

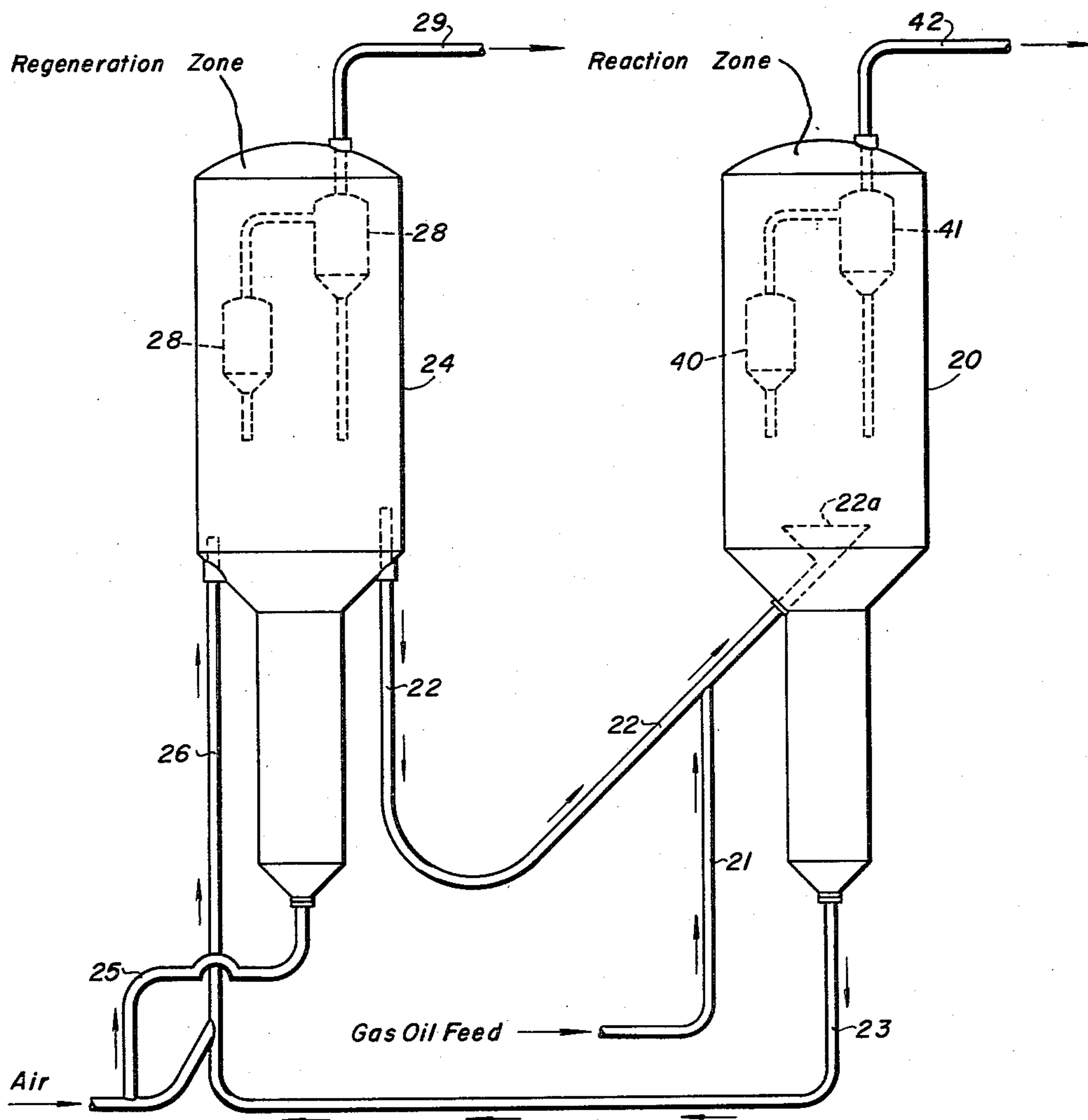
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PROCESS FOR CONTROLLING CATALYTIC CRACKING PROCESS

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PROCESS FOR CONTROLLING CATALYTIC CRACKING PROCESS

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This invention concerns a novel technique for operating a catalytic cracking operation. The invention is of particular application to the catalytic cracking of feed stock containing metals which contaminate the cracking catalyst. In accordance with this invention, a control technique is provided by which the process can be conducted so as to alleviate difficulties caused by catalyst contamination.

One of the principal refining operations in commercial use at this time concerns the catalytic cracking of gas oil fractions of a petroleum oil. Until relatively recently, the gas oil distillate fraction employed as a catalytic cracking feed stock was a fraction boiling in the relatively low boiling range of about 500° to 800°. However, in order to secure greater yields of cracked products and to reduce the portion of the petroleum oil constituting the residual portion higher boiling than gas oil, there has been a great deal of incentive for extending catalytic cracking to higher boiling feed stocks. Toward this end, the end point of the gas oil fraction subjected to catalytic cracking has risen to greater than 900° F. Difficulties have been encountered in attempting to crack gas oils of this character including a substantial portion boiling above about 900° F. It has heretofore been appreciated that one of the difficulties involved in cracking such feed stocks is the presence of metal contaminants in the feed stocks. These metal contaminants include nickel, vanadium and iron compounds which are particularly deleterious. High boiling fractions for catalytic cracking have also been produced by deasphalting, and deasphalted oils thus produced are also very high in such metal contaminants.

The metal compounds are inherently and unavoidably carried over into the high boiling gas oils when including products boiling above about 900° F., because of entrainment and volatility of metal compounds in high temperature fractionators and because of the solubility of metal compounds in deasphalted oil produced from deasphalting higher boiling fractions. Heavy gas oils derived from typical crude oils will contain about 10 to 20 pounds of metal contaminants per 1000 barrels. When segregating heavier boiling gas oils or when deriving such oils from particular crude oils, contaminant concentrations as high as 50 pounds per 1000 barrels may be encountered. The presence of these metal contaminants in the catalytic cracking zone apparently causes poisoning of the catalyst, adversely affecting the conversions obtained, product distribution, and catalyst life.

While attempts are being made with some degree of success to reduce the concentration of metal contaminants in a catalytic cracking feed stock, this objective has not yet been completely met. As a consequence, the need exists for a technique or process by which heavy gas oils containing more than about 3 to 4 pounds per 1000 barrels of metal contaminants can be satisfactorily catalytically cracked. The present invention is concerned with a technique for overcoming plant upsets caused by

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contamination of the catalyst. In providing this objective, the present invention makes it possible to process heavy gas oils having somewhat higher concentrations of metal contaminants while alleviating the difficulties normally encountered. In this connection, the present process eliminates the economic waste ordinarily occurring in a catalytic cracking plant which encounters operating difficulties due to metal contamination of the cracking catalyst.

In order to fully illustrate the nature of the present invention, the invention will be described with specific reference to a fluidized catalytic cracking process. The general nature and a specific flow plan for such a cracking process is illustrated in the accompanying drawing.

Referring to the drawing, a hydrocarbon fraction boiling in the gas oil boiling range is introduced into a fluidized solids catalytic reactor 20 by means of line 21. This stream is mixed with fluidized solids catalyst which is introduced into zone 20 by means of line 22 through a distributing head 22a. Temperature and pressure conditions as well as gas velocities and catalyst holdup are adjusted in zone 20 to secure the desired conversion of the relatively high boiling hydrocarbon constituents to lower boiling constituents. Spent catalyst is removed from zone 20 by means of line 23 and passed into a fluidized solids regeneration zone 24. Air or other oxygen containing gas is introduced into zone 24 by means of lines 25 and 26. Temperature and pressure conditions in regeneration zone 24 and catalyst holdup are adjusted to secure the desired burning of the catalyst and to regenerate the same. Regenerated catalyst is removed from zone 24 by means of line 22 and recycled to reaction zone 20. Combustion gases are passed through suitable cyclones 28 positioned in the top of or above regeneration zone 24 and are removed overhead by means of line 29. Cracked products are removed overhead from reaction zone 20 through cyclones 40 and 41, and are introduced into a fractionation zone, not shown, through line 42.

The fluidized solids technique for cracking hydrocarbons comprises a reaction zone and a regeneration zone, employed in conjunction with a fractionation zone. The reactor and the catalyst regenerator are or may be arranged at approximately an even level. The operation of the reaction zone and the regeneration zone is conventional, which preferably is as follows:

An overflow pan is provided in the regeneration zone at the desired catalyst level. The catalyst overflows into a withdrawal line which preferably has the form of a U-shaped seal leg connecting the regeneration zone with the reaction zone. The feed stream introduced is usually preheated to a temperature in the range from about 500° to 650° F. in exchangers in heat exchange with regenerator flue gases which are removed overhead from the regeneration zone, or with cracked products. The heated feed stream is withdrawn from the exchangers and introduced into the reactor. The seal leg is usually sufficiently below the point of feed oil injection to prevent oil vapors from backing into the regenerator in case of normal surges. Since there is no restriction in the overflow line from the regenerator, satisfactory catalyst flow will occur as long as the catalyst level in the reactor is slightly below the catalyst level in the regenerator when the vessels are maintained at about the same pressure. Spent catalyst from the reactor flows through a second U-shaped seal leg from the bottom of the reactor into the bottom of the regenerator. The rate of catalyst flow is controlled by injecting some of the air into the catalyst transfer line to the regenerator.

The pressure in the regenerator may be controlled at the desired level by a throttle valve in the overhead line from the regenerator. Thus, the pressure in the regen-

erator may be controlled at any desired level by a throttle valve which may be operated, if desired, by a differential pressure controller. If the pressure differential between the two vessels is maintained at a minimum, the seal legs will prevent gases from passing from one vessel into the other in the event that the catalyst flow in the legs should cease.

The reactor and the regenerator may be designed for high velocity operation involving linear superficial gas velocities of from about 2.5 to 4 feet per second. However, the superficial velocity of the upflowing gases may vary from about 1-5 and higher. Catalyst losses are minimized and substantially prevented in the reactor by the use of multiple stages of cyclone separators. The regeneration zone is provided with cyclone separators. These cyclone separators usually include 2 to 3 or more stages.

Distributing grids may be employed in the reaction and regeneration zones. Operating temperatures and pressures may vary appreciably depending upon the feed stocks being processed and upon the products desired. Operating temperatures are, for example, in the range from about 800° to 1000° F., preferably about 850° to 950° F. in the reaction zone. Elevated pressures may be employed, but in general, pressures below 100 pounds per square inch gauge are utilized. Pressures generally in the range from 1 to 30 pounds per square inch gauge are preferred. A catalyst hold-up corresponding to a space velocity of 1 to 20 weights per hour of feed per weight of catalyst is utilized. A preferred ratio is 2 to 4. Catalyst to oil ratios of about 3 to 10, preferably about 6 to 8 by weight are used.

The catalytic material used in the fluidized catalyst cracking operation are conventional cracking catalysts. These catalysts are oxides of metals of groups II, III, IV and V of the periodic table. A preferred catalyst comprises silica-alumina wherein the weight percent of the alumina is in the range from about 5 to 20%. Another preferred catalyst comprises silica-magnesium where the weight percent of the magnesia is about 5% to 20%. These catalysts may also contain a third constituent, as for example, ThO₂, WO₃, MoO₃, BeO, Bi₂O₃, CdO, UO₃, B₂O₃, SnO₂, Fe₂O₃, V₂O₅, MnO, Cr₂O₃, CaO, TiO, MgO and Ce₂O₃ present in the concentration from 0.05% to 0.5%.

The size of the catalyst particles is usually below about 200 microns. Usually at least 50% of the catalyst has a micron size in the range from about 20-80. Under these conditions with the superficial velocities as given, a fluidized bed is maintained where in the lower section of the reactor, a dense catalyst phase exists while in the upper area of the reactor a disperse phase exists.

The process of this invention is the outcome of basic research work directed to the general problem of catalyst contamination in a catalytic cracking process of the nature described. In studying this problem, a variety of feed stocks were subjected to catalytic cracking in pilot plant facilities so as to determine the full consequences of metal contamination of the feed stock. All operating variables were meticulously controlled and determined. This entailed, for example, complete analysis of the cracking catalyst so as to identify and trace any significant correlations among all of the process parameters involved in the catalytic cracking operation.

This exhaustive study unearthed certain unexpected and surprising facts relating to catalytic cracking with metal contaminated cracking catalysts. For one thing, it was discovered that of the metal contaminants normally present in a catalytic cracking feed stock, nickel is particularly effective in causing abnormal yields of hydrogen. It was established that the amount of hydrogen production varies logarithmically with the nickel contamination of the cracking catalyst. Identification of this fact explains the mechanism by which difficulties are frequently

encountered when catalytic cracking feed stocks contain metal contaminants.

Thus one of the problems that frequently is encountered in such a case is that normal operation of the catalytic cracking process is upset by production of excessive hydrogen. From the relationship identified, it is apparent that since the hydrogen produced varies logarithmically with the metal contamination of the catalyst, a snowballing effect can result in more and more production of hydrogen. This occurs since formation of excess hydrogen beyond normal proportions is inherently accompanied by additional carbon formation which increases the carbon burning requirement and, in turn, results in increased carbon on regenerated catalyst as will be described subsequently. Increased carbon on regenerated catalyst results in formation of more hydrogen and thus the situation becomes progressively worse. Such increased hydrogen production causes a number of operating problems. Excess hydrogen production can increase the velocity in the catalytic cracking reactor to such an extent that catalyst entrainment becomes excessive and limits the operation. Again the excess hydrogen produced may cause flooding of the product fractionator or exceed the capacity of gas handling facilities. In other cases, the gravity of light gases from the catalytic cracking unit may change sufficiently due to excess hydrogen that centrifugal gas compressors will fail to operate.

It is one of the specific objects of this invention to minimize the problem of excess hydrogen production in catalytic cracking and to provide a means for most economically preventing the difficulties referred to.

It is apparent from what has been said that the problems due to metal contamination of cracking catalyst could be eliminated by replacing the contaminated catalyst with fresh catalyst or by reducing the concentration of metal contaminants on the catalyst. However, there is no practical or economic method of accomplishing these solutions. Thus in a typical commercial catalytic cracking plant the catalyst inventory in the cracking operation may constitute about 500 tons. It is clearly impossible to discard this quantity of catalyst or even to replace enough of it to drop materially the average weight of metal contaminants present in less than several days operations at normal catalyst replacement rates. Again there is no means known for removing metal contaminants from the cracking catalyst after these contaminants are deposited on the catalyst. The present invention serves to solve this dilemma by establishing a control process for maintaining operation with contaminated catalyst while avoiding the serious operational upsets referred to.

In the basic study of the catalytic cracking referred to, one of the correlations which was established showed that the amount of hydrogen production with the same feed stock at the same conversion level and with all other variables maintained constant was also a function of the carbon content of the regenerated catalyst. Under these conditions, it was found that the amount of hydrogen produced during catalytic cracking at constant nickel concentration on the catalyst varied in proportion to the amount of carbon on the catalyst. As a result of this discovery a fundamental relationship exists expressing the occurrence of hydrogen production as a function of both nickel contamination of the catalyst and the carbon content of the catalyst. This relationship can be mathematically expressed by the following formula:

$$\log_{10} H = 19.4(Ni) + 0.793 \log_{10} C + \text{constant}$$

where H is the hydrogen index, Ni is the weight percent of nickel on the catalyst, and C is the weight percent of carbon on regenerated catalyst. The hydrogen index referred to is an arbitrary index used to express the relative hydrogen production. Thus, the hydrogen index can be defined at the ratio of hydrogen production with

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a contaminated catalyst to the hydrogen production from an uncontaminated catalyst at the same conversion level. The constant in the equation identified is a value which is set by the particular catalytic cracking apparatus employed, the feed stock processed and the catalytic cracking conversion.

From the fundamental relationship expressed by the equation set forth, it is unexpectedly apparent that the amount of hydrogen production in a catalytic cracking process is a function of both the carbon content and the nickel content of the cracking catalyst. It is this discovery and the unexpected relationship between hydrogen production and nickel and carbon content of the catalyst which provides the basis for the process of this invention.

In order to appreciate the control process embodying this invention, a graph can be drawn plotting hydrogen production logarithmically against the nickel content of a particular cracking catalyst. At any given value of carbon on the catalyst, a substantially linear plot of data is attainable. By drawing similar plots for different proportions of carbon on the catalyst, a family of curves is obtained. In this family it is apparent that for a given amount of hydrogen production with a catalyst having a particular nickel content a substantially decreased hydrogen production is obtainable by reducing the carbon content of the catalyst. In other words, it becomes possible to correct operating conditions in a catalytic cracking operation due to metal contaminated catalyst by adjusting these conditions so as to reduce the carbon content of the catalyst. Since, as pointed out, it is practically impossible to change the amount of metal contamination, it becomes practical to achieve precisely the same result by changing the carbon content of the catalyst which can be practically accomplished.

In accordance with this invention, therefore, a catalytic cracking control process is provided in which variation in the carbon content of regenerated catalyst is deliberately employed for the first time. In order to appreciate the practical significance of this control process, let it be assumed that a commercial cracking plant is operating at a capacity of 40,000 barrels per day processing a feed stock boiling in the range of about 500° to 1000° F. and containing about 0.15 pound of nickel per 1000 barrels. Successful operation of this plant can be maintained normally making about 40-60 s. c. f. of hydrogen per barrel of feed in operating at a carbon content on regenerated catalyst of about 0.8 wt. percent. In this connection, it must be appreciated that a commercial catalytic cracking plant is ordinarily controlled so as to maintain a substantially constant carbon on catalyst value. The precise magnitude of carbon content on the catalyst may vary from plant to plant within the range of about 0.3 wt. percent to 1.0 wt. percent but at any one plant operation has heretofore been carried out by maintaining a particular fixed carbon content at all times. This is carried out by frequent catalyst analysis and also by controlling the amount of oxygen in the flue gas. Thus operation will be carried out with reference to the flue gas analysis so that a particular and constant value of oxygen is maintained chosen from the range of about 0.2% to 1%. Operating in this manner, the typical plant referred to in this example will continue to operate well under stable conditions at 0.8 wt. percent carbon on regenerated catalyst until the metal contamination of the catalyst builds up to a value of about 0.014 wt. percent. At this time excessive hydrogen production will begin to occur and plant operating difficulties will be encountered. As indicated formerly, a variety of operating difficulties due to the excessive hydrogen production will result creating the necessity of cutting off cracking feed to the cracking operation so as to overcome the excessive amounts of hydrogen produced. Heretofore a cutback in the feed rate has been the only practical way to continue operation when excessive hydrogen production is encountered.

In accordance with this invention, however, when ex-

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cessive hydrogen production is encountered, this is overcome by reducing the carbon content of the catalyst. As pointed out, it has never been appreciated formerly that control of the carbon content of the regenerated catalyst can be a critical control variable. The process of this invention is, therefore, uniquely characterized by this feature. Thus, as pointed out formerly, reducing the carbon content of the catalyst will serve to completely offset increased hydrogen production caused by the unavoidable nickel contamination of the catalyst.

In order to lower the carbon content of the regenerated catalyst a variety of operating expedients may be employed. Whatever is done to successfully reduce the carbon content is indicated by and can be followed by the increase in oxygen content of the flue gas. It can, therefore, be said that the operating conditions are varied so as to increase the proportion of oxygen present in the flue gas of the catalytic cracking regenerator. The particular steps by which this is accomplished are a matter of choice on the part of the operator, chosen with regard to the particular plant facilities and limitations. Thus, for example, carbon on the catalyst can be reduced by employing more air in the regenerator. Again the hold-up of the catalyst in the regenerator can be increased resulting in more carbon being burned from the catalyst. Again the catalyst inventory in the catalytic cracking reaction zone can be decreased so that conversion is dropped, having the ultimate effect of reducing the carbon content of the catalyst. These and other operating expedients such as reducing reaction temperature can be used in order to reduce the amount of carbon on the catalyst, in order to increase the amount of oxygen in the flue gas of the regenerator, and thus to provide the ultimate function of overcoming the effects of nickel concentration of the catalyst.

By deliberately varying the catalytic cracking conditions so as to decrease the carbon content of the regenerated catalyst, it is thus possible to avoid the basic problem of excess hydrogen production due to nickel contamination of the catalyst. By this process serious plant upsets are avoided and satisfactory maintenance can be continued. It is apparent, therefore, that this process is of great practical and economic value.

The equation set forth formerly; namely,

$$\log_{10} H = 19.4(Ni) + 0.798 \log_{10} C + \text{constant}$$

can be directly used in using the control process of this invention. For example, for a unit operating under conditions of 50% conversion to 430° F. and lighter products, 0.005 weight percent of nickel on catalyst, 0.8 weight percent carbon on regenerated catalyst, and 40 s. c. f./bbl. of hydrogen production, the hydrogen index for the unit under consideration as calculated from the above equation is 5.55. The constant for the equation, determined experimentally, is 0.724. From experience on this unit, it was found that hydrogen production becomes a limiting factor at a rate of 60 s. c. f./bbl. corresponding to a hydrogen index of 8.3. Assume that the nickel content of the catalyst starts to increase as a result of increased nickel content of the feed stock. The weight percent nickel on the catalyst at which the unit will be limited by hydrogen production when the carbon on regenerated catalyst is 0.8 weight percent. From the above equation:

$$\begin{aligned} \log_{10} 8.3 &= 19.4(Ni) + 0.798 \log_{10} 0.8 + 0.724 \\ 0.919 &= 19.4(Ni) + (0.798)(-0.097) + 0.724 \\ Ni &= \frac{0.919 - 0.724 + 0.077}{19.4} = 0.014 \text{ weight percent nickel} \end{aligned}$$

Thus as the nickel increases from 0.005 to 0.014 weight percent on catalyst at constant 0.8 weight percent carbon on regenerated catalyst, the hydrogen production will increase from 40 s. c. f./bbl. of feed to 60 s. c. f./bbl. of feed. At this point if the nickel continues to increase, the carbon on regenerated catalyst must be decreased to maintain the hydrogen at 60 s. c. f./bbl. of feed. From

the aforementioned equation, it is seen that the nickel-carbon on regenerated catalyst relationship above 0.014 weight percent nickel must be as follows:

Ni (weight percent on catalyst)	C (Weight percent on regenerated catalyst)
0.014	0.80
0.020	0.57
0.025	0.44
0.030	0.33

In summary the sequence of operations would be as follows:

Nickel, weight percent on catalyst	0.005	0.014	0.020	0.025	0.30
Carbon, weight percent on regenerated catalyst	0.8	0.8	0.57	0.44	0.33
H ₂ , s. c. f./bbl. of feed	40	60	60	60	60

It will be seen from this data that the problem of excess hydrogen production is completely met by lowering the carbon content of the regenerated catalyst from a value of 0.8 weight percent to 0.33 weight percent. This is achieved even though the nickel content of the catalyst continued to increase during the operational change and is achieved while preventing the snowballing effect of excess hydrogen production.

What is claimed is:

1. A process for overcoming the deleterious effect of nickel catalyst contamination in the fluidized catalytic cracking of a nickel-contaminated hydrocarbon feed stock containing a substantial portion of components boiling above 900° F. which comprises conducting said fluidized catalytic cracking during a first period of operation while maintaining a substantially constant amount, within the range of about 0.3 to 1 weight percent, of carbon on the catalyst to thereby provide for the production of not more than a predetermined maximum amount of hydrogen and thereafter reducing the amount of carbon on the catalyst to successively lower levels as the amount of nickel deposited on the catalyst by the feed stock is increased, to thereby prevent excess hydrogen production due to nickel contamination of the said catalyst.

2. The process defined by claim 1 in which the carbon content of the catalyst is controlled in accordance with the equation:

$$\log_{10} H = 19.4(Ni) + 0.798 \log_{10} C + \text{constant}$$

where H is the hydrogen index, Ni is the weight percent of nickel on the catalyst, and C is the weight percent of carbon on regenerated catalyst.

3. In the fluidized catalytic cracking of a nickel-contaminated petroleum hydrocarbon feed stock containing a substantial portion of components boiling below 900° F. wherein said feed stock is contacted with a regenerated cracking catalyst containing an initially constant amount of carbon within the range of about 0.3 to 1 weight percent to provide for a predetermined reaction equilibrium and for the production of not more than a predetermined amount of hydrogen, the improved method of operation which comprises progressively reducing the carbon-on-catalyst value as the nickel content of said catalyst increases by an amount sufficient to permit the production of not more than said predetermined maximum amount of hydrogen.

4. The process of claim 3 in which the said carbon-on-catalyst value is reduced by supplying additional air to the regenerator.

5. The process of claim 3 in which the said carbon-on-catalyst value is reduced by increasing the hold-up time of the catalyst in the regenerator.

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