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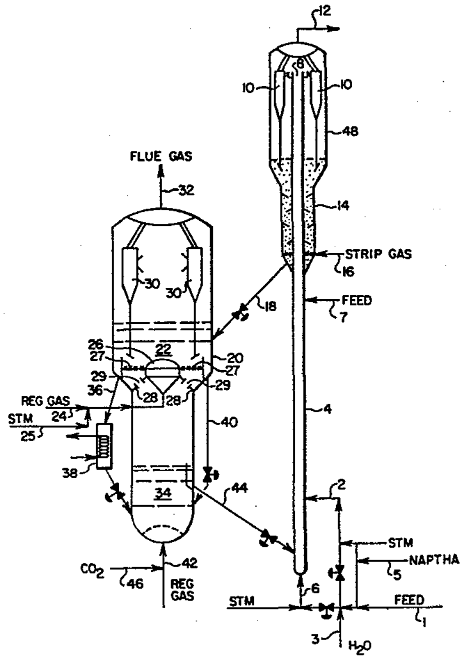
(54) Regeneration of catalyst used in the conversion of carbo-metallic containing residual oils.

(57) Steam (25) is added to the air that passes through the dense bed of the deactivated coked catalyst. Steam acts by removing adsorbed heavy hydrocarbons and reacting with the coke to yield carbon monoxide. The overall effect is to lower the regenerator temperature by removing oxidizable material and convert coke to carbon monoxide and hydrogen via endothermic reaction. This allows operation at higher Conradson carbon feed (10–14% Conradson carbon). Air (42) is added at the bottom of the lower regenerator (34) and also an additional air inlet is placed in the upper part of the lower regenerator section.



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ACTORUM AG

REGENERATION OF CATALYST USED IN THE CONVERSION OF CARBO-METALLIC CONTAINING RESIDUAL OILS

The present invention is particularly concerned with the method and technique for regenerating a cracking catalyst comprising relatively high levels of deposited hydrocarbonaceous materials and metal contaminants. Sulfur and nitrogen contaminants are also included as deposited contaminants.

The well-known process of relatively clean gas oil feed fluid catalytic cracking (FCC) is not designed or tailored for use in the catalytic conversion of carbo-metallic containing oil feeds known as residual oils or reduced crudes comprising carbo-metallic high molecular weight hydrocarbon components boiling above 522°C (1025°F) and effecting regeneration of catalyst particles used therein. Gas oil fluid catalytic cracking operations are generally restricted to processing relatively clean feeds comprising less than one weight percent of Conradson carbon and comprising small amounts of metal contaminants of Ni, V, Fe and Cu in amounts preferably less than about 0.5 ppm. The zeolite containing catalysts employed currently in gas oil fluid catalytic cracking operations are generally discarded when their catalytic MAT activity if below about 70% and a contaminant metals loading has reached from 1000 to 3000 Ni + V.

The development of fluid catalytic cracking was for the conversion of select relatively clean fractions or portions obtained from crude oils to produce particularly gasoline and heating fuels. The select feedstock for FCC gas oil operations comprise predominantly atmospheric and vacuum gas oils, generally boiling below about 552°C (1025°F) and most desirably comprise a low Conradson carbon content, below 1 wt%, a low metals content, below 0.5 ppm Ni + V and are also low in sulfur and nitrogen components and obtained by prehydrogenation of the feed. More typical (GO) gas oil feedstocks comprising atmospheric and vacuum gas oils contain less than 0.5 wt% Conradson carbon and 0.1-0.2 ppm Ni + V. The boiling range of gas oil is generally above about 221°C

(430°F) up to about 552°C (1025°F) but may go to 566°C (1050°F) with some clean crude oils. The gas oil feed for an FCC operation is preheated to a temperature in the range of 260-427°C (500-800°F) and thus is substantially completely vaporized immediately upon contact with hot regenerated catalyst at temperatures in the range of 621-787°C (1150-1450°F). This complete vaporization of the feed by the catalyst in a riser reactor results in a relatively high conversion (>70%), high gasoline product selectivities (>70%) and most usually low carbon values (<1 wt% on catalyst, about 4 wt% on feed). The catalyst so utilized gradually accumulates some metal contaminants after an extended period of operation in the range of about 500-3,000 ppm Ni + V before the catalyst is gradually and/or continuously replaced with fresh catalyst added to maintain an equilibrium state of conversion and metals level. The FCC process as practiced today provides high coke and gas makes at the elevated metal levels with a lowered gasoline selectivity, thus necessitating considerable catalyst withdrawal and additions of fresh catalyst as makeup. Secondly, the coke make or carbon deposition as hydrocarbonaceous material on the catalyst in gas oil cracking is relatively low by comparison with more severe operations such as provided by reduced crude cracking operations. Also for metallurgical reasons and preservation of catalyst activity, it is desirable to restrict regeneration temperatures generally below 815°C (1500°F) and more usually in the range of 677 to 760°C (1250 to 1400°F). However, processing reduced crudes and residual oils of high Conradson carbon under FCC operating conditions and particularly restricted catalyst regeneration conditions with known FCC catalysts is a most difficult problem because of the high levels of carbonaceous material on the catalyst contributing to reduced catalyst life and requiring relatively high catalyst inventory. Reduced crude catalytic processing goes against substantially all processing principles practiced in gas oil FCC technology in that (1) reduced crudes charged for catalyst contact are only partially vaporized; (2) reduced crudes have a higher metals content resulting in high metals deposition and rapid accumulation on catalyst particles; (3) reduced crudes have a high Conradson carbon value contributed by naphthenes and asphaltenes; and (4) processing reduced crudes and residual oils comprising materials boiling above 552°C (1025°F) contributes to high deposition of hydrocarbonaceous material on the catalyst and thus high temperatures generated by oxygen combustion thereof during regeneration is the norm in the absence of elaborate control systems.

In reduced crude processing one must necessarily give consideration to high metals loading on catalyst, high carbon and hydrogen deposition on catalyst, maintaining unit heat balance, avoiding catalyst inactivation temperatures, and more particularly maintaining catalyst activity under the severity of conditions encountered.

The processing of residual oils and reduced crudes comprising carbo-metallic high molecular weight components such as asphaltenes, polycyclic naphthenes and porphyrins in a reduced crude cracking (RCC) operation deposits a large amount of coke in the form of hydrocarbonaceous material on the RCC catalyst. Also deposited are metal deposits of the cracking operations such as nickel, vanadium, sodium, iron, copper, sulfur and nitrogen compounds in various quantities depending upon feed source. Following cracking of such reduced crude feeds and mechanical separation of the vaporous products of cracking from catalyst, the separated catalyst is stripped usually with steam to remove entrained vaporous material before passing the stripped catalyst to catalyst regeneration for removal of deposited hydrocarbonaceous material by burning with an oxygen containing gas such as air.

A review of pertinent prior art having a bearing on reduced crude cracking and particularly the regeneration of metals contaminated catalyst comprising high levels of deposited hydrocarbonaceous materials has been less than lucrative for teachings directed to dissapating high levels of carbon burning heat to provide a regenerated catalyst of low or no residual carbon residue.

U.S. Patent 2,606,430 teaches high temperature carbonization 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 that 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 hycrocracking 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 hdavy deposits of reduced crude cracking.

U.S. Patent 4,009,121 directed to the control of 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.

Summary of the Invention

The present invention is directed to the regeneration of fluid catalyst particles contaminated with hydrocarbonaceous deposits, metals, sulfur and nitrogen compounds such as obtained in reduced crude cracking operations. In a particular aspect the present invention is directed to a regeneration technique which relies upon two separate stages of fluid catalyst regeneration positioned one above the other and following a catalyst stripping operation in which the first stage of catalyst regeneration relies in substantial measure upon the partial removal of hydrocarbonaceous material with a steam oxygen mixture comprising hot flue gas combustion products under conditions to form CO and hydrogen at least partially combined therein in combination with a second stage of catalyst regeneration relied upon to complete substantially complete removal of residual carbonaceous material (coke) with oxygen rich gas under temperature conditions restricted to preferably limit the temperature below 815°C (1500°F) and more usually below about 760°C (1400°F).

The use 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 up to about 732°C (1350°F) 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 regeneration 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 regeneneration 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.

The use of a relatively large quantity of steam in the first stage of catalyst regeneration in combination with some oxygen providing combustion heat is of such quantity and temperature when combined with the hot flue gas products of the second stage of regeneration at a temperature up to about 760°C (1400°F) to effectively remove a substantial portion of the hydrocarbonaceous deposits at temperatures up to 732°C (1350°F) by reacting steam with carbonaceous deposits to form carbon monoxide and hydrogen. Thus, 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.

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 observed to be 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 irreversably 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 aggrevated 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 fluidize 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.

In order to reduce the problems above identified and improve the technique for removing high levels of carbonaceous material deposits in a sequence of at least two stacked regeneration zones as herein provided, a portion of the required regeneration air if introduced to a bottom portion of each of a dense fluid bed of catalyst in each zone. Thus, the distribution of regeneration air to each zone may be of equal portion or a higher or lower portion may be employed in the lower catalyst bed than in the upper bed of catalyst depending on condition desired. In the regeneration arrangement of this invention it is contemplated employing a greater portion of oxygen containing regeneration gas such as air in the lower most bed of catalyst being regenerated to remove residual carbon of the first stage regeneration so that combustion products thereof and any unreacted oxygen will pass upwardly into the bottom portion of the upper catalyst bed being regenerated in the presence of steam charged to the first stage of regeneration to produce CO and hydrogen. Utilizing an additional air inlet to the upper bed of catalyst, added in admixtures with steam or separately thereto, is provided in a volume sufficient to provide exothermic combustion heat to support the endothermic steam partial regeneration of the catalyst along with second stage hot combustion products according to the concepts of this invention.

In one specific embodiment steam is added with some supplemental air and charged for contact with a bottom portion of the upper catalyst bed to be regenerated. Regeneration of catalyst in the upper bed with oxygen (air) steam mixture is preferably effected 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 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 as herein provided. 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 catalytic cracking of more higher Conradson carbon crudes without worrying about high regeneration temperatures in the absence of attendant processes for removal of these coke producing materials as in now the current practice by propane deasphalting, coking, vacuum distillation, hydrogenation and other processes suitable for the purpose and combinations thereof. Thus, it is clear that one following the concepts of this invention can process reduced crudes and other portions of crude oils of high Conradson carbon levels above about 8 such as feed materials of Conradson carbon levels in the range of 10 to 15 or more.

The fluid catalyst composition contemplated for use in this invention is a high activity cracking catalyst comprising a crystalline aluminosilicate or zeolite 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 of silica, alumina, or silica alumina to which matrix material is added a clay material selected from the group consisting of kaolin, holloysite, montmorilonite, heat and chemically modified clays such as meta kaolin and acid treated holloysite 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 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 is 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 concommitantly 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 recognized 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 of about 20 pounds per cubic foot up to about 35, 40 or even more pounds per cubic foot. Generally, the concentration of particles will be within the range of 35 to 40 pounds per cubic foot. In the regeneration sequence contemplated by this invention, it is intended to reduce residual carbon of regenerated catalyst to a level of at least 0.05 wt% or less without exceeding catalyst regeneration temperatures of about 760°C (1400°F) or significantly hydrothermally deactivating the catalyst.

Brief Description of the Drawings

Figure I is a diagrammatic sketch in elevation of one arrangement of apparatus for practicing the catalytic concession of reduced crudes and effecting regeneration of the catalyst so used in a plurality of dense fluid catalyst beds following the concepts and techniques of this 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.

Discussion of Specific Embodiments

Referring now to Figure 1 by way of example, there is shown a riser cracking zone, a catalyst disengaging and stripping zone adjacent to a two stage catalyst regeneration arrangement stacked one above the other so that flue gas products of the bottom regeneration section can pass upwardly into the bottom portion of a dense fluid bed of catalyst being regenerated in the upper regeneration section.

In this arrangement of the drawing, Figure 1, a reduced crude is charged by conduit 1 in admixture with one or more of steam naphtha and water, as a diluent material, temperature adjustment material, velocity providing material feed partial pressure reducing material and a combination thereof to assure intimate rapid atomized and vaporized contact of the reduced crude with charged finely divided fluidizable catalyst particles 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. Short residence time may also be provided by charging the reduced crude through inlet means above the riser bottom as by inlet 2 and 7 shown in the presence of suitable diluent material. Steam, naphtha or other light hydrocarbons may initially fluidize the catalyst charged to the riser bottom before contact with reduced crude charge by either conduit 2 or 7. At the riser exit 8, the suspension following traverse of the riser is separated so that vaporous materials pass through cyclones for removal by conduit 12 and separation in downstream equipment not shown. Separated catalyst particles are collected in an annular stripping zone 14 for countercurrent contact with stripping gas such as steam introduced by conduit 16. Stripped catalyst particles comprising a heavy load of hydrocarbonaceous deposits and metal contaminants pass from stripper 14 by conduit 18 to a dense bed of catalyst 22 in the upper portion of regeneration zone 20. Catalyst bed 22 comprises the first stage of regeneration in accordance with the processing concepts of this invention. That is, regeneration gas such as air introduced by conduit 24 is mixed with steam introduced by conduit 25 and the mixed gasiform material, predominantly steam at a temperature in the range of 143°C to 238°C (290°F to 460°F) is charged to plenum chamber 26 and thence by distributor arms 27 to a bottom portion of bed 22 for admixture with flue gases obtained as provided below and charged through openings 29. That is, separator baffle means 28 is provided with a plurality of small openings represented by 29 for passage of flue gases therethrough and obtained from the second stage of catalyst regeneration discussed below.

It is contemplated modifying the arrangement above discussed so that the baffle 28 is now porous and the flue gases of the second stage regeneration comprising bed 34 are caused to flow into the plenum 26 for admixture with steam prior to entering bed 22 by distributor arms 27. On the other hand flue gases from bed 34 may be passed through external cyclones for removal of catalyst fines returned to bed 34 before passing the flue gases freed of catalyst in admixture with steam to a bottom portion of bed 22.

In any of the above arrangements, the catalyst in dense fluid bed 22 is partially regenerated with oxygen containing gases furnished by the flue gases obtained from the lower bed 34 and being enriched with an air-steam mixture added by gas distributor arms 27 connected to plenum 27. Partial regeneration of the catalyst in bed 22 is accomplished under steam reforming conditions at temperatures within the range of 677°C to 815°C (1250°F to 1500°F). Flue gas products of regeneration pass through cyclone separator means 30 before being withdrawn by conduit 32 for use as desired.

The partially regenerated catalyst in bed 22 is passed to suitable withdrawal wells communicating with standpipes 36 and 40. All or a portion of the catalyst may be passed by either one or both of standpipes 36 and 40 to catalyst bed 40 in the lower regenerator section. Heating or cooling of the catalyst in standpipe 36 may be accomplished in zone 38 as desired.

In the lower catalyst regeneration zone comprising bed 34, complete regeneration of the catalyst to provide a residual carbon content less than 0.1 wt% and preferably no more than 0.05 wt% is accomplished with an oxygen containing regeneration gas such as air, air modified with CO2, CO2 modified with oxygen and a combination thereof as required to effect removal of residual carbonaceous material 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 2, 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 coke 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 3 and 4 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 then 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. Catalyst 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, heat dissipation and restrict temperature sequential burning in a plurality of regeneration zones, all of which techniques are less than desirable. It will be recognized 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 realization 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.

Having thus generally described the new and novel concepts of this invention with respect to regenerating catalyst particles to reduce the temperature of the operation and discussed specific examples in support thereof, it is to be understood that no undue restrictions are to be imposed by reasons thereof except as defined by the following claims.

We Claim:

1. In a hydrocarbon conversion process where carbonaceous material deposited on a hydrocarbon conversion catalyst is of a quantity to produce upon combustion thereof temperatures exceeding 760°C (1400°F), the improvement for reducing catalyst regeneration temperatures which comprise,
   - (a) partially regenerating a conversion catalyst comprising high levels of carbonaceous material deposits by contact with a gaseous mixture comprising a relatively large quantity of high temperature steam in admixture with an oxygen containing gas and flue gas combustion products of residual carbon removal,
   - (b) said high temperature steam reacting with said carbonaceous deposits under conditions to form CO and hydrogen which are combusted upon contact with said oxygen containing gas,
   - (c) recovering partially regenerated catalyst from said steam contacting step for transfer to a second stage of catalyst regeneration to remove residual carbon by combustion with oxygen containing gas,
   - (d) removing residual carbon on the partially regenerated catalyst by combustion with oxygen containing gas under temperature conditions restricted below about 787°C (1450°F) to produce high temperature flue gases comprising CO, CO2 and unconsumed oxygen,
   - (e) passing said high temperature flue gases with said gaseous mixture comprising steam to contact with said catalyst partially regenerated as above provided, and
   - (f) recovering a regenerated catalyst comprising less than 0.05 wt% residual carbon at a temperature below about 760°C (1400°F) separately from flue gas products of said two stage regeneration operation.

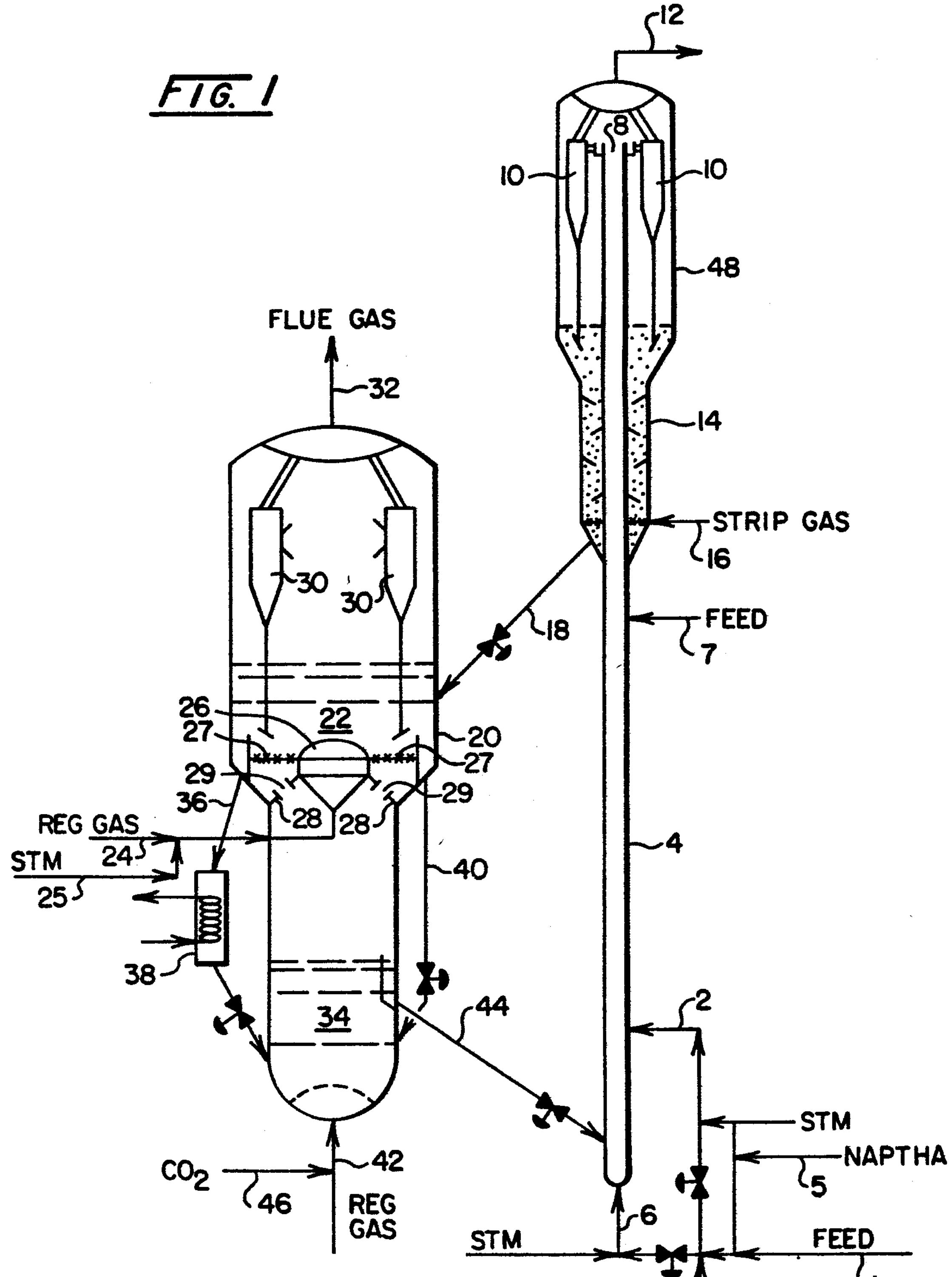
2. The catalyst regeneration operation of Claim 1 wherein each stage of regeneration is accomplished in a dense fluid bed of catalyst positioned one above the other so that flue gas products of said second stage may pass directly into the bottom of the bed of catalyst comprising the first stage of catalyst regeneration.

3. The regeneration operation of Claim 2 wherein the gaseous mixtures of steam and oxygen containing gas are separately introduced to a bottom portion of said catalyst bed comprising said first stage of regeneration.

4. The catalyst regeneration operation of Claim 1 wherein up to about 40 percent of the carbonaceous deposit is removed by steam under endothermic reaction conditions at temperature below 815°C (1500°F) and a residual carbon on the partially regenerated catalyst is removed by oxygen combustion at a temperature of about 746°C (1375°F).

5. The catalyst regeneration operation of Claim 1 wherein the carbonaceous materials are deposits obtained by the catalytic conversion of a residual oil boiling above about 343°C (650°F) and comprising carbo-metallic impurities providing Conradson carbon deposits in excess of 8 wt%.

FIG. 1


12
8
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48
14
STRIP GAS
16
FEED
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FLUE GAS
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REG GAS
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3
H_2O

FIG. 2

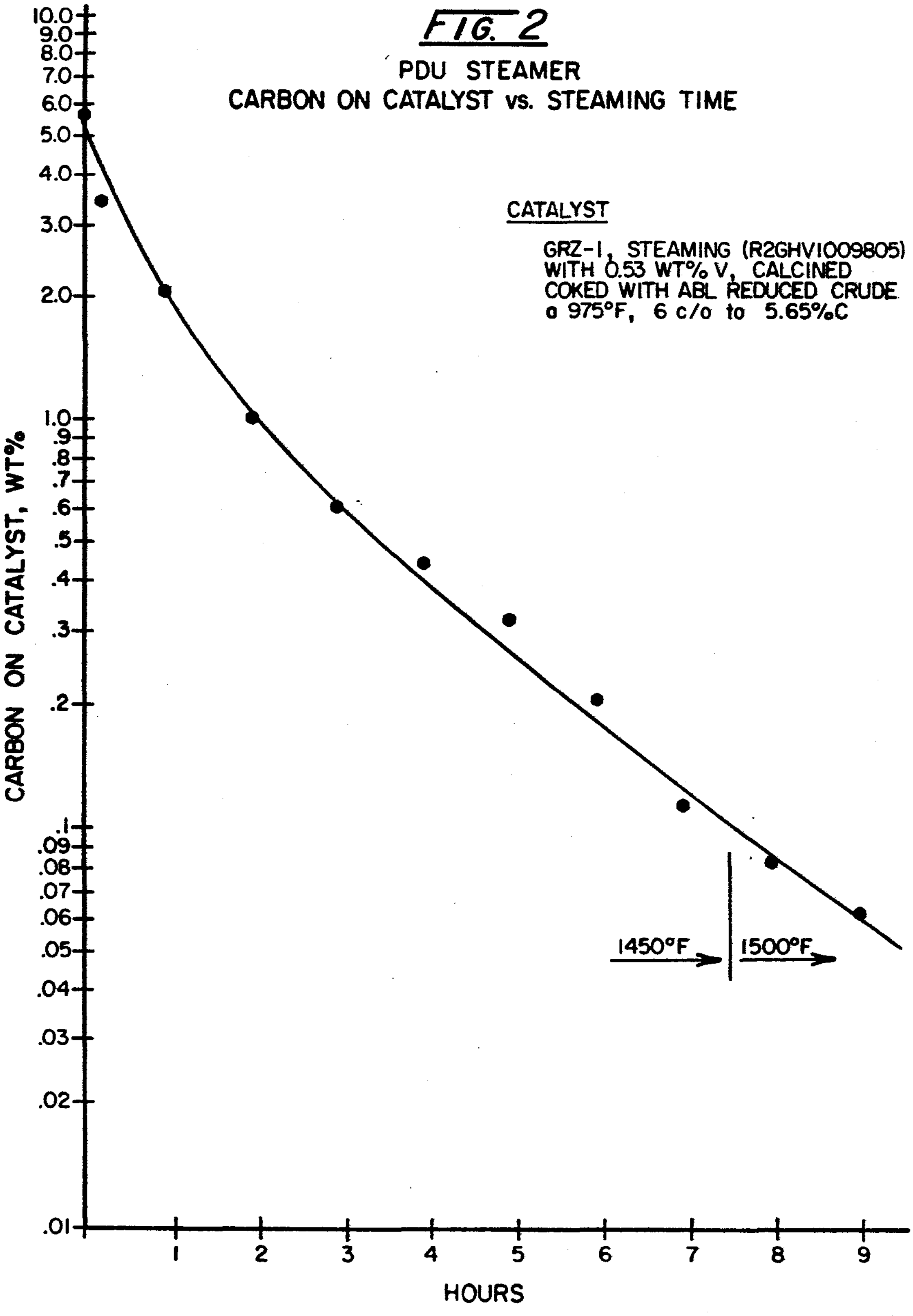

PDU STEAMER
CARBON ON CATALYST vs. STEAMING TIME
CATALYST
GRZ-1, STEAMING (R2GHV1009805)
WITH 0.53 WT% V, CALCINED
COKED WITH ABL REDUCED CRUDE
@ 975°F, 6 c/o to 5.65%C
1450°F
1500°F
CARBON ON CATALYST, WT%
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.09
.08
.07
.06
.05
.04
.03
.02
.01
1
2
3
4
5
6
7
8
9
HOURS

FIG. 3

EFFECT OF STEAM
COKED CATALYST vs. UNCOKED CATALYST
SURFACE AREA vs. TIME

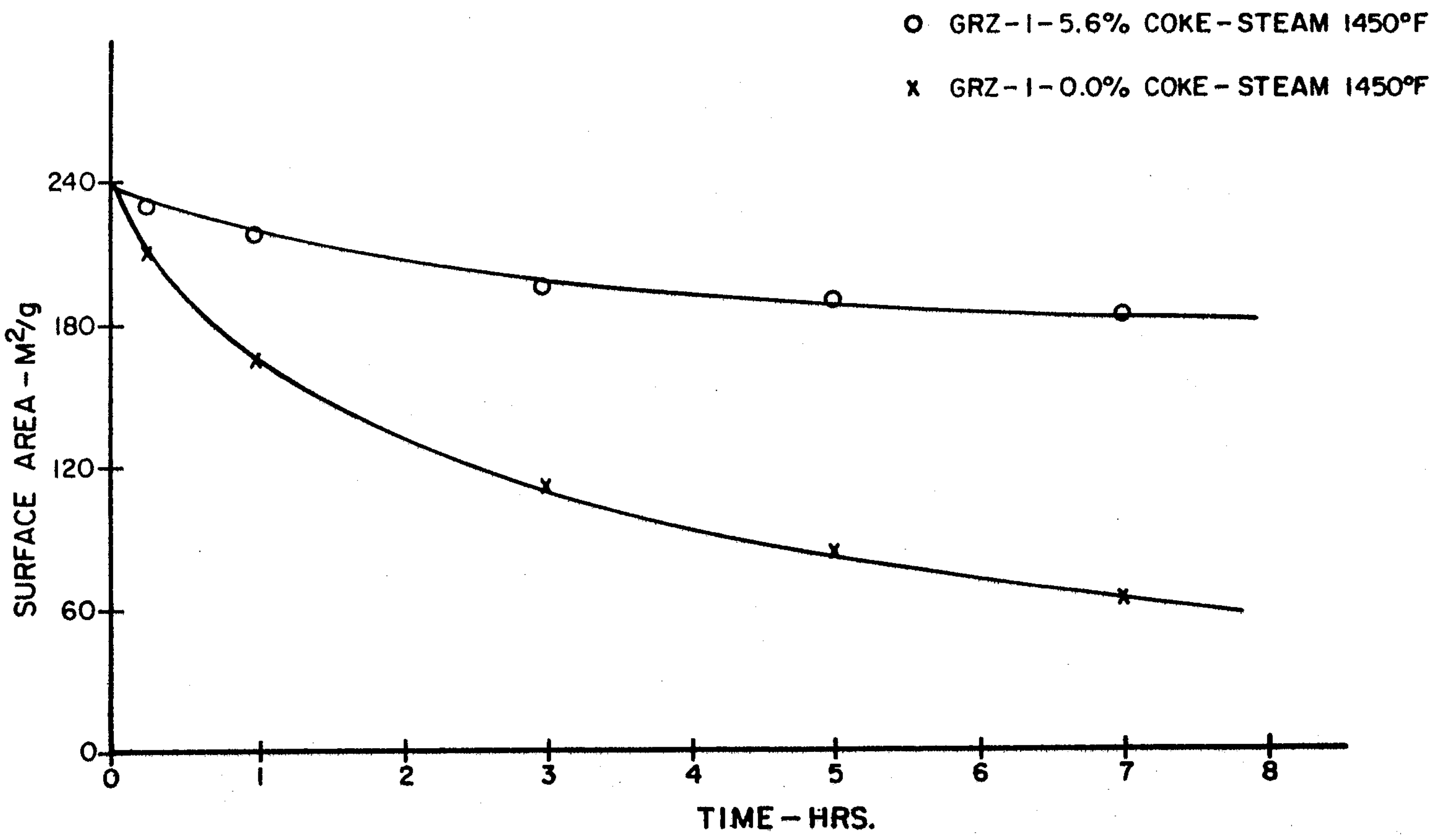
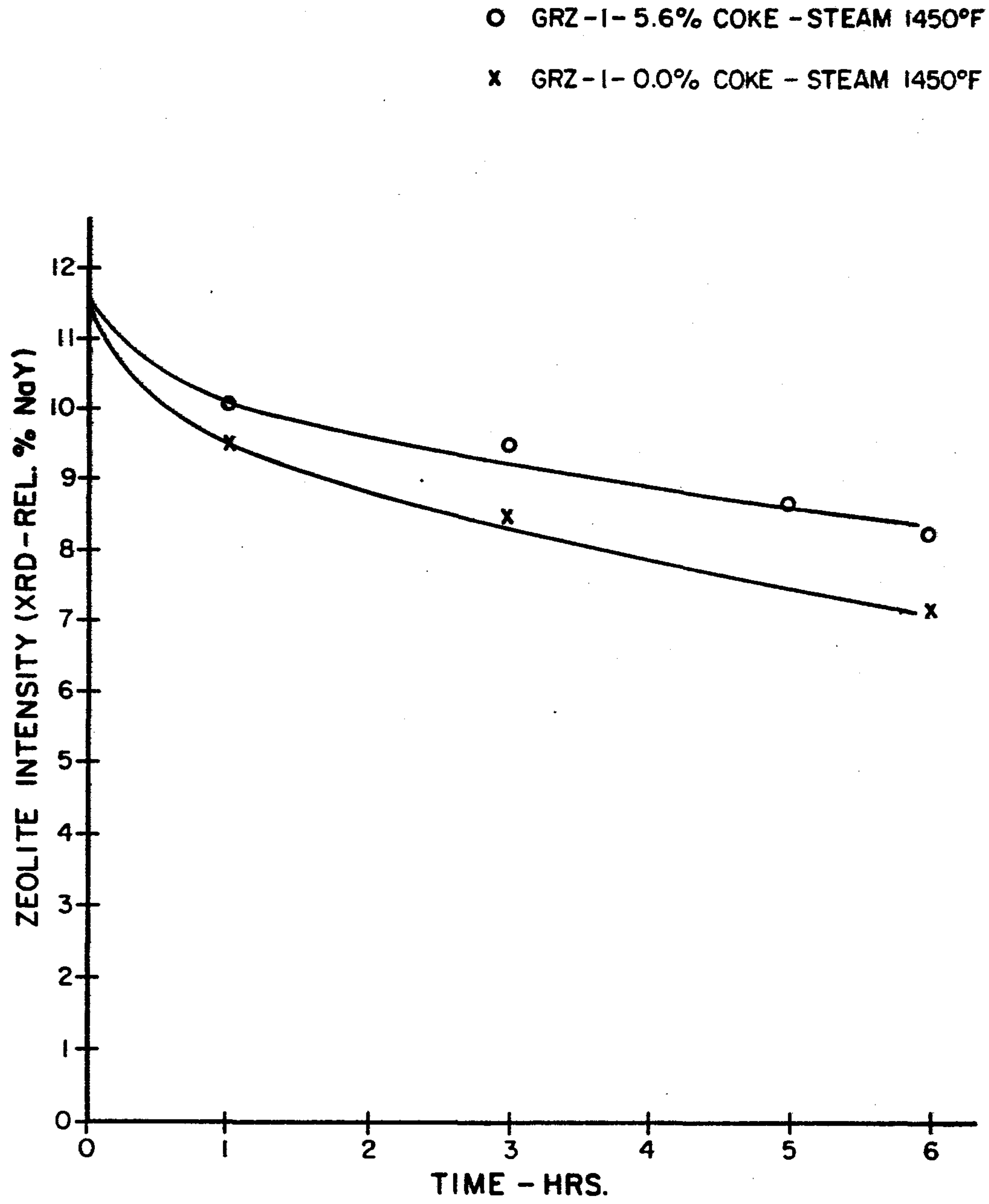


FIG. 4
EFFECT OF STEAM
COKED CATALYST vs. UNCOKED CATALYST
ZEOLITE INTENSITY vs. TIME



European Patent
Office

EUROPEAN SEARCH REPORT

Application number
0092065

EP 83102928.5

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
P,A	US - A - 4 336 160 (ROBERT R. DEAN et al.) * Claims; column 6, line 55 - column 9, line 68 * --	1	C 10 G 11/14 //B 01 J 29/38
P,A	US - A - 4 274 942 (BARTHOLIC et al.) * Claims; column 5, line 9 - column 6, line 2 * --	1	
A	US - A - 4 062 759 (CASTAGNOS, JR. et al.) * Claims; column 1, line 60 - column 3, line 55 * --	1	
A	US - A - 4 056 486 (BUNN, JR. et al.) * Claims; column 1, line 60 - column 3, line 5 * --	1	
A	GB - A - 2 001 545 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) * Claims; page 2, line 15 - page 3, line 74 * --	1	
A	GB - A - 1 569 467 (TEXACO DEVELOPMENT CORPORATION) * Claims; page 1, line 89 - page 3, line 112 * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
C 10 G 11/00
C 10 G 47/00
B 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	21-07-1983	STÖCKLMAYER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document