocarbon feed resulting from the formation of carbon. In other words, a higher yield of valuable hydrocarbon products is achieved.

Particularly advantageous is the use of a regeneration gas containing not less than 95% by volume of oxygen. Under such circumstances, all of the aforementioned advantages of my invention are not only materially enhanced but also I realize an additional benefit. The

flue gases resulting from the regeneration of spent catalyst with oxygen of not less than 95% purity are predominantly a mixture of carbon monoxide and dioxide, usually in the proportions of about 1 part by volume of carbon monoxide to 2 parts of carbon dioxide. Such a gas mixture has commercial value in that the carbon dioxide may be utilized in the manufacture of dry ice or fire extinguishers. The carbon monoxide may be used as one of the reactants in a Fischer-type process wherein carbon monoxide is hydrogenated to form liquid hydrocarbons. The mixture is also useful as a fuel gas since it has a heating value of about 100 B.t.u. per cubic foot. Those skilled in the art will appreciate that a substantially pure mixture of carbon monoxide and dioxide may be utilized in various ways industrially.

When using oxygen of not less than 95% purity, it is sometimes desirable to supplement the oxygen with the oxides of carbon and/or steam. The oxides of carbon are of course formed during regeneration and therefore may be in part recycled to the regenerator to supplement the incoming oxygen. Steam is a convenient extender of the oxygen used for regeneration since by condensation it is easily separated from the effluent gases of the regenerator. Recourse to recycled carbon oxides and steam as extenders of high purity oxygen is advisable where, because of temperature and other limitations in a process, the feed rate of oxygen is not sufficient to fluidize properly the mass of spent catalyst undergoing regeneration. High purity oxygen admixed with extenders of the class of carbon monoxide, carbon dioxide and steam has the advantage that the rate of introduction of oxygen into the regenerator may be varied over a considerable range without detracting from the value of the regeneration product gases as is the case when oxygen is admixed with nitrogen. In all instances, however, the oxygen content of the regeneration gas must be not less than about 35% by volume.

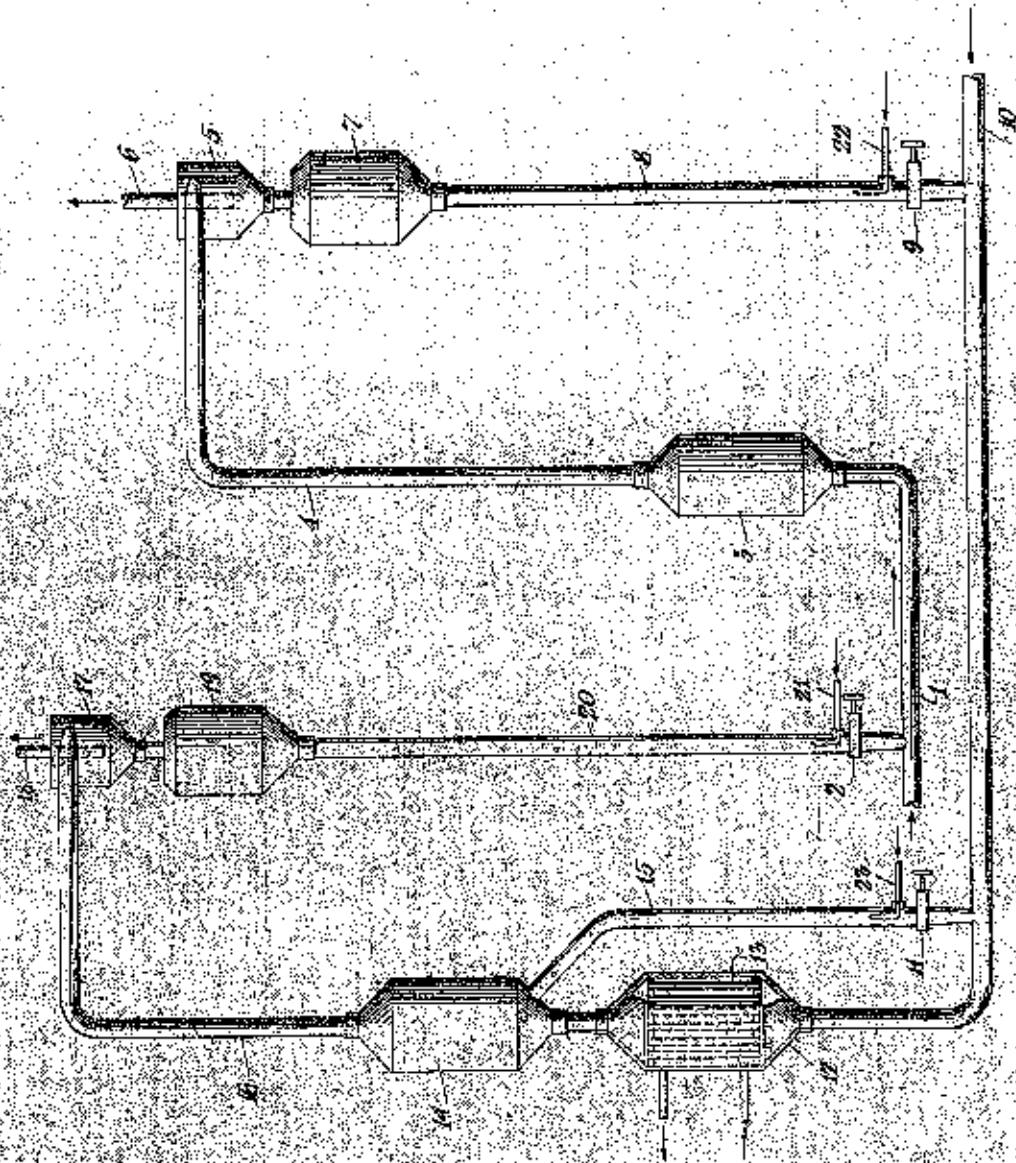
Depending upon the particular catalyst used in the process, the regeneration temperature will be controlled in relation to the de-

activation temperature of the catalyst. While a temperature of about 1100°F. is a desirable limit for activated clays, the limit may be raised to about 1300°F. with some synthetic silica-alumina type catalysts. My invention is applicable to catalytic processes of the type known as hydroforming, dehydrogenation, desulfurization, aromatization, and the like. All of these reactions are characterized by the cracking or decomposition of at least a small portion of the hydrocarbon vapors that are treated and by the deposition on the catalyst of carbonaceous matter which is removed by oxidation in order to revivify the catalyst. The regeneration gas should flow through the regeneration zone at linear velocities within the range ordinarily practiced in fluidized operations. I generally select a velocity of the order of magnitude of 1 foot per second. As is well established in the fluidization art, the powdered catalyst should be of such particle size that it lies predominantly between the sizes of 100 mesh and 325 mesh, although coarser and finer particles may be utilized in some instances.

In the foregoing description, the examples have been presented for illustrative purposes only and in no way are to be considered as representative of the limitations of my invention. Those skilled in the art will appreciate that my process will permit of many alterations and adaptations. For example, my process may be carried out in a fluid catalyst plant of the type wherein the catalyst is circulated by bottom draw-off instead of by overhead entrainment as shown in the attached drawing. Fluid catalyst plants which operate by bottom draw-off of the catalyst are represented in recent patents, e.g., U. S. 2,345,487 and U. S. 2,358,688. As disclosed in my copending Canadian patent application, Serial No. 529,551, and United States patent 2,445,327, the catalyst regeneration process of my present invention may be conducted in a unitary, two-zone reactor, also, heat exchangers like cooling coils and tubes may be built within the regenerator so as to remove directly excess heat of combustion or regeneration. Accordingly,

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all modifications of my basic process, which conform to the spirit of the invention, are to be considered within the scope of the claims.



Certified to be the drawings referred to
in the specification herewith annexed.

OTTAWA, Canada, October 9, 1945

PERCIVAL G. REUBEN
INVENTOR

By *[Signature]*
ATTORNEY