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54 **Regeneration of catalyst used in the conversion of carbo-metallic containing residual oils.**

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US-A-4 056 486
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Description

The present invention relates to the regeneration of cracking catalysts used in the catalytic conversion of carbo-metallic containing residual oils, or reduced crudes, and as a result of which the used catalysts will contain relatively high levels of deposited carbon and metal contaminants and possible sulfur and nitrogen-containing compounds, depending on the source of the crude.

More particularly the residual oils, or reduced crudes, used as feedstocks in reduced crude cracking (RCC) operations comprise relatively large amounts of carbo-metallic high molecular weight components with boiling points in excess of about 522°C (1025°F) such as asphaltenes, polycyclic naphthenes and porphyrins which deposit a large amount of coke on the RCC catalyst. Also deposited are metals such as nickel, vanadium, sodium, iron and copper, and sulfur and nitrogen-containing compounds. Following cracking used catalyst is mechanically separated from the vaporised products of the cracking process and regenerated before recycling the regenerated catalysts to the cracking operation. This is in contrast to the fluidised catalytic cracking (FCC) of gas oil feeds which are relatively clean, i.e. low in carbo-metallic impurities with Conradson carbon values generally less than 1.0% by weight and metallic contamination, i.e. Ni, Fe, V and Cu, less than about 0.5 ppm, and wherein the zeolite catalysts used are generally discarded when their catalytic MAT activity falls below about 70% or the contaminant metal loading reaches from 1000 to 3000 ppm Ni and V. This procedure, however, is uneconomical and impractical in RCC operations where catalyst inventories are much higher and catalyst activity is reduced that much more quickly by the rapid build up of carbonaceous deposits. Additional factors leading to the relatively rapid build up of carbonaceous deposits on the catalyst in RCC operations are that the cracking conditions required in RCC operations are that much more severe than in FCC operations and that the feed to the cracking zone is only partially vaporised. Thus regeneration of the catalyst is in the norm in RCC operations.

Current regeneration procedures generally involve steam stripping of the mechanically separated RCC catalyst and then regeneration of the stripped catalyst by burning off the carbonaceous deposits with an oxygen-containing regeneration gas, usually air. For metallurgical reasons, and to avoid permanent deactivation of the catalyst, it is preferred to keep the regeneration temperatures below about 815°C (1500°F) and more usually in the range 677 to 760°C (1250—1400°F). However, the high levels of coke deposit on the catalyst create problems in the control of temperature during the regeneration process since the high levels of coke deposit result in the absence of elaborate control systems, in the creation of excessively high temperatures during

burning off of the deposit. Thus in RCC processing one must necessarily give consideration to the high metal loadings on the catalyst, the high carbon deposits, the maintenance of unit heat balance, the avoidance of catalyst inactivation temperatures, and the maintenance of catalyst activity under the severity of the conditions encountered.

A review of pertinent prior art having a bearing on RCC processes, and particularly the regeneration of RCC catalysts comprising high levels of deposited carbonaceous material is not particularly helpful when it comes to the problem of heat dissipation during the regeneration process.

Thus: U.S. Patent 2,606,430 teaches high temperature carbonisation and gasification of coke produced by cracking to produce synthesis gas. Temperatures of about 1093°C (2000°F) are contemplated in the gasification zone.

U.S. Patent 3,726,791 teaches the high Conradson carbon feeds are coked to lay down carbonaceous deposits on a gasification catalyst. The catalyst so coked is then steam gasified to produce hydrogen.

U.S. Patent 3,433,732 teaches catalytic hydrocracking and steam regeneration of the catalyst to produce hydrogen.

Canadian Patent 875,528 teaches contacting a coked catalyst with oxygen and carbon dioxide to produce carbon monoxide. The carbon monoxide is reacted with steam over a catalyst to form hydrogen and carbon dioxide.

U.S. Patent 2,414,002 teaches a two-stage catalyst regeneration operation which separates regeneration flue gases from each stage of controlled oxygen regeneration. This patent does not speak to the problems of regenerating catalyst comprising the heavy deposits of reduced crude cracking.

U.S. Patent 4,009,121 directed to the control or regeneration temperatures relies upon the use of steam coils in the catalyst bed.

U.S. Patent 3,563,911 describes a two-stage catalyst regeneration operation employing oxygen containing gas in each stage to remove up to 65% of carbonaceous deposits in the first stage.

U.S. Patent 3,821,103 discloses a two-stage regeneration operation with oxygen containing gas such as air. The flue gas of the second stage does not contribute heat to the first stage of catalyst regeneration nor is the use of steam therewith contemplated in the first stage of regeneration.

U.S. Patent 4,118,337 discloses two stages of catalyst regeneration with oxygen containing gas wherein hot regenerated catalyst of the second stage is added to the first stage regeneration to increase the heat level thereof.

U.S. Patent 4,276,150 teaches cracking of a reduced crude and effecting a first partial regeneration thereof with steam and oxygen in a gasifier at a temperature in the range of 593 to 1204°C (1100 to 2200°F). In this operation the

second stage regeneration flue gases are separated rather than contributing heat to the first stage of regeneration by utilization with a steam air mixture in the first regeneration step referred to as a stripper gasifier.

GB—A—2,001,545 teaches the regeneration of a cracking catalyst by means of two regeneration zones placed vertically one above the other. Partial regeneration takes place in the first zone, which is preferably the upper of the two, by contact of the spent catalyst with a mixture of oxygen, steam and CO₂ at 900—1200°F (482—649°C). The partially regenerated catalyst is then passed to the second zone where residual coke is burned off with an oxygen-containing gas, preferably air, at a temperature in the range 1250—1400°F (677—760°C). Flue gases from the second stage are separately processed for the recovery of sensible heat.

In connection with the above art, and as has already been said, the processing of a reduced crude in a fluid catalytic cracking reaction zone deposits relatively large amounts of coke on the catalyst. The amount of coke deposited on the catalyst is a function of the catalyst cracking activity and the Conradson carbon content of the reduced crude feed. This can be expressed as 4 wt % plus the feed Conradson carbon content. The ability of a catalyst single stage regeneration operation to handle coke on catalyst is considered limited to approximately an 8 Conradson carbon or approximately (4+8) 12 wt % coke on catalyst. To remove such coke levels from catalyst particles in a single stage is most difficult because of excessive regeneration temperature potentially encountered above 815°C (1500°F), which can irreversibly damage the catalyst activity and selectivity of a crystalline zeolite catalyst in the presence of steam as well as provide severe apparatus metallurgical problems requiring the use of expensive alloys and refractory linings.

In a two stage, stacked, one above the other, catalyst regeneration operation or other arrangement it is difficult to control oxygen combustion regeneration conditions and such is aggravated when one zone is positioned above the other so that the flue gas products of the bottom second stage pass upwardly through the catalyst in the first stage of catalyst regeneration and necessarily contribute heat thereto. Also, if one charges all of the oxygen required for coke combustion as air to the bottom regeneration zone, the quantity and velocities of regeneration gas and flue gas products will necessarily be high in order to fluidise a catalyst bed in the upper first regeneration zone and such high velocities can entrain or transport an undesired substantial amount of regenerated catalyst from the bottom bed up into the upper catalyst bed comprising the first stage of regeneration.

The present invention provides an improved process for the regeneration of RCC catalysts particularly from the point of view of improved temperature control of the regeneration process.

In this process the contaminated catalyst is

regenerated in two stages by contact with an oxygen-containing gas. In the first stage at least 40% of the deposited carbon originally present is removed by contact of the contaminated catalyst at a temperature in the range 1250—1500°F (677—815°C) with a hot regeneration gas comprising an oxygen-containing gas, steam and the hot flue gases emanating from the second stage of the regeneration process, following which the partially regenerated catalyst is passed to the second stage in which regeneration is completed to a residual carbon content of less than 0.5% by weight, based on the weight of the regenerated catalyst, by contacting the partially regenerated catalyst with an oxygen-containing gas under controlled temperature conditions not exceeding 1500°F (815°C), thereby producing the regenerated catalyst and a flue gas containing CO, CO₂ and unconsumed oxygen which is then fed to the first regeneration stage.

The use of a relatively large amount of steam in the presence of oxygen and combustion flue gas products of the second stage of catalyst regeneration in a first stage of catalyst regeneration effectively provides carbonaceous material removal temperatures not exceeding 1500°F (815°C) preferably in the range 1250 to 1350°F (677 to 732°C) and reduces the carbonaceous material level of the catalyst by at least about 40 percent before being subjected to oxygen regeneration higher temperature conditions in the second stage of regeneration. The regenerating operating technique of this invention permits restricting the overall regeneration temperatures below about 815°C (1500°F) and preferably below 760°C (1400°F) which is not possible in a single stage dense fluid bed catalyst regeneration operation for removal of high levels of hydrocarbonaceous material deposit such as obtained in cracking reduced crudes to provide catalyst particles of low residual coke. Thus, the particular combination regeneration operation of this invention because of temperature constraints provided by the operation permits one to increase the amount of Conradson carbon content of the feed that can be processed over the catalyst with high levels of carbonaceous material deposition also permits one to use poorer quality feeds under catalytic conversion conditions to more suitable products. In particular, the hot flue gas components of CO, CO₂ and oxygen recovered from the second stage of regeneration and charged with steam as herein provided to the first regeneration stage are balanced to particularly promote the removal of hydrocarbonaceous material under controlled endothermic and exothermic reaction conditions to achieve the results desired. That is, the flue gas product stream of the first stage of catalyst regeneration will include reaction products of restricted oxygen combustion including steam reforming products of CO and hydrogen in the presence of CO₂.

The removal of sulfur and nitrogen components in the hydrocarbonaceous deposits will also

accompany the flue gas products of the first stage regeneration.

In the preferred technique for removing high levels of carbonaceous material deposits in accordance with this invention two stacked regeneration zones are utilized and a portion of the required regeneration air is introduced to a bottom portion of the dense fluid bed of catalyst in each zone. The regeneration air can be distributed between the zones in equal proportions or can be lower in one bed than the other depending on the conditions desired. In the preferred regeneration arrangement of this invention it is contemplated employing a greater proportion of the oxygen-containing regeneration gas such as air in the lowermost bed of catalyst.

In the upper bed, partial regeneration of the catalyst is preferably effected with an oxygen (air) steam mixture and in the presence of the flue gases comprising CO, CO₂ and any unreacted oxygen from the lower bed at a temperature within the range of 677°C to 732°C (1250°F to 1350°F). The steam-air mixture has the dual function of removal of large amounts of hydrocarbonaceous deposits and comprising some high molecular weight polynuclear aromatic material by the combination of partial combustion at a temperature up to 732°C (1350°F) and steam reforming to produce gaseous components comprising CO and hydrogen which is partially combusted in the first stage of regeneration.

In a more particular aspect, the addition of steam performs the function of removing heavy adsorbed hydrocarbons by endothermic conversion to CO and hydrogen under restricted temperature conditions. The overall effect of the two stage regeneration operation is to lower the regenerator temperature by removing a substantial portion of the oxidizable carbonaceous material under endothermic temperature conditions. Thus, regeneration of the catalyst at any given level of hydrocarbonaceous deposits in the presence of heavy residual hydrocarbons can be accomplished at lower temperatures than is possible with oxygen regeneration alone. Furthermore, one can now effect the catalytic cracking of reduced crudes with high Conradson carbon values, i.e. in the range 10 to 15 or more, without worrying about high regeneration temperatures thus avoiding the current practices of propane deasphalting, coking, vacuum distillation, hydrogenation and other processes used to remove such coke producing materials from such reduced crudes prior to catalytic cracking.

The cracking catalyst to which the present invention applies, i.e. high activity RCC catalysts, include crystalline aluminosilicates and zeolites such as a crystalline "Y" faujasite catalytically activated by exchange with ammonia or one or more rare earth metals to remove sodium therefrom. The zeolite is dispersed in an amount in the range of about 5 to 60 wt % in a matrix material comprising one or more silica, alumina, or silica alumina to which matrix material is added a clay

material selected from the group consisting of kaolin, hollloysite, montmorillonite, heat and chemically modified clays such as metal kaolin and acid treated hollloysite and bentonite. One or more various large pore zeolites may be employed in the catalyst particle complex in combination with providing a matrix material of large pore volume in excess of 0.22 cc/gm and more usually at least about 0.3 cc/gm.

The combination operation of this invention is directed to a temperature controlled heat balance regeneration operation which employs a novel combination of processing steps for removing high levels of hydrocarbonaceous deposits of reduced crude cracking from catalyst particles in the absence of significant hydrothermal degradation of the catalyst particles.

Thus, it has been found, contrary to the teachings of the prior art that the high levels of carbonaceous material deposits can be used to advantage as a protector of the catalyst, cracking actively during partial removal thereof with steam under conditions to form syngas comprising CO and hydrogen. In this operating environment it is found possible to remove from 40 to 60 wt % of the deposited carbonaceous material in the first stage of regeneration by the combination of steam reforming and oxygen combustion for supplying the endothermic heat requirements of the steam reforming operation without significantly contributing to hydrothermal degradation of the catalyst cracking activity concomitantly with maintaining desired low regeneration temperatures preferably below about 760°C (1400°F).

In yet another embodiment, the present invention contemplates the removal of at least a portion of the hydrocarbonaceous deposits in the first stage regeneration operation at temperatures of at least 760°C (1400°F) by contact with steam and by the reactions of CO₂ with hydrogen and carbon in the hydrocarbonaceous deposits. Thus, the competing reactions of oxygen combustion of carbonaceous deposits to provide a substantial portion of the endothermic heat requirements of steam reforming and the reactions of CO₂ with carbon and hydrogen in the first regeneration zone so that a majority or greater than 50 wt % of the deposited hydrocarbonaceous material is intended to be removed in the first stage of catalyst regeneration wherein the catalyst contacted is maintained in a dense fluid catalyst bed phase providing relatively uniform temperature in this first regenerator dense catalyst phase operation operates to minimize hydrothermal degradation of catalyst particles not so guardedly contacted.

The catalyst thus partially regenerated and comprising residual carbonaceous material and more appropriately referred to as residual carbon is then contacted with an excess of oxygen containing gas such as air or oxygen modified regeneration gas relying upon a second dense fluid catalyst bed phase contributing to uniform temperature combustion of residual carbon on

the catalyst particles. It will be recognised by those skilled in the art that the concentration of catalyst particles forming the dense fluid beds of catalyst particles may be varied over a considerable range, e.g. from 20 to 40 lb/ft³ (320 to 640 kg/m³) or more, but more usually from 35 to 40 lb/ft³ (560 to 640 kg/m³).

In general the regeneration sequence contemplated by this invention is effective to reduce the residual carbon content of the regenerated catalyst to 0.1 wt % or less, and preferably less than 0.05 wt % without exceeding a catalyst regeneration temperature of 1500°F (815°C), more preferably 1400°F (760°C) or significantly hydrothermally deactivating the catalyst.

The regeneration process of the present invention is further described with reference to the accompanying drawings in which:

Figure I is a diagrammatic sketch of an apparatus for the catalytic cracking (RCC) of reduced crudes and incorporating the catalyst regeneration feature of the present invention.

Figure II is a graph depicting a first study directed to the removal of coke from a catalyst with steam.

Figure III is a graph depicting the effect of steam at 787°C (1450°F) on surface area of a commercially available catalyst with and without coke deposits identified as GRZ-1 by Davidson Chemical Company.

Figure IV is a graph depicting the effect of steam contact time on the catalyst zeolite intensity whether coked or not coked.

Referring now to Figure I, by way of example, the cracking apparatus comprises a riser cracking zone 4, and a catalyst disengaging and stripping zone 14, 48 adjacent to a two stage catalyst regeneration vessel 20 comprising two regeneration zones or beds 22, 34 located one above the other so that the flue gas products of the bottom bed 34 can pass upwardly into the bottom portion of the upper bed 22.

In the cracking part of the apparatus, reduced crude feed is charged to the riser cracking zone 4 via conduits 1 and 6 in admixture with one or more of steam (STM) naphtha and water via conduits 5 and 3. The steam, naphtha and water act as diluent materials, temperature adjustment materials, velocity providing materials, feed partial pressure reducing materials and a combination thereof to assure intimate rapid atomized and vaporised contact of the reduced crude feed with charged finely divided fluidizable catalyst particles fed from the regeneration vessel via line 44 to provide an upwardly flowing suspension at a temperature of at least about 510°C (950°F) and sufficiently elevated to provide a riser outlet temperature in the range of 510°C to 566°C (950°F to 1050°F). The upwardly flowing suspension in riser 4 is at a velocity to provide a hydrocarbon residence time within the range of 0.5 to 4 seconds and more usually in the range of 1 to 2 seconds. A short residence time may also be provided by alternatively charging the reduced crude feed through additional inlet conduits 2 and

7 located above the riser bottom. In this case the steam, naphtha or other light hydrocarbons introduced to the riser bottom initially fluidize the catalyst charged to the riser via conduit 44 before contact with the reduced crude fed through the conduit 2 or 7.

At the top of the riser 4, the existing suspension of catalyst particles in the cracked vaporous product passes to the cyclones 10 for the separation of the spent catalyst particles from the vapour phase cracked product which is withdrawn from the cracker for further processing (not shown) via conduit 12. Separated catalyst particles are connected in an annular stripping zone 14 for countercurrent contact with a stripping gas such as steam introduced by conduit 16. Stripped catalyst particles comprising a heavy load of hydrocarbonaceous deposits and metal contaminants then pass from the stripper 14 by conduit 18 to a dense, fluidised bed of catalyst particles 22 in the upper portion of the regeneration vessel 20. Catalyst bed 22 comprises the first stage of regeneration in accordance with the process of this invention.

Introduced into the bottom of the fluidized bed 22 of spent catalyst particles via a plenum chamber 26 and associated distributor arms 27 is a mixture of a regeneration gas (REG) fed via conduit 24 and premixed with steam (STM) fed via conduit 25, the resulting mixture being predominantly steam at a temperature in the range 143°C to 238°C (290°F to 460°F). Also, and specifically in accordance with this invention, flue gas from the lower of the two catalyst beds 34 passes upwardly through apertures 29 in baffle plates 28 separating the two sections of the regeneration vessel and directly into the upper of the two catalyst regeneration beds 22.

In an alternative it is contemplated that the baffle plates 28 be of a porous construction or that the flue gases from the lower bed pass into the plenum chamber 26 for distribution with the regeneration gas and steam via the distributor 27, rather than directly into the bed 22.

In yet another variation it is contemplated that the flue gases from the lower bed may be passed through external cyclones for the removal of catalyst fines before passing to the bottom of the bed 22, in admixture with steam.

Whatever the actual arrangement employed, the catalyst particles in the dense fluidised bed 22 are partially regenerated by contact with the mixture comprising the oxygen-containing regeneration gas and steam fed via lines 24 and 25 and the flue gases obtained from the lower bed 34. Partial regeneration of the catalyst in bed 22 is accomplished under steam reforming conditions at temperatures within the range 677°C to 815°C (1250°F to 1500°F). Flue gas products of regeneration pass through cyclone separator 30 before being withdrawn by conduit 32 for use as desired.

The partially regenerated catalyst from bed 22 then passes to suitable withdrawal wells communicating with standpipes 36 and 40 for passage to the lower bed 34 with optional heating

or cooling of the catalyst in standpipe 36 in a heat exchanger 38.

In the lower catalyst regeneration bed 34, regeneration of the catalyst is completed to provide a residual carbon content less than 0.1 wt % and preferably no more than 0.05 wt % by further contact with oxygen containing regeneration gas (REG) such as air or oxygen fed via conduit 42 optionally in combination with CO₂ fed via line 46. In the second regeneration bed 34 residual carbonaceous material is removed without exceeding a temperature of 815°C (1500°F) and preferably without exceeding a temperature of 760°C (1400°F).

The transfer of catalyst from upper bed 22 to lower bed 34 may also be accomplished by one or more internal standpipes rather than by the external standpipes shown.

The catalyst regenerated to a desired low level of residual carbon by the combination operation above discussed and at a desired elevated temperature is passed from catalyst bed 34 by standpipe 44 to a lower portion of riser 4 for re-use in the system as above described.

Referring now to Figure II, by way of example, there is provided a graph directed to presenting data directed to carbon removal with steam from a GRZ-1 cracking catalyst (commercially available catalyst from W. R. Grace & Co.—Davidson Chemical Division) which had been coked with Arabian Light Reduced Crude. The graph shows that the reaction of steam to remove coke or carbonaceous material is relatively just for significant amounts of coke removal within a time span commensurate with that obtainable in a dense fluid catalyst bed regeneration operation. For example, a catalyst comprising about 5.8 wt % carbon on catalyst is reduced to a residual carbon level of about 1.0 wt % when contacted with 787°C (1450°F) steam for 2 hours. More significant, coke removal is achievable with steam at temperatures of about 760°C (1400°F) to form CO and hydrogen which are combustible with added oxygen to generate needed endothermic heat.

Figures III and IV on the other hand show the effect of 787°C (1450°F) steam on a coked and uncoked GRZ-1 catalyst with respect to surface area and zeolite intensity. Zeolite intensity is identified with the active zeolite component or the catalyst, the greater the intensity, the more of the active crystalline zeolite component. The graphical data of Figures 3 and 4 show that steaming of the uncoked catalyst gave a much larger drop in surface area and zeolite intensity than obtained when contacting a coked catalyst with high temperature steam. Thus, the coke on the catalyst guards the deactivation of the catalyst against high temperature steam. This finding is used to advantage in pursuit of the concepts of this invention which is directed to reducing the temperature of regeneration of catalysts used in reduced crude cracking. Catalysts so used are known to accumulate large amounts of carbonaceous material attributable in substantial

measure to the Conradson carbon level of the feed being processed and such high levels of deposited carbonaceous materials are instrumental in causing high temperatures to be encountered by burning removal thereof with oxygen containing gas such as air in the absence of extreme caution, head dissipation and restrict temperature sequential burning in a plurality of regeneration zones, all of which techniques are less than desirable. It will be recognised by those skilled in the art that the regeneration combination of this invention is not only a unique approach to the removal of relatively large amounts of carbonaceous deposits but so also is the amount of carbonaceous material to be removed by burning with oxygen containing gas sufficiently reduced to permit maintaining desired temperature restrictions below 760°C (1400°F) and more preferably at the lowest temperature conditions promoting extended catalyst life and usage. Perhaps more important is the realisation that the regeneration concept of sequence of performance permits the processing of higher Conradson carbon feeds than previously considered possible at relatively low temperatures particularly suitable for achieving desired hydrocarbon conversion results. Thus the endothermic conversion of carbonaceous deposits (coke) with steam to a more favorable level for complete removal of residual carbon with oxygen containing gas measurably improves the economics restraints with respect to processing more of the bottom of the barrel of the crude oil and identified more particularly as a reduced crude comprising carbo-metallic impurities.

Claims

1. A method for the regeneration of metal and carbon contaminated cracking catalysts used in the catalytic conversion of carbo-metallic containing residual oils, which comprises contacting the contaminated catalyst in two stages with an oxygen containing regeneration gas, characterised in that in the first stage at least 40% of the deposited carbon originally present is removed by contact of the contaminated catalyst at a temperature in the range 1250—1500°F (677—815°C) with a hot regeneration gas comprising an oxygen-containing gas, steam and the hot flue gases emanating from the second stage of the regeneration process, following which the partially regenerated catalyst is passed to the second stage in which regeneration is completed to a residual carbon content of less than 0.5% by weight, based on the weight of the regenerated catalyst, by contacting the partially regenerated catalyst with an oxygen-containing gas under controlled temperature conditions not exceeding 1500°F (815°C), thereby producing the regenerated catalyst and a flue gas containing CO, CO₂ and unconsumed oxygen which is then fed to the first regeneration stage.

2. A method according to claim 1, wherein the temperature in the first regeneration stage is

maintained in the range 1250° to 1350°F (677° to 732°C).

3. A method according to claim 1 or 2, wherein the temperature of the second regeneration stage is kept below 1400°F (760°C).

4. A method according to claim 1, 2 or 3, wherein at least 50% of the carbon present in the contaminated catalyst is removed in the first regeneration stage.

5. A method according to any one of claims 1—4, wherein the first and second stages of the regeneration process are effected, respectively, in fluidised beds of catalyst located one above the other in a catalyst regeneration vessel with the partially regenerated catalyst passing from the upper bed to the lower bed, and the hot flue gases passing from the lower bed to the upper bed.

6. A method according to claim 5, wherein the hot flue gases from the lower bed are passed directly upward in the regeneration vessel into the upper bed, the additional oxygen-containing gas and steam being separately fed to the base of the upper bed.

7. A method according to claim 5, wherein the hot flue gases from the lower bed are premixed with the additional oxygen-containing gas and steam prior to feeding the mixture to the base of the upper bed.

8. A method according to claim 5, 6 or 7, wherein the temperature of at least a portion of the partially regenerated catalyst is adjusted by separately heating or cooling the partially regenerated catalyst on its passage from one bed to the other.

9. A process for the catalytic cracking of carbometallic containing residual oils, which comprises contacting the residual oil with a regenerated cracking catalyst under conditions effective to cause catalytic cracking of the feedstock, and which includes regenerating and recycling catalyst contaminated with carbometallic deposits during the cracking process, characterised in that the contaminated catalyst is regenerated by a method as claimed in any one of claims 1—8.

Patentansprüche

1. Verfahren zur Regenerierung von mit Metall und Kohlenstoff vereunreinigten Spaltkatalysatoren bei der katalytischen Umwandlung von karbometallische Verbindungen enthaltenden Restölen, bei dem der verunreinigte Katalysator in zwei Stufen mit einem sauerstoffenthaltenden Regenerationsgas in Berührung gebracht wird, dadurch gekennzeichnet, daß bei der ersten Stufe wenigstens 40% des ursprünglich niedergeschlagenen Kohlenstoffs durch Inberührungbringen des verunreinigten Katalysators bei einer Temperatur im Bereich von 677 bis 815°C mit einem heißen Regenerationsgas, das aus sauerstoffenthaltendem Gas, Dampf und den aus der zweiten Stufe des Regenerationsverfahrens austretenden heißen Heizgasen entfernt werden, und im Ausfluß hieran der

teilweise regenerierte Katalysator zu der zweiten Stufe geführt wird, in der die Regeneration bis auf einen restlichen Kohlenstoffgehalt von weniger als 0,5 Gew. %, bezogen auf das Gewicht des regenerierten Katalysators abgeschlossen wird durch Inberührungbringen des teilweise regenerierten Katalysators mit einem sauerstoffenthaltenden Gas unter gesteuerten Temperaturbedingungen, die 815°C nicht überschreiten, wobei der regenerierte Katalysator und ein Heizgas, das CO, CO₂ und nicht verbrauchten Sauerstoff enthält, gewonnen werden, die sodann der ersten Regenerierungsstufe zugeführt werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Temperatur der ersten Regenerierungsstufe in einem Bereich von 677 bis 732°C gehalten wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Temperatur der zweiten Regenerierungsstufe unter 760°C gehalten wird.

4. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß wenigstens 50% des in dem verunreinigten Katalysator vorliegenden Kohlenstoffs in der ersten Regenerierungsstufe entfernt werden.

5. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die erste und zweite Regenerierungsstufe des Regenerierungsverfahrens in entsprechend fluidisierten Katalysatorbetten durchgeführt werden, die übereinander in einem Katalysator-Regenerierungsgefäß, wobei der teilweise regenerierte Katalysator von dem oberen Bett in das untere Bett tritt und die heißen Heizgase von dem unteren Bett in das obere Bett aufsteigen.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die heißen Heizgase von dem unteren Bett direkt nach oben in dem Regenerierungsgefäß in das obere Bett geführt werden und das zusätzliche, sauerstoffenthaltende Gas und Dampf getrennt auf den Grund des oberen Bettes geführt werden.

7. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die heißen Heizgase aus dem unteren Bett vorher mit zusätzlichem, sauerstoffenthaltendem Gas und Dampf vermischt werden, bevor das Gemisch dem Grund des oberen Bettes zugeführt wird.

8. Verfahren nach einem der Ansprüche 5 bis 7, dadurch gekennzeichnet, daß die Temperatur wenigstens eines Teils des teilweise regenerierten Katalysator durch getrenntes Erhitzen oder Kühlen des teilweise regenerierten Katalysators bei seinem Durchgang von einem zu dem anderen Bett eingestellt wird.

9. Verfahren zum katalytischen Spalten von carbometallischen Verbindungen enthaltenden Restölen, bei dem das Restöl mit einem regenerierten Spaltkatalysator unter Bedingungen in Berührung gebracht wird, die zu einem katalytischen Spalten der Beschickung führen und bei dem ein mit carbometallischen Ablagerungen verunreinigter Katalysator während des Spaltverfahrens regeneriert und zurückgeführt wird, da-

durch gekennzeichnet, daß der verunreinigte Katalysator gemäß dem Verfahren nach den Ansprüchen 1 bis 8 regeneriert wird.

Revendications

1. Un procédé pour la régénération de catalyseurs de craquage contaminés par des métaux et du carbone, utilisés dans la conversion catalytique d'huiles résiduelles carbo-métalliques, qui consiste à mettre en contact le catalyseur contaminé en deux stades avec un gaz de régénération contenant de l'oxygène, caractérisé en ce qu'au premier stade, on élimine au moins 40% du carbone déposé primitivement présent, par contact du catalyseur impur, à une température de l'intervalle de 677 à 815°C (1250 à 1500°F), avec un gaz de régénération chaud comprenant un gaz contenant de l'oxygène, de la vapeur d'eau et les gaz de carneau chauds provenant de deuxième stade du processus de régénération, après quoi on amène le catalyseur partiellement régénéré au deuxième stade dans lequel on complète la régénération jusqu'à une teneur résiduelle en carbone de moins de 0,5% en poids, sur la base du poids du catalyseur régénéré, en mettant en contact le catalyseur partiellement régénéré avec un gaz contenant de l'oxygène dans des conditions réglées de température ne dépassant pas 815°C (1500°F), formant ainsi le catalyseur régénéré et un gaz de carneau contenant du CO, du CO₂ et de l'oxygène non consommé, qui est alors amené au premier stade de régénération.

2. Un procédé selon la revendication 1, dans lequel on maintient la température au premier stade de régénération dans l'intervalle de 677 à 732°C (1250 à 1350°F).

3. Un procédé selon l'une des revendications 1 ou 2, dans lequel on maintient la température du deuxième stade de régénération en-dessous de 760°C (1400°F).

4. Un procédé selon l'une des revendications 1, 2 ou 3, dans lequel on élimine au premier stade de

régénération au moins 50% du carbone présent dans le catalyseur contaminé.

5. Un procédé selon l'une quelconque des revendications 1 à 4, dans lequel on effectue respectivement les premier et deuxième stades du processus de régénération dans des couches fluidisées de catalyseur situées l'une au-dessus de l'autre dans un récipient de régénération de catalyseur, le catalyseur partiellement régénéré passant de la couche supérieure à la couche inférieure et les gaz de carneau chauds passant de la couche inférieure à la couche supérieure.

6. Un procédé selon la revendication 5, dans lequel on amène directement le gaz de carneau chauds venant de la couche inférieure, vers le haut, dans le récipient de régénération, à la couche supérieure, le gaz supplémentaire contenant de l'oxygène et la vapeur d'eau étant amenés séparément à la base de la couche supérieure.

7. Un procédé selon la revendication 5, dans lequel on prémélange les gaz de carneau chauds venant de la couche inférieure au gaz supplémentaire contenant de l'oxygène et à de la vapeur d'eau avant d'amener le mélange à la couche supérieure.

8. Un procédé selon l'une des revendications 5, 6 ou 7 dans lequel on ajuste la température d'au moins une partie du catalyseur partiellement régénéré en chauffant ou en refroidissant séparément le catalyseur partiellement régénéré à son passage d'une couche à l'autre.

9. Un procédé pour le craquage catalytique d'huiles résiduelles carbo-métalliques, qui consiste à mettre en contact l'huile résiduelle avec un catalyseur de craquage régénéré, dans des conditions efficaces pour causer le craquage catalytique de la matière d'alimentation, et qui comprend la régénération et le recyclage de catalyseur contaminé par des dépôts carbo-métalliques pendant le processus de craquage, caractérisé en ce que l'on régénère le catalyseur contaminé par un procédé selon l'une quelconque des revendications 1 à 8.

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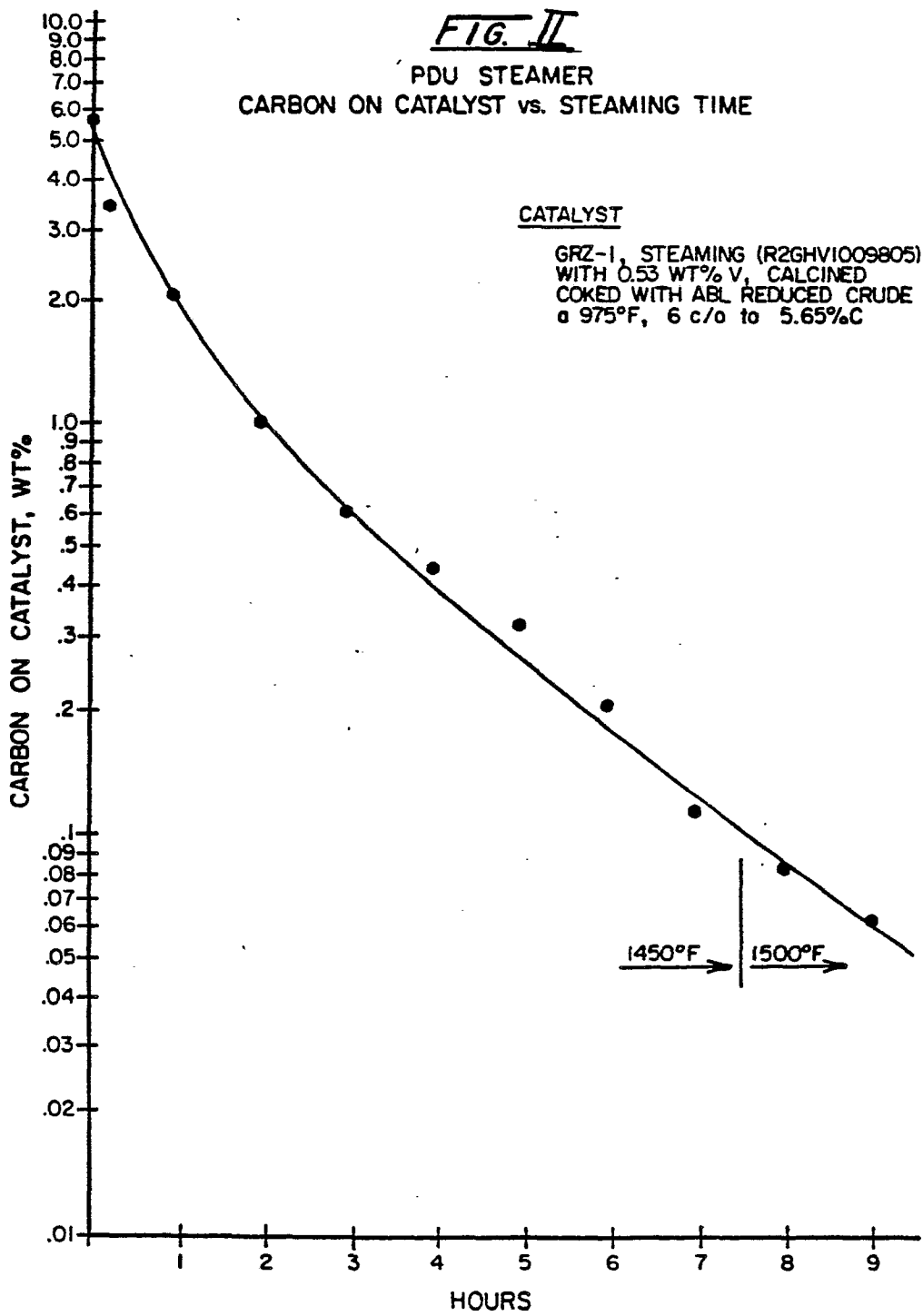


FIG. III
EFFECT OF STEAM
COKED CATALYST vs. UNCOOKED CATALYST
SURFACE AREA vs. TIME

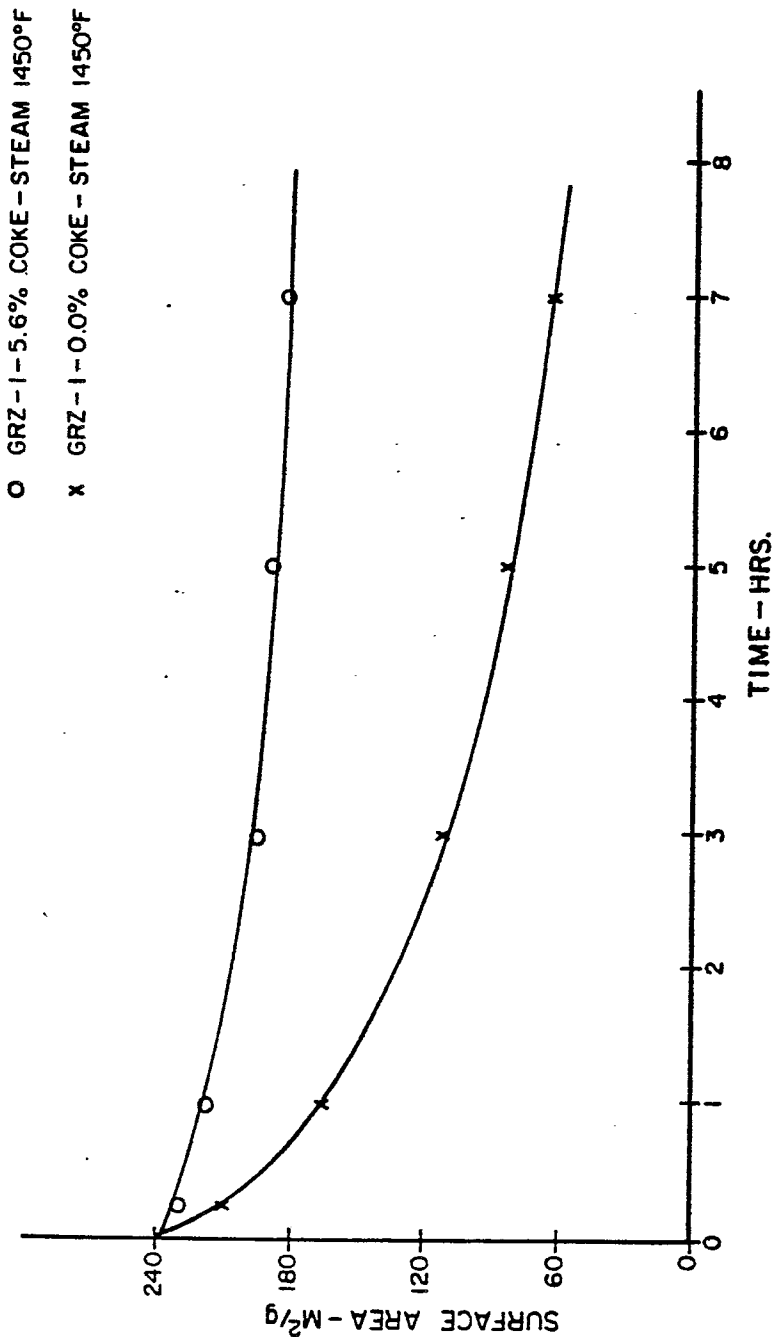


FIG. IV
EFFECT OF STEAM
COKED CATALYST vs. UNCOCKED CATALYST
ZEOLITE INTENSITY vs. TIME

O GRZ-1- 5.6% COKE - STEAM 1450°F

X GRZ-1- 0.0% COKE - STEAM 1450°F

