

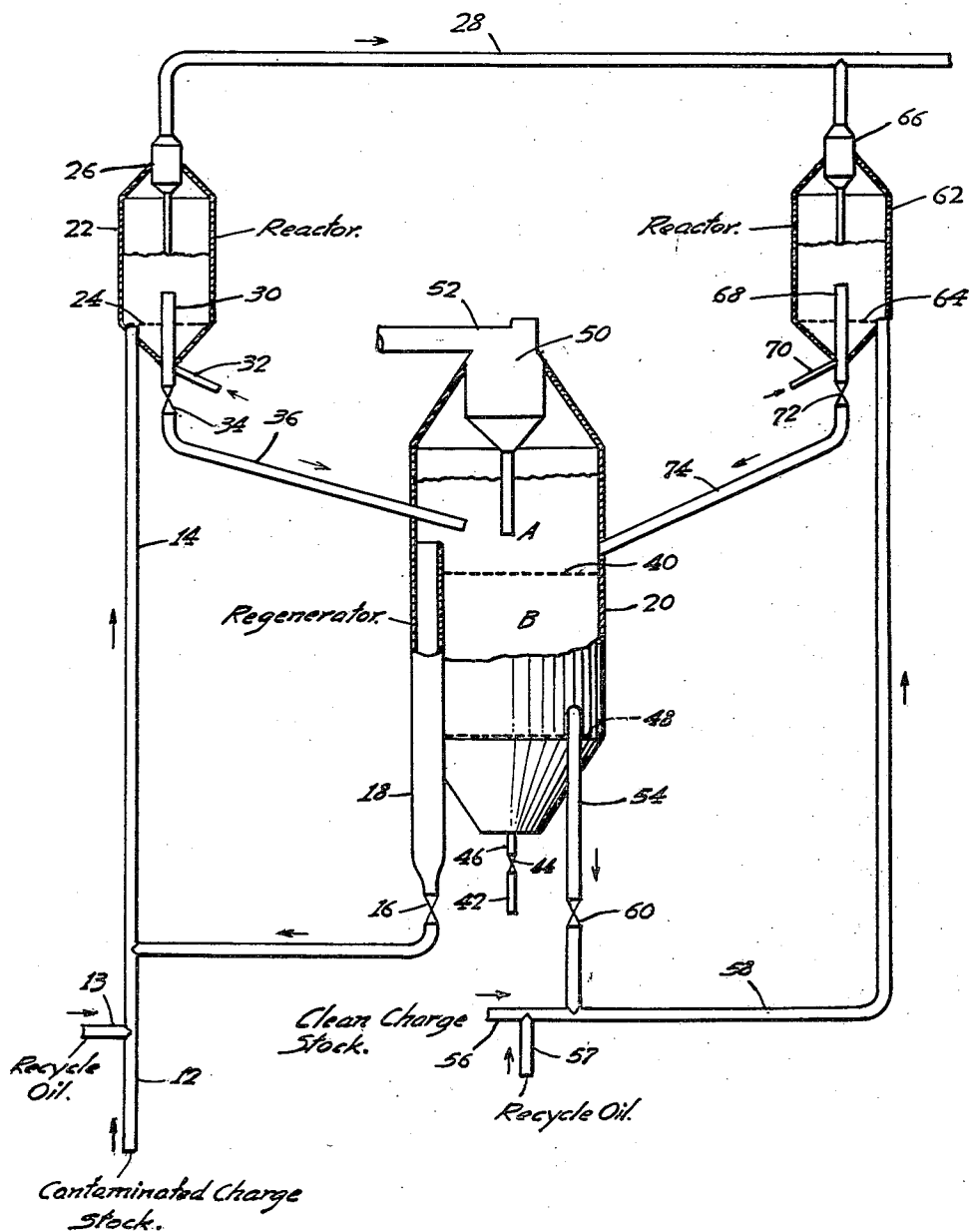
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CATALYTIC CRACKING PROCESS AND APPARATUS

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CATALYTIC CRACKING PROCESS AND APPARATUS

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This invention relates to a fluid catalytic cracking process and apparatus and more particularly to an improved process and apparatus for the catalytic conversion of hydrocarbons.

Hydrocarbon charge stocks containing appreciable amounts of deleterious materials, such as sulfur compounds and/or nitrogen bases, are not ordinarily desirable as charge stocks for conventional catalytic cracking operations because these charge stocks, under conventional catalytic cracking conditions, normally tend to deposit upon the cracking catalyst excessive amounts of catalyst contaminant. The catalyst deposits tend to build up on the cracking catalyst at an alarming rate, with the result that the cracking catalyst may quickly be poisoned and the cracking reaction adversely affected or the cracked products may be contaminated with the undesirable contaminants.

In accordance with the invention, a hydrocarbon charge stock containing appreciable amounts of deleterious materials, such as sulfur compounds and/or nitrogen bases, is contacted in a first reaction zone under relatively mild cracking conditions with partially regenerated fluidized cracking catalyst obtained from an upper portion of a regeneration zone; and a hydrocarbon charge stock substantially free of objectionable materials, such as sulfur compounds and/or nitrogen bases, and which may, in fact, comprise the cracked products comprising the effluent from the first reaction zone, is contacted in a second reaction zone under conventional cracking conditions with regenerated fluidized cracking catalyst obtained from a lower portion of said regeneration zone.

By operating in accordance with my invention, the above-noted difficulties are avoided by removing in the first reaction zone, maintained under relatively mild cracking conditions, the objectionable materials from such a charge stock, and thereafter passing the remainder of the charge stock to a second reaction zone where conventional catalytic cracking conditions are maintained. When the charge oil contains large amounts of sulfur, H_2S vapors are released and heavy combustible deposits not vaporized are deposited on the cracking catalyst in the first reaction zone. Since the H_2S vapors pass overhead from the first reaction zone and may be detrimental to natural catalysts in subsequent cracking operations, it may be advisable to remove H_2S vapors from the effluent. This can be done by means known in the art, as for example, by passing the effluent carrying the H_2S vapors through a vapor-liquid separator. Treating charge stocks containing large amounts of nitrogen bases in the first reaction zone will result in deposits of combustible nitrogen-containing compounds on the cracking catalyst and some formation of nitrogen and ammonia vapors. The nitrogen and ammonia vapors are not detrimental to subsequent cracking operations and need not be removed from the effluent in the first reaction zone. When the charge stock contains both sulfur and nitrogen compounds, volatile products as well as combustible deposits containing both of these compounds are formed in the

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first reaction zone. For simplicity, these combustible deposits resulting from the cracking of the deleterious compounds noted, in particular sulfur compounds and/or nitrogen bases, as well as the combustible hydrocarbonaceous deposits generally formed on the catalyst during catalytic cracking, sometimes known as "coke," will be termed hereinafter "contaminant."

It is important in the practice of my invention that (1) cracking catalyst employed in the first reaction zone, wherein mild cracking conditions are maintained, be partially regenerated cracking catalyst obtained from the upper portion of the regenerator; (2) cracking catalyst employed in the second or conventional catalytic cracking zone be regenerated cracking catalyst obtained from a lower portion of said regenerator; (3) spent catalyst from each of the reaction zones be continuously passed to the upper part of said regenerator; and (4) an oxidizing gas, like air, be passed upwardly through the base of the regenerator for the purpose of regenerating the catalyst therein.

By operating in this manner, and, as will be explained in detail hereinafter, as the catalyst moves downwardly from the upper portion of the regenerator and is regenerated by the oxidizing gas moving upwardly, the oxygen in the oxidizing gas is substantially consumed with the result that the gas in the uppermost portion of the regenerator contains little or no oxygen and "after-burning" is avoided.

In obtaining partially regenerated catalyst from an upper zone of the regenerator for the first reactor and regenerated catalyst from a lower zone of the regenerator for the second reactor, an efficient and reliable means of obtaining sufficient amounts of the proper catalyst for each of the reaction zones is assured. Since the cracking catalyst passed to the first reaction zone is to be employed under relatively mild cracking conditions only, and thus need not be unduly active, it is apparent that, by obtaining partially regenerated catalyst from the upper part of the regeneration zone, I am able to control the supply of such catalyst as well as the level of the contaminant thereon. Similarly, the catalyst needed in the second or conventional catalytic cracking zone is preferably a relatively active cracking catalyst substantially free of contaminant, and by obtaining the catalyst for such latter zone from a lower portion of the regenerator I am able to control the amount and quality of catalyst passed to such latter zone.

The novel apparatus employed in carrying out my process comprises a regenerator provided with a plurality of regeneration zones, superposed one upon another; a first and second reactor; means for removing a partially regenerated fluidized cracking catalyst from one of the upper regeneration zones, admixing it with a charge stock containing appreciable amounts of objectionable materials, such as the aforementioned sulfur compounds and/or nitrogen bases, and moving the resulting mixture to the first reactor; means for removing a regenerated fluidized cracking catalyst from one of the lower regeneration zones, admixing it with a charge stock containing substantially less objectionable materials than are present in the charge stock passed to the first reactor, and moving the resulting mixture to the second reactor; means for removing cracked products from each of the two reactors; and means for continuously recycling catalyst contaminated with carbonaceous material from each of the two reactors to the regenerator.

Any conventional cracking catalyst, natural or synthetic, can be employed in the process of my invention, as for example silica-alumina cracking catalyst comprising an acid-activated halloysite such as "Filtrol SR," montmorillonite clay such as "Filtrol D," synthetic silica-alumina cracking catalyst such as synthetic composites containing

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between 80 to 90 percent of silica and 10 to 20 percent of alumina, and so forth. The aforementioned catalysts should be of conventional particle size used in fluid catalytic cracking systems.

In order to illustrate the process and apparatus of my invention, reference should be had to the accompanying figure which is a diagrammatic representation of a fluid conversion system in accordance with my invention. The accompanying figure is hereby incorporated into my invention and made a part thereof.

A charge stock comprising a heavy gas oil containing appreciable amounts of sulfur compounds and/or nitrogen bases is introduced into the system through line 12. The charge stock has been preheated (by means not shown) to a temperature somewhat below the cracking temperature maintained in reactor 22. If desired, the charge stock in line 12 can be joined by recycle oil from line 13. The combined feed enters line 14 and is joined therein by partially regenerated cracking catalyst particles, such as silica-alumina cracking catalyst, entering through valve 16 from standpipe 18 extending upwardly through the base of regenerator 20 into upper portion A thereof. The partially regenerated cracking catalyst entering standpipe 18 is at a temperature somewhat above the cracking temperature present in reactor 22 and serves to heat the mixture of charge stock and recycle oil to this cracking temperature. The mixture of partially regenerated catalyst, charge stock and recycle oil, if any, passes upwardly through line 14 into the base of reactor 22, which contains a dense phase bed of silica-alumina cracking catalyst particles.

Within reactor 22 the mixture passes through grid 24 and the feed is mildly cracked through contact with the catalyst particles in reactor 22. The dense phase fluidized bed of catalyst particles within reactor 22 is maintained at a temperature in the range of about 750° to about 900° F. and a pressure of about 15 pounds per square inch for a time sufficient to obtain mild cracking of the total charge and the release of a major portion of the sulfur and/or nitrogen in the charge in the form of hydrogen sulfide, combustible catalyst deposits, etc. The cracked products, together with the uncracked effluent, are withdrawn from reactor 22 through cyclone separator 26, which returns entrained catalyst to the dense phase catalyst bed in reactor 22, and are led through line 28 to a fractionator (not shown) where they subsequently undergo such additional refining and processing as is readily apparent to one skilled in the art.

The rate of introduction of feed and catalyst into reactor 22 and the rate of withdrawal of products and contaminated catalyst from reactor 22 is preferably so regulated that the average level of contaminant upon the catalyst in reactor 22 is maintained preferably in the range of about 0.5 to about 1.2 percent by weight. The withdrawal of contaminated catalyst from reactor 22 is effected through stripper 30. The contaminated catalyst passes through stripper 30 or strippers of other designs known to those familiar with the art, and is stripped of entrained hydrocarbons by an inert gas such as steam entering stripper 30 through steam line and nozzle 32.

From stripper 30 the contaminated catalyst passes through valve 34 and line 36 to regenerator 20. Regenerator 20 is at a lower level than reactor 22 so that flow from reactor 22 to regenerator 20 can be readily effected without the necessity of adding appreciable quantities of aerating gas to line 36. However, some aerating gas can be added to facilitate proper flow of the contaminated catalyst from reactor 22 to regenerator 20.

Regenerator 20 comprises a two-zone regenerator with upper zone A being located above a perforated plate member or grid 40 and lower zone B being located below grid 40. The contaminated catalyst from line 36 enters zone A and is regenerated by oxygen-containing regenerating gas leaving zone B. This oxygen-containing regenerating gas, originally comprised an oxygen-rich gas,

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such as air, which is introduced into regenerator 20 by means of line 42, valve 44 and line 46 or by other suitable means. The air passes upwardly through the base of regenerator 20 and grid 48 into regeneration zone B. In regeneration zone B, partially regenerated catalyst which has passed downwardly from regeneration zone A through grid 40 is further regenerated by oxidatively burning contaminant from the catalyst to produce a regenerated catalyst containing preferably in the range of about 0.1 to about 0.6 weight per cent of contaminant. Grid 40 redistributes catalyst and regenerating gas in their movement through the regenerator and thus provides a means for eliminating channeling and permitting intimate contact between the catalyst and the regenerating gas. In this way temperatures throughout the regenerator are easily maintained at a temperature in the range of 950° to about 1125° F., and temperatures above about 1150° F., which may occur in conventional single-zone regenerators because of hot spots and which may result in permanent deactivation of the catalyst, are avoided. Redistribution, moreover, provides for rapid disengagement and removal of nitrogen gases and H₂S vapors that might have been occluded from reactor 22. The regeneration effected in regeneration zone B is more severe than that effected in regeneration zone A, and accordingly a major portion of the oxygen content of the regenerating gas is consumed in regeneration zone B.

As a result of the foregoing, the regenerating gas entering regeneration zone A has a relatively low concentration of oxygen. This concentration of oxygen should be sufficient to insure that the contaminant level on the spent catalyst from reactor 22 and reactor 62, hereinafter noted, is reduced to a value of about 0.4 to about 1.0 percent by weight in regeneration zone A.

However, the oxygen content of the regenerating gas in regeneration zone A should be sufficiently low, preferably less than about 2 percent, as to eliminate the danger of "after-burning" in the upper part of regenerator 20. After-burning can occur when a combustible mixture exists in the section of the regenerator known as the dilute phase, which is the region above the more dense fluid bed where the concentration of the catalyst particles is relatively low. In the regeneration of the spent catalyst, the burning of the carbon results in the formation of combustion products such as carbon monoxide, carbon dioxide and water and, in addition, any oxygen not consumed during regeneration is also present. When the oxygen and carbon monoxide are in the proper proportions, the mixture is readily combustible. The gas may then burn in the top of the regenerator or in the flue gas ducts, resulting in very high temperature, above about 1100° F., which is extremely damaging to the cyclone separators and the flue gas ducts, and may also affect the activity of the catalyst. After-burning can usually be avoided if the oxygen content of the combustion gas in the dilute phase of zone A is kept below about 2 percent.

By operating in accordance with my invention, the amount of oxygen present in the oxidizing gas in the dilute phase of zone A is easily maintained below about 2 percent. The oxidizing gas moving upwardly from zone B may contain more than 2 percent oxygen but the excess oxygen, or that amount over 2 percent, is consumed in burning off combustible deposits on the catalyst surface in zone A. Thus, by regenerating the contaminated catalyst in the regenerator while maintaining the catalyst in a plurality of beds, the excess oxygen which would ordinarily be present in the upper portion of the regenerator is substantially consumed in an upper catalyst bed, and after-burning is avoided.

The regeneration flue gases are withdrawn from regenerator 20 through cyclone separator 50 and line 52. Cyclone separator 50 returns regenerating catalyst to the dense phase bed of catalyst in regenerator 20.

While standpipe 18 extends upwardly through the base of regenerator 20 into upper zone A for the purpose of

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withdrawing partially regenerated catalyst preferably containing about 0.4 to about 1.0 weight percent of contaminant for use in reactor 22, a second standpipe 54 extends upwardly through the base of regenerator 20 into lower zone B for the purpose of withdrawing regenerated catalyst containing preferably about 0.1 to about 0.6 weight percent of contaminant for use in reactor 62, where charge stocks containing little or no deleterious materials, such as objectionable sulfur and/or nitrogen compounds, are catalytically cracked.

A charge stock comprising a heavy gas oil containing substantially less of the deleterious materials present in the charge stock passed to reactor 22, which has previously been heated (by means not shown) to a temperature somewhat below the cracking temperature maintained in reactor 62, is introduced into line 56. This charge stock may be joined, if desired, by recycle oil and/or desulfurized oil through line 57, particularly that obtained as a result of cracking in reactor 22. The combined charge in line 58 is joined by regenerated silica-alumina cracking catalyst containing preferably about 0.1 to about 0.6 weight percent of contaminant from standpipe 54 through valve 60. The regenerated catalyst from standpipe 54 is at a temperature somewhat above the cracking temperature maintained in reactor 62 and serves to heat the mixture of total charge to this cracking temperature. The mixture of regenerated catalyst and charge passes upwardly from line 58 into the base of reactor 62. Reactor 62 contains a dense phase bed of silica-alumina cracking catalyst particles.

Within reactor 62 the mixture passes through grid 64 and the feed is catalytically cracked through contact with the catalyst particles in reactor 62. The dense phase fluidized bed of catalyst particles within reactor 62 is maintained at cracking temperatures in the range of about 800° to about 1100° F., such as about 900° F. As a result of contact with the catalyst particles in reactor 62 the feed is catalytically cracked to relatively low-boiling hydrocarbons such as gasoline boiling range hydrocarbons, butanes, butenes, propane and propylene. Simultaneously, contaminant is deposited upon the silica-alumina cracking catalyst. The cracked products are withdrawn from reactor 62 through cyclone separator 66, which returns entrained catalyst to the dense phase catalyst bed in reactor 62, and the cracked products then pass through line 28, where they join the products from reactor 22, to a fractionator (not shown). If desired, the cracked products from reactor 62 may be sent to a fractionator other than that to which the products from reactor 22 are sent. In the fractionator, these cracked products undergo such additional refining and processing as is readily apparent to one skilled in the art.

The rate of introduction of feed and catalyst into reactor 62 and the rate and withdrawal of cracked products and contaminated catalyst from reactor 62 preferably are so regulated that the average level of contaminant upon the catalyst in reactor 62 is maintained in the range of about 0.5 to about 1.2 percent by weight. The withdrawal of contaminated catalyst from reactor 62 is effected through stripper 68 or strippers of other designs known to those familiar with the art. The contaminated catalyst passes through stripper 68 and is stripped of entrained hydrocarbons by an inert gas such as steam entering stripper 68 through steam line and nozzle 70.

From stripper 68 the contaminated catalyst passes through valve 72 and line 74 to regenerator 20. Regenerator 20 is at a lower level than reactor 62 so that flow from reactor 62 to regenerator 20 can be readily effected without the necessity of adding appreciable quantities of aerating gas to line 74. However, some aerating gas can be added to facilitate proper flow of the contaminated catalyst from reactor 62 to regenerator 20. Operating conditions in regenerator 20 are maintained as previously described.

In order to illustrate a specific embodiment in accord-

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ance with the process of my invention, a charge stock comprising a gas oil charge having the following inspection data:

Characterization factor	11.8
Sulfur, wt. percent	3
Nitrogen, wt. percent	0.4
ASTM distillation, ° F. (D-158):	
Initial boiling point—end point	600–1050

- 10 is contacted with cracking catalyst in reactor 22 at a temperature in the range of approximately 750° to about 900° F. and a pressure of about 15 pounds per square inch gauge for a time sufficient to obtain mild cracking therein. As a result of such cracking, substantially all of the desirable gas oil fractions are vaporized and the heavy components of the gas oil charge are mildly cracked, resulting in the formation of lighter hydrocarbons, which are removed from the reactor along with the vaporized gas oil fractions, and deposits of heavy combustible material on the catalyst therein.

In reactor 62, a gas oil charge stock, relatively free of deleterious materials found in the charge stock entering reactor 22, and having the following inspection data:

Characterization factor	11.8
ASTM distillation, ° F. (D-158):	
Initial boiling point—end point	600–1050

- is catalytically cracked at a temperature of about 900° F. and a pressure about 15 pounds per square inch gauge, while maintaining a catalyst to oil ratio of about 10:1 and a space velocity of about 1.5 (weight per hour of oil per weight of catalyst). As a result of cracking in reactor 62, relatively low-boiling hydrocarbons such as gasoline boiling range hydrocarbons, butanes, butenes, propane and propylene are obtained in the effluent therefrom and carbonaceous contaminant is deposited on the cracking catalyst.

- While I have disclosed specific operating conditions which are preferably maintained in reactors 22 and 62, it is understood that these conditions are to be considered illustrative only and not limitative. The operating conditions necessary in practicing my invention are not critical but may be varied over a wide range and may be considered to be dependent on many variables, such as the composition of the charge stocks employed, the cracked products desired, a balance of economic costs involved, and so forth. For example, in reactor 22, the temperature may vary from about 700° to about 1000° F., the pressure from about atmospheric to 100 pounds per square inch gauge or more but preferably at atmospheric pressure, and the space velocity may range from about 5 to 15; while in reactor 62 the temperature may range from about 800° to about 1100° F., the pressure from about atmospheric to about 100 pounds per square inch gauge or more, and the space velocity may range from about 0.5 to about 10 or more. It has been found that the poisoning effect of H₂S is a function of its partial pressure and time of contact. Therefore, it is preferred to operate at low pressures and high space velocities in reactor 22 to minimize deactivation of the catalyst. The catalyst oil ratio employed in reactors 22 and 62 may be as low as 1:1 or as high as 15:1 or more.

- While the character of the invention has been described in detail and examples given, this has been done by way of illustration only, and the invention is not to be considered to be so limited. Numerous modifications and variations of my invention may be apparent to one skilled in the art, and these modifications should be construed as included within the scope of the claims appended hereto. For example, standpipes 18 and 54 need not be located as shown in the drawing but may penetrate the base of regenerator 20 at other points as well, and, in fact, may even run exteriorly of regenerator 20 before penetrating zones A and B, respectively. If desired, regenerator 20 may be located at a higher level than either

of reactors 22 and 62, or both, and additional aerating gas may be introduced into lines 36 and 74 for the purpose of aiding the movement of spent catalyst from reactors 22 and 62 to regenerator 20. In addition, the regenerator may include more than two regenerator zones if desired.

The fluid catalytic process and apparatus of my invention permit the processing of distillates having an appreciable amount of deleterious materials, such as sulfur compounds and/or nitrogen bases, without materially affecting the activity of the cracking catalyst employed in the conventional catalytic cracking zone and at the same time permit higher yield of valuable low boiling point hydrocarbons to be obtained while simultaneously decreasing both the deposition of undesirable contaminant upon the catalyst in said cracking zone and the yield of undesirable low boiling point gaseous hydrocarbons.

While I have described my invention by reference to certain improvements thereof, the same is not limited thereto except as defined by the appended claims.

I claim:

1. A fluid catalytic cracking process which comprises regenerating contaminated fluidized cracking catalyst particles by removing the contaminant by oxidative combustion from the catalyst particles in a regenerator provided with a plurality of regeneration zones, superposed one upon another, in which the amount of contaminant present on the cracking catalyst in an upper zone is greater than that which is present on the cracking catalyst in a lower zone thereof, the amount of contaminant in said upper zone being about 0.4 to about 1.0 weight percent and the amount of contaminant in said lower zone being about 0.1 to about 0.6 weight percent; admixing a hydrocarbon charge stock containing appreciable amounts of deleterious materials with partially regenerated cracking catalyst obtained from an upper regeneration zone; subjecting such mixture to relatively mild cracking conditions in a first reaction zone for a time sufficient to release a major portion of said deleterious materials in said first reaction zone and deposit contaminant on the cracking catalyst therein; admixing a hydrocarbon charge stock containing substantially less of the deleterious materials than is present in the charge stock passed to first reaction zone with a regenerated cracking catalyst obtained from a lower regeneration zone; subjecting said last named mixture to elevated temperatures in a second reaction zone, thereby forming a relatively lower boiling hydrocarbon product and depositing contaminant on the catalyst particles therein; continuously recycling contaminated catalyst from each of the two reaction zones to the regenerator and continuously withdrawing the cracked product from each of the two reaction zones.

2. A process in accordance with claim 1 in which the charge stock entering the first reaction zone contains appreciable amounts of deleterious sulfur and nitrogen-containing compounds.

3. A process in accordance with claim 1 in which the charge stock entering the first reaction zone contains appreciable amounts of deleterious sulfur-containing compounds.

4. A process in accordance with claim 1 in which the charge stock entering the first reaction zone contains appreciable amounts of deleterious nitrogen-containing compounds.

5. A process in accordance with claim 1 in which the charge stock entering the second reaction zone comprises the effluent from the first reaction zone.

6. A process in accordance with claim 1 in which an oxygen-containing gas is passed upwardly through the regenerator and the catalyst being regenerated is passed downwardly through the regenerator.

7. A fluid cracking unit comprising a regenerator provided with a plurality of regeneration zones, superposed one upon another; means for separating an upper regeneration zone from a lower regeneration zone and permitting movement of catalyst and regenerating gas therethrough; a reactor; means for removing a partially regenerated fluidized cracking catalyst from an upper regeneration zone, admixing it with a hydrocarbon charge stock, and moving the resulting mixture to the reactor; means for removing cracked products from the reactor; means for removing a regenerated fluidized cracking catalyst from a lower regeneration zone; means for continuously recycling contaminated catalyst from the reactor to an upper regeneration zone; and means for introducing an oxygen-containing gas upwardly through the base of the regenerator.

8. A fluid cracking unit comprising a regenerator provided with a plurality of regeneration zones, superposed one upon another; means for separating an upper regeneration zone from a lower regeneration zone and permitting movement of catalyst and regenerating gas therethrough; a first reactor and a second reactor; means for removing a partially regenerated fluidized cracking catalyst from an upper regeneration zone, admixing it with a hydrocarbon charge stock containing appreciable amounts of deleterious materials, and moving the resulting mixture to the first reactor; means for removing a regenerated catalyst from a lower regeneration zone, admixing it with a hydrocarbon charge stock containing substantially less of the objectionable materials than is present in the charge stock passed to the first reaction zone, and moving the resulting mixture to the second reactor; means for removing cracked products from each of the two reactors; means for continuously recycling contaminated catalyst from each of the two reactors to an upper regeneration zone; and means for introducing an oxygen-containing gas upwardly through the base of the regenerator.

9. A fluid catalytic cracking unit in accordance with claim 8 in which the zones in the regenerator are separated by at least one grid.

10. A fluid cracking unit in accordance with claim 8 in which the regenerator is provided with at least two regeneration zones.

11. A fluid catalytic cracking unit in accordance with claim 8 in which the means for removing catalyst from the regeneration zones in the regenerator include standpipes extending upwardly through the base of the regenerator into the upper and lower regeneration zones, respectively.

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