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(54) CATALYST REGENERATION IN CATALYTIC CRACKING OF HYDROCARBONS

(71) We, MOBIL OIL CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with the catalytic cracking of hydrocarbons in the absence of added hydrogen. It particularly refers to an improved method for controlling the combustion of carbon monoxide in the regenerator of a catalytic cracking apparatus by the addition of minute amounts of an oxidation catalyst such as platinum to the cracking catalyst. In one embodiment a side-stream of cracking catalyst is contacted with a solution of metal compound, thereby controlling the combustion of carbon monoxide in the regenerator of the catalytic cracking apparatus.

One typical example of industrially practised moving bed hydrocarbon catalytic cracking is known as thermofor catalytic cracking (TCC). In this process the catalyst is in the shape of beads or pellets having an average particle size of about 1/64 to 1.4 inch, preferably about 1/8 inch. Active, hot catalyst beads progress downwardly cocurrent with a hydrocarbon charge stock through a cracking reaction zone. In this zone hydrocarbon feed is endothermically cracked to lower molecular weight hydrocarbons while coke is deposited on the catalyst. At the lower end of the reaction zone the hydrocarbon products are separated from the coked catalyst, and recovered. The coked catalyst is then passed downwardly to a regeneration zone, into which air is fed such that part of the air passes upwardly countercurrent to the coked catalyst and part of the air passed downwardly cocurrent with partially regenerated catalyst. Two flue gases comprising carbon oxides are produced. Regenerated catalyst is disengaged from the flue gas and is then lifted, pneumatically or mechanically, back up to the top of the reaction zone.

Fluid catalytic cracking of hydrocarbon oils is a major refinery process. The installed plants are usually designed to process from about 5,000 to 135,000 bbls/day of fresh feed. Most of the plants are quite large, and are capable of handling at least 40,000 bbls/day. The catalyst section of the plant consists of a cracking section where a heavy hydrocarbon feed is cracked in contact with fluidized cracking catalyst and a regenerator section where fluidized catalyst coked in the cracking operation is regenerated by burning with air. All of the plants utilize a large circulating inventory of cracking catalyst which is continuously circulating between the cracking and regenerator sections. The size of this circulating inventory in most existing plants is within the range of 50 to 600 tons.

Although the design and construction of individual plants vary, the essential elements, particularly the flow of catalyst, are illustrated by Figures 1 and 2 of the accompanying drawings which show a conventional catalyst section of a fluid catalytic cracking plant.

Figure 1 and the sectional element thereof shown in Figure 2 are representative of the catalyst section of a commercial fluid catalytic cracking unit. Referring now to Figure 1, a hydrocarbon feed 2 such as a gas oil boiling from 600°F up to 1000°F is passed after preheating thereof to the bottom portion of riser 4 for admixture with hot regenerated catalyst introduced by standpipe 6 provided with flow control valve 8. A suspension of catalyst in hydrocarbon vapors at a temperature of at least 950°F but more usually at least 1000°F is thus formed in the lower portion of riser 4 for flow upwardly therethrough under hydrocarbon conversion conditions. The suspension initially formed in the riser may be retained during flow through the riser for a hydrocarbon residence time in the range of 1 to 10 seconds.

The hydrocarbon vapor-catalyst suspension formed in the riser reactor is passed upwardly through riser 4 under hydrocarbon conversion, conditions of at least 900°F and more usually at least 1000°F before discharge into one or more cyclonic separation zones about the riser discharge, represented by cyclone separator 14. There may be a plurality of such cyclone separator combinations comprising first and second cyclonic separation means attached to or spaced apart from the riser discharge for separating catalyst particles from hydrocarbon vapors. Separated hydrocarbon vapors are passed from separator 14 to a plenum chamber 16 for withdrawal therefrom by conduit 18. These hydrocarbon vapors together with gasiform material separated by stripping gas as defined below are passed by conduit 18 to fractionation equipment not shown. Catalyst separated from hydrocarbon vapors in the cyclonic separation means is passed by diplegs represented by dipleg 20 to a dense fluid bed of separated catalyst 22 retained about an upper portion of riser conversion zone 4. Catalyst bed 22 is maintained as a downwardly moving fluid bed of catalyst countercurrent to rising gasiform material. The catalyst passes downwardly through a stripping zone 24 immediately therebelow and counter-current to rising stripping gas introduced to a lower portion thereof by conduit 26. Baffles 28 are provided in the stripping zone to improve the stripping operation.

The catalyst is maintained in stripping zone 24 for a period of time sufficient to effect a high temperature desorption of feed deposited compounds which are then carried overhead by the stripping gas. The stripping gas with desorbed hydrocarbons pass through one or more cyclonic separating means 32 wherein entrained catalyst fines are separated and returned to the catalyst bed 22 by dipleg 34. The hydrocarbon conversion zone comprising riser 4 may terminate in an upper enlarged portion of the catalyst collecting vessel with the commonly known bird cage discharge device or an open end "T" connection may be fastened to the riser discharge which is not directly connected to the cyclonic catalyst separation means. The cyclonic separation means may be spaced apart from the riser discharge so that an initial catalyst separation is effected by a change in velocity and direction of the discharged suspension so that vapors less encumbered with catalyst fines may then pass through one or more cyclonic separation means before passing to a product separation step. In any of these arrangements, gasiform materials comprising stripping gas hydrocarbon vapors and desorbed sulfur compounds are passed from the cyclonic separation means represented by separator 32 to a plenum chamber 16 for removal with hydrocarbon products of the cracking operation by conduit 18. Gasiform material comprising hydrocarbon vapors is passed by conduit 18 to a product fractionation step not shown. Hot stripped catalyst at an elevated temperature is withdrawn from a lower portion of the stripping zone by conduit 36 for transfer to a fluid bed of catalyst being regenerated in a catalyst regeneration zone. Flow control valve 38 is provided in coked catalyst conduit 36.

This type of catalyst regeneration operation is referred to as a swirl type of catalyst regeneration due to the fact that the catalyst bed tends to rotate or circumferentially circulate about the vessel's vertical axis and this motion is promoted by the tangential spent catalyst inlet to the circulating catalyst bed. Thus, the tangentially introduced catalyst at an elevated temperature is further mixed with hot regenerated catalyst or catalyst undergoing regeneration at an elevated temperature and is caused to move in a circular or swirl pattern about the regenerator's vertical axis as it also moves generally downward to a catalyst withdrawal funnel 40 (sometimes called the "bathtub") adjacent the regeneration gas distributor grid. In this catalyst regeneration environment, it has been found that the regeneration gases comprising flue gas products of carbonaceous material combustion tend to move generally vertically upwardly through the generally horizontally moving circulating catalyst to cyclone separators positioned above the bed of catalyst in any given vertical segment. As shown by Figure 2, the catalyst tangentially introduced to the regenerator by conduit 36 causes the catalyst to circulate in a clockwise direction in this specific embodiment. As the bed of catalyst continues its circular motion some catalyst particles move from an upper portion of the mass of catalyst particles suspended in regeneration gas downwardly therethrough to a catalyst withdrawal funnel 40 in a segment of the vessel adjacent to the catalyst inlet segment. In the regeneration zone 42 housing a mass of the circulating suspended catalyst particles 44 in upflowing oxygen-containing regeneration gas introduced to the lower portion thereof by conduit distributor means 46, the density of the mass of suspended catalyst particles may be varied by the volume of regeneration gas used in any given segment or segments of the distributor grid. Generally speaking, the circulating suspended mass of catalyst particles 44 undergoing regeneration with oxygen-containing gas to remove carbonaceous deposits by burning will be retained as a suspended mass of swirling catalyst particles varying in density in the direction of catalyst flow and a much less dense phase of suspended catalyst particles 48 will exist thereabove in an upper portion of the regeneration zone. Under carefully selected relatively low regeneration gas velocity conditions, a rather distinct line of demarcation may be made to exist between a dense fluid bed of suspended catalyst particles and a more dispersed suspended phase (dilute phase) of catalyst thereabove. However, as the regeneration gas velocity conditions are increased there is less of a demarcation line and the suspended catalyst passes through regions of catalyst particle density generally less than 30 lbs. per cu. ft. A lower catalyst bed density of at least 20 lb/cu. ft. is preferred.

A segmented regeneration gas distributor grid 50 positioned in the lower cross-sectional area of the regeneration vessel 42 is provided as shown in Figure 1 and is adapted to control the flow of regeneration gas passed to any given vertical segment of the catalyst bed thereabove. In this arrangement, it has been found that even with the generally horizontally circulating mass of catalyst, the flow of regeneration gas is generally vertically upwardly through the mass of catalyst particles so that regeneration gas introduced to the catalyst bed by any given grid segment or portion thereof may be controlled by grid openings made available and the air flow rate thereto. Thus, oxygen-containing combustion gases after contact with catalyst in the regeneration zone are separated from entrained catalyst particles by the cyclonic means provided and vertically spaced thereabove. The cyclone combinations diagrammatically represented in Figure 1 are intended to correspond to that represented in Figure 2. Catalyst particles separated from the flue gases passing through the cyclones are returned to the mass of catalyst therebelow by the plurality of provided catalyst diplegs.

As mentioned above, regenerated catalyst withdrawn by funnel 40 is conveyed by standpipe 6 to the hydrocarbon conversion riser 4.

The regenerator system shown in Figures 1 and 2 is usually designed for producing a flue gas that contains a substantial concentration of carbon monoxide along with carbon dioxide. In fact, a typical CO_2/CO ratio is about 1.2.

As noted above, there has recently been a marked increase in the desire to reduce carbon monoxide emissions from the regenerator of a reflexive non-hydrogenative catalytic cracking process. Prior proposed solutions, of increasing the temperature of the regenerator sufficient to thermally burn CO, or of incorporating chromium or iron with the cracking catalyst to support catalytic CO combustion, have not accomplished a sufficient reduction in CO emissions or, when this reduction has approached sufficiency, it has been at the expense of a great detriment to the operation and product distribution of the cracking reaction side of this process. In addition to the fact that increased production of coke on the cracking side throws this entire reflexive system into heat imbalance, the increased production of light gas unduly strains the capacity of the compressors and the entire gas plant, that is the series of separation operation in which the $\underline{C4}$ gasiform part of the product is resolved into its component parts.

It is therefore an important object of this invention to provide a novel means of reducing carbon monoxide emissions from a reflexive, non-hydrogenative catalytic cracking process.

It is another object of this invention to provide a novel catalyst for such a process.

It is another object of this invention to provide an improved process for the fluid catalytic cracking of gas oils in the absence of added hydrogen.

According to the present invention there is provided a cyclic, regenerative, catalytic cracking process of the known kind, in which catalyst, having contacted feed in a reactor under cracking conditions, in the absence of added hydrogen, traverses an external circuit which includes a regenerator and which returns the catalyst to the reactor in regenerated form, the moving mass of catalyst containing a concentration of a platinum group metal, or of rhenium, which is sufficient to catalyse oxidation of carbon monoxide in the regenerator but insufficient to act as a poison under said cracking conditions, (i.e. to substantially increase coke and hydrogen production, based on feed) under said cracking conditions, characterized by the fact that the platinum group metal or rhenium is applied to the catalyst while (but not before) the catalyst is traversing said circuit.

It will be clear from Figure 1 that the term "circulating inventory of catalyst" referred to herein includes the catalyst in riser 4, in the dense bed 22, in the dense bed in stripper 24, and in the dense bed in the regenerator 44 as well as the catalyst material in lines 36 and 6 and the catalyst material suspended in the dilute phase and cyclones in the reactor section and the regenerator section. This circulating inventory is everywhere very hot, substantially above 600°F, since the regenerator operates at a temperature higher than 1000°F and the reactor at higher than 800°F.

In actual operation, because the catalytic activity of the circulating inventory of catalyst tends to decrease with age, fresh makeup catalyst usually amounting to one to two percent of the circulating inventory is added per day to maintain optimal catalyst activity, with daily withdrawal plus losses of about like amount of aged circulating inventory. This catalyst makeup is usually added via a hopper and conduit (not shown) into the regenerator.

The platinum group metal may be a component of all catalyst particles or only of some of the catalyst particles. In terms of its concentration in the entire system, it must be present in a large enough proportion to be able to effect the reaction of carbon monoxide with oxygen to carbon dioxide, provided the conditions in the regenerator are otherwise sufficient to support this combustion; e.g., sufficiently high temperature and sufficient air. Yet it must not be present in a proportion so large that it substantially adversely affects the operation of the cracking side of the process. This latter, upper limit on platinum group metal content is to some extent a reflection of the design capacity of the cracking system including auxiliaries and downstream product resolution facilities compared to actual operating throughput. The upper level of platinum group metal content must be less than that which would cause this design capacity to be exceeded.

Further, as a practical consideration each of the seven metals of the platinum group as defined herein has a different degree of effectiveness for their intended use in this system. Therefore, numerical upper and lower limits of metal proportions are blanketing numbers for the entire group. They are not necessarily applicable as a proper range for any given species within this genus. Thus, for example, an appropriate upper limit for the proportion of metal of the entire platinum group metal genus is 100 parts by weight per million based upon the finished catalyst formulation. While it is clear that this is a proper upper limit for the genus, it is also clear that this numerical value may be quite high for certain species of the genus, notably platinum and iridinium in which case a preferred upper limit might better be set at 10 parts per million on the same basis.

It is also clear that although a lower numerical limit can be applied to the proportion of "platinum group metal" used in this catalyst, this value must also be considered as applied to the genus and should be carefully reconsidered as to each individual species. Thus, a lower limit of 0.1 part per million of platinum group metal is considered to be appropriate with respect to the use of some metals, such as platinum, but this value may be lower than the minimum suitable for the application of other metals such as rhenium for example.

In any case, however, the most appropriate measure of the amount of any particular platinum group metal is related exclusively to how it performs in reflexive, endothermic, non-hydrogenative catalytic cracking. There should be a sufficient quantity to support as much combustion of carbon monoxide as is desired considering the inherent limitations of any given operating system, such as temperature limitations based upon equipment metallurgy and/or coke producing propensities of a particular feed.

In this regard it is important to note that in some instances it may be desirable to cause substantially all of the carbon burned in the regenerator to be oxidized all the way to carbon dioxide. In other instances, it may be desirable to cause only part of the carbon to be oxidized all the way to carbon dioxide and permit some substantial amount to be only partially oxidized to carbon monoxide. The use of the instant catalyst now permits the refiner to select the exact amount of heat to be generated in the regenerator as a function of efficient carbon monoxide burning. It permits him to increase the regenerator temperature by burning some of the carbon monoxide therein, (thereby reducing residual coke on regenerated catalyst and increasing the activity of regenerated catalyst) and burning the rest outside the regenerator, for example in a steam generating CO boiler.

Since the amount of platinum group metal employed is so very small, it is extremely difficult to analyze the form of the metal on the catalyst in operation, particularly after it has been on stream for a while and has gone through many cycles of cracking and regeneration.

The platinum group metal is incorporated with the cracking component when the latter is contained in the cracking/regeneration system. In preferred embodiments of the invention, spent catalyst is periodically withdrawn from the moving mass of catalyst and replaced by fresh catalyst in known manner, and the metal is applied to the catalyst at intervals so as to maintain the concentration of said metal substantially constant. The metal may also be added into the reflexive endothermic cracking/regeneration system as an emulsion, suspension or solution in the oil feed, for example. The metal, i.e. Pt, Pd, Ru, Ir, Os, Rh or Re may be in any one of a large number of metallic or non-metallic forms collectively described herein as "decomposable". Included as decomposable metal compounds, for example, are: suspensions of colloidal platinum; dispersions of platinum on an inorganic base such as alumina, such base having a particle size substantially smaller, i.e. less than half, than the average particle size of the catalyst, such as colloidal alumina; suspensions of the aforesaid dispersions in a fluid carrier such as fuel oil, air or water; emulsions of aqueous solutions of platinum compounds; and vapors of the volatile metal compounds in a suitable carrier such as an inert gas. Thus, the term "decomposable" as used herein broadly encompasses all forms of the metal suitable for incorporation into and in association with the cracking component, whether or not the said cracking component is contained within the cracking/regeneration system. In general, the decomposable metal compound, on contact with the cracking component in the cracking/regeneration system, undergoes transformation such that an intimate, irreversible association is formed with the cracking component, i.e. the decomposable metal compound loses its identity and cannot readily be recovered as such by ordinary physical means of separation.

The decomposable metal compounds that may be introduced directly into the unit, i.e. the cracking/regeneration system, include those hereinabove mentioned, by way of example, alternatively, an oil-soluble or oil-dispersible compound of the metal may be added in suitable amount of a hydrocarbon feedstock, such as a gas oil charge stock, for incorporation in the catalyst as the charge is cracked. Such compounds include metal diketonates, carbonyl, metallocenes, olefin complexes of 2 to 20 carbons, acetylene complexes, alkyl or aryl phosphine complexes and carboxylates of 1 to 20 carbons. Specific examples of these are platinum acetylacetonate, tris(acetylacetanato) rhodium (III), triiodoiridium (III) tricarbonyl, η - cyclopentadienylrhenium (I) tricarbonyl, ruthenocene, η - cyclopentadienylosmium (I) dicarbonyl dimer, dichloro(ethylene)palladium (II) dimer, η - cyclopentadienyl) - (ethylene)rhodium (I), diphenylacetylenebis(triphenylphospino) - platinum (O), bromomethylbis(triethylphosphino)palladium (II), tetrakis(triphenylphosphino)palladium (O), chlorocarbonylbis(triphenylphosphino)iridium (I), palladium acetate, and palladium naphthenate.

The feedstocks which may be cracked using the catalysts of this invention include any conventional hydrocarbon stocks, such as naphthas, gas oil, light and heavy distillates, residual oils and the like.

There are several other ways to introduce the above-described decomposable metal compounds into the unit other than with the oil feed. The metal may be applied to the catalyst in the regenerator. Referring now to Figure 1, by way of illustration for an FCC unit, the decomposable metal compound may be introduced suspended in the air feed 46 to the regenerator; or with the steam introduced to the stripping section of the reactor via 26; or directly into spent catalyst transfer conduit 36; or into regenerated catalyst standpipe 6; or into dense fluid bed 22; or into the upper portion of riser conversion zone 4; or into cyclone separating means 32; or dipleg 34; or into catalyst bed 44; or into suspended catalyst particles 48; or into separating means such as diplegs 60, 62, 64 and 66 contained within housing 42. Direct injection into the dense bed of the regenerator 44 is a preferred means of introduction.

The application of the metal to the catalyst may comprise mixing with the catalyst a composite of said metal and a refractory support. The support may be an inorganic oxide such as alumina, silica-alumina or clay, and the support may be particulate and of substantially the same dimensions as the catalyst.

Whereas optional methods for introducing a decomposable metal compound have been illustrated for an FCC (fluid catalytic cracking) unit, moving bed systems likewise provide numerous locations for injection. Also, if the "swirl" regenerator of Figure 1 is replaced with a riser-regenerator, more fully described hereinafter, the decomposable metal compound may be introduced into the riser itself, the dense bed of regenerated catalyst, or into the conduit for recycle of regenerated catalyst to spent catalyst, as well as into other locations of the apparatus equivalent to those described for Figure 1.

The minute quantities of the metal compound catalysts used in this invention affect the overall catalytic cracking process to a different extent and in a different manner than prior catalysts used by the petroleum industry in attempts to burn CO in the regenerator. They also cause different results as compared with non-catalytic CO-burning. Nickel and vanadium are both known to be deposited on cracking catalyst from the hydrocarbon feed and both are known to be carbon monoxide oxidation catalysts. Yet these materials are considered by the petroleum industry to be catalyst poisons. To understand this, one must consider that the aim of catalytic cracking is increased production of gasoline and other lower boiling distillate fractions from whole crude oil.

When a catalyst component, such as nickel or vanadium, is considered to be a poison even thought it has some activity for accomplishing a desirable objective, e.g. catalyzing CO oxidation, it is because its overall effect is to reduce the gasoline yield from the entire system. In the case of nickel and vanadium, and perhaps to a lesser extent other transition metals such as manganese and/or chromium, there is a significant increase in the coke produced on the cracking side of a reflexive catalytic cracking process as defined herein. This increased coke production may result in a higher residual carbon on regenerated catalyst in spite of the somewhat increased catalytic CO combustion. With higher residual carbon, the net effect of the deposition of these metals is to reduce the catalytic activity and gasoline selectivity of the cracking component. To the contrary, the miniscule amounts of the special CO oxidation catalyst components of the instant invention have a net effect of reducing the equilibrium coke levels on the cracking catalyst. These novel catalysts also have the net effect of increasing gasoline selectivity.

Consideration of thermal (non-catalytic) CO oxidation shows that initiating and sustaining non-catalytic CO oxidation requires and produces much higher temperatures than in the presence of a catalyst. It would appear that zeolite cracking catalyst may be adversely affected by exposure to high temperatures, such as those encountered in thermal (non-catalytic) CO burning. Therefore, the net effect of non-catalytic CO burning in the regenerator of a reflexive non-hydrogenative cracking system may be to decrease gasoline production.

In conventional reflexive, non-hydrogenative, endothermic catalytic cracking of hydrocarbons coupled with rapid cyclic regeneration (coke burn-off) of catalyst, the regenerator operates in one of several general modes. In FCC type of operations one regenerator scheme, exemplified by Figure 1, utilizes a dense fluidized bed of catalyst into which cooled, coked catalyst is fed from the cracking reaction zone and from which regenerated, heated catalyst is taken for transfer to the feed inlet point of the cracking side reaction zone. It is usual for the dilute phase temperature in such regenerators to be higher, sometimes as much as 100°F or more, than the dense bed temperature. The flue gas may be at a still higher temperature. One marked advantage of using a platinum group metal modifier catalyst, in combination with increasing the oxygen input to the regeneration zone, is that it tends to cause carbon monoxide to burn in the dense phase rather than in the dilute phase whereby reducing the temperature differential (ΔT) between the two phases. The temperature of the dilute phase can be markedly reduced while the temperature of the dense phase is only moderately increased. This permits the additional heat generated by CO combustion to be invested in the catalyst being returned to the cracking zone to a greater extent.

There exist, in the market today, new designs for FCC units which operate with conventional catalysts and conversion of CO is accomplished thermally rather than catalytically. However, there are many problems in actual operation of these units. These problems may be eliminated through the use of the catalyst of this invention. With catalysts containing suitable low concentrations, usually well under 10 ppmw total, of one or more metals chosen from Pt, Pr, Rh, Ru, Ir, Os and Re, several advantages become apparent in the operations of these units. The ΔT values decrease; that is, the dense bed temperature increases and these is sharp decrease in the dilute phase, cyclone and effluent gas temperature. More process heat is thereby retained by the dense bed for use in the reactor. With the increased dense bed temperature, a lower rate of catalyst circulation is required to supply the same amount of heat to the reactor. The reduced catalyst circulation results in less attrition and lower particulate emissions with the effluent regeneration gas, and may also reduce catalyst makeup requirements to maintain a given activity. With the higher dense bed temperature, the residual carbon on the catalyst returning to the reactor is reduced. It has been established that lower residual carbon will result in a higher effective catalyst activity. The lower catalyst circulation rate and the lower residual coke will improve selectivity, particularly by lowering yield of coke based on charge and a corresponding increase on recoverable products. With the catalyst of this invention, steam injection to lower high cyclone temperatures is unnecessary. Injection of torch oil to raise the temperature of the dense bed to sustain thermal conversion of CO is also unnecessary. Aside from the cost of the steam and torch oil, both of these controls accelerate the deactivation of the catalyst and make the process more difficult to control. A further advantage to decreased catalyst circulation rate is less erosion of the internals of the system. Although preheat of the feed to the cracking unit can also effect or allow a reduction in catalyst circulation rate, the efficiency of energy transfer in the form of heat to the reactor is greater when the heat is generated directly in the bed of catalyst.

In some fluid cracking units as well as in moving bed units, insufficient coke is deposited on the catalyst during the cracking cycle to generate enough heat when the coke is burned in the regenerator. In such cases, the temperature in the regenerator is too low to effectively reduce the residual carbon to a desirable level (e.g., below 0.2% wt. C). Furthermore, new, higher selectivity cracking catalysts, which produce more high-valued liquid products at the expense of coke, cannot be used in these units, since they would be even more difficult to regenerate. With the catalyst of this invention sufficient additional heat is generated by oxidation of carbon monoxide to take advantage of any such improved selectivities.

Another type of FCC regeneration system utilizes a lower dense fluidized bed of catalyst to which cooled, coked catalyst is added from the cracking zone and an upper dispersed or dilute phase into which all of the catalyst from the dense phase is projected. Some of the hot regenerated catalyst from the upper dilute phase may be recycled to the lower dense bed in order to keep the temperature of the dense bed hot enough to at least start coke combustion. In this configuration, substantially all of the regenerated catalyst returned to the cracking zone is taken from the upper dispersed phase and substantially none comes directly from the lower dense bed. The use of a platinum group metal modified cracking catalyst, together with sufficient oxygen feed to the regenerator to support carbon monoxide combustion, results in increasing the dense bed temperature, decreasing the residual coke level on the catalyst in the dense bed and decreasing or perhaps even eliminating the need for hot catalyst recycle from the upper dilute phase to the lower dense phase.

In moving bed reflective catalytic cracking exemplified by TCC referred to above, the coked catalyst is transferred from a cracking zone to a regeneration zone which is sometimes called a kiln. The kiln itself has an upper zone and a lower zone. Oxygen containing gas, preferably air, is fed between the zones while coked catalyst is fed to the topmost of the two zones. The air passes countercurrent to the coked catalyst in the upper zone burning off some coke creating a flue gas comprising carbon oxides, including substantial quantities of carbon monoxide. The partially decoked catalyst from the upper zone now passes cocurrent to a portion of the fed air in the lower zone where further coke deposits are burned off creating a flue gas comprising carbon oxides. When a catalyst incorporating a platinum group metal as set forth herein is used, and sufficient oxygen is introduced into the kiln, small changes are observed in carbon dioxide to carbon monoxide ratio in the flue gas from the upper, countercurrent degeneration zone. Under these same conditions, however, the flue gas from the lower, cocurrent regeneration zone is observed to retain substantially no carbon monoxide, it having been substantially all oxidized to carbon dioxide. The regenerated catalyst leaving the kiln is substantially hotter than without the instant platinum group metal modification and the total flue gas, which is a composite of the upper and lower kiln zone flue gases, may have somewhat less carbon monoxide.

In the present invention a decomposable compound of a platinum group metal is brought into contact with the cracking catalyst during its use in the cracking process. For example in a TCC process a decomposable compound of a platinum group metal can be applied directly to coked cracking catalyst between the cracking reaction zone and the regeneration kiln zone. This type of operation, coupled with feeding sufficient air, will cause at least some of the carbon monoxide generated by coke burning in the upper counter-current regeneration zone to be burned to carbon dioxide thereby at least reducing the carbon monoxide content of the flue gas from the upper regeneration zone. In this regard it should be understood that there is substantial competition, particularly in the upper regeneration zone, between the coke and the carbon monoxide, for the available oxygen. Therefore, in the upper zone, where relatively low temperatures and high coke levels prevail, it is difficult to burn CO with any high degree of efficiency.

Another aspect of this invention which tends to enable one to increase the utility of the cracking catalyst hereof modified with the addition of minute quantities of platinum group metal, particularly in moving bed type cracking, is to recycle some small amount of regenerated catalyst from the kiln exit to the kiln inlet. Recycle proportions may be up to 10 weight percent or perhaps even more. It is appropriate to keep this recycle down to a minimum since it increases the necessary catalyst inventory. It is advantageous, however, in that it results in hotter and cleaner regenerated catalyst and in less carbon monoxide in the flue gas.

A further aspect of this invention, in conjunction with moving bed, e.g. TCC, cracking systems utilizing platinum group metal modified cracking catalyst, involves a change in the conventional flue gas venting scheme. In conventional operation, the flue gas from the lower kiln is admixed with the flue gas from the upper kiln and the mixture vented. According to this aspect of this invention, the flue gas from the upper kiln, which contains substantial quantities of carbon monoxide, is fed into the lower kiln regeneration zone along with the air feed thereto. This permits the carbon monoxide laden upper flue gas to contact partially and fully regenerated platinum group metal containing catalyst and excess air and therefore permits and encourages carbon monoxide to be burned to carbon dioxide to a greater extent than has heretofore been possible.

It is conventional in moving bed catalytic cracking systems to operate the entire cycle of cracking followed by regeneration with a continual downward flow of catalyst, and then to pneumatically or mechanically lift the regenerated catalyst from the bottom of the regenerator kiln to the top of the cracking reactor. Some refiners use air in the pneumatic lift, some use a combination of steam and flue gas. With the incorporation of minute amounts of platinum group metal with the cracking catalyst an opportunity presents itself for substantially reducing, or perhaps even eliminating, carbon monoxide from the flue gas. According to this aspect of this invention, hot regenerated catalyst is lifted, as slowly as practical, with a mixture of flue gas and air. The platinum group metal on the hot regenerated cracking catalyst will catalyze the combustion of carbon monoxide in the lift pipe. This will not only purify the vented flue gas, but it will also further heat the regenerated catalyst so as to enable it to more efficiently catalyze the hydrocarbon cracking reactions.

The oils fed to this process are principally the petroleum distillates commonly known as gas oils, which boil in the temperature range of 650°F to 1000°F, supplemented at times by coker gas oil, vacuum tower overhead, etc. These oils generally are substantially free of metal contaminants.

The charge stock, which term herein is used to refer to the total fresh feed made up of one or more oils, is cracked in the reactor section in a reaction zone maintained at a temperature of 800°F to 1200°F, a pressure of 1 to 5 atmospheres, and with a usual residence time for the oil of from about one to ten seconds with a modern short contact time riser design. The catalyst residence time is from one to fifteen seconds.

Because the chargestock contains trace amounts of metal principally nickel and vanadium, the circulating inventory of catalyst accumulates these metals until a balance is struck between the metals removed from the inventory by catalyst withdrawal and losses, and the amount introduced with fresh feed. It is common to refer to circulating inventory of catalyst which has been in use for some time and has acquired a normal complement of nickel and vanadium as "equilibrium catalyst". Equilibrium catalyst usually is characterized by metals content in the range of 200 to 600 ppmw Nickel Equivalents of metal, which is defined as

$$\text{ppmw Nickel Equivalent} = \text{ppmw nickel} + 0.25 \text{ ppmw vanadium}$$

A preferred embodiment of the invention comprises taking a side-stream of the circulating inventory of cracking catalyst and impregating it in a contacting zone with a solution of a compound of said combustion-promoter-metal dissolved in a solvent boiling above 140°F but below 600°F, which contacting effects deposition of the metal compound on the catalyst. Before or during contacting, the side-stream is cooled to a temperature less than 600°F. Thereafter, the side-stream is returned to the circulating inventory of catalyst. The side stream may be confined to a single vessel which is closed, apart from its communication with the catalyst circuit. The vessel may open into the reactor regenerator, coked catalyst conduit is regenerated catalyst standpipe. The side-stream may thus originate in different parts of the catalyst section. However, it is preferred that it be taken from the reactor section or coked catalyst conduit to provide a side-stream of coked catalyst. It is also preferred that at least some of the contacting be effected at about or above the boiling point of the solvent, as described hereinbelow.

In order to provide intimate contacting with consequent deposition of or impregnating by metal combustion promoter compound, it is preferred that the catalyst be fluidized in the contacting zone during the contacting period. Useful solvents include water and liquid organic compounds with the described boiling specifiications.

It has been discovered that according to this embodiment of the invention the effectiveness of the combustion-promoter-metal for promoting combustion of carbon monoxide is enhanced and the possible loss of a portion of the promoter metal or deposition of some of that metal elsewhere than on the catalyst is avoided. Although the effectiveness of a particular metal may depend on the particular way in which it is introduced into the catalyst, an indication is given in Figure 3 of the relative effectiveness obtained with a series of cracking catalysts that contain the different metal combustion promoters deposited in the conventional fashion during preparation of these catalysts. For the purposes of this invention, it is preferred to use platinum.

The metal compounds useful in the present invention include the metal halides, preferably chlorides, nitrates, ammine halides, oxides, sulfates, phosphates and other water-soluble inorganic salts; also, the metal carboxylates of from 1 to 5 carbon atoms; or, the alcoholates. Specific examples include palladium chloride, chloroplatinic acid, tetrammine platinum(II) dichloride, ruthenium pentaammine chloride, osmium chloride perrhenic acid, dioxobis(ethylenediamine)rhenium(V) chloride and rhodium chloride. Metal organic compounds or organometallic compounds of the described metals also may be used, including metal diketonates, carbonyls, metallocenes, olefin complexes of 2 to 20 carbons, acetylene complexes, alkyl or aryl phosphine complexes and carboxylates of 1 to 20 carbons. Specific examples of these are platinum acetylacetonate, tris(acetylacetonato)rhodium (III), tri - iodoiridium (III) tricarbonyl, η - cyclcpentadienylrhenium (I) tricarbonyl, ruthenocene, η - cyclopentadienylosmium (I) dicarbonyl dimer, dichloro(ethylene)palladium (II) dimer, (η - cyclopentadienyl) - ethylene)-rhodium (I), diphenylacetylenebis(triphenylphosphino) - platinum (O), bromomethylbis(triethylphosphino)palladium (II), tetrakis(triphenylphosphino)palladium (O), chlorocarbonylbis(triphenylphosphino)iridium (I), palladium acetate, and palladium naphthenate.

It is a feature of this invention that relatively simple and inexpensive metal compounds may be used, such as chloroplatinic acid or tetra-ammine platinum dichloride.

The solvents useful in the process of this invention include water, polar organic solvents and liquid hydrocarbons, and in general any organic or inorganic fluids which are solvents for the chosen metal compound. Representative examples of organic solvents include alcohols such as methanol, ethanol, isopropanol, tert-butanol, 2 - ethylhexanol, octanol, glycerol, and ethylene glycol; esters such as ethyl acetate, butyl acetate, amyl acetate; ethers such as diethylene glycol, di - isopropyl ether, di - n - butyl ether, "Cellosolve" (registered Trade Mark), methyl "Cellosolve", butyl "Cellosolve"; hydrocarbons such as octane, nonane, decane, dodecane, hexadecane, benzene, toluene, xylene, cumene; and mixtures thereof.

Mixtures of solvents may be used to advantage as will be hereinafter described in more detail. Such mixtures include, for example, water and ethylene glycol, benzene and cumene, and tertiary butyl alcohol and water. Such mixtures are recited only by way of illustration and are not to be construed as limiting.

The preferred solvents or mixtures thereof useful in the present invention are those that boil above 140°F but below 600°F at contact zone pressure.

It is believed essential for the purpose of this invention to cool the side-stream of hot circulating inventory of cracking catalyst which is at a temperature substantially higher than 600°F, and to cool it to a temperature below 600°F. While not wishing to be bound by theoretical considerations, it is believed that the method of this invention is effective, at least in part, because it avoids premature decomposition of the combustion - promoter - metal compound, i.e., decomposition of the compound before it has had adequate opportunity to contact the catalyst and achieve optimal distribution on the surface thereof. Therefore, it will be understod that the precise temperature for contacting the solution of combustion-promoter-metal and the side-stream of cracking catalyst in order to achieve maximum effectiveness of the promoter metal may vary, depending on the thermal stability of the metal compound itself and the choice of solvent, and in some cases perhaps the nature of the cracking catalyst itself. Unusual effectiveness has been observed, for example, as illustrated hereinbelow, with tetra-ammine platinum dichloride using water as a solvent at about or above 275°F, which is about the boiling point of water under contact zone pressure of about 30 p.s.i. gage. In general, it is preferred to conduct the contacting step under conditions such that at least a portion of the solvent wets the catalyst.

Prior to the contacting step, the side-stream of cracking catalyst may be indirectly cooled by a cooler employing air or other heat transfer fluid to remove heat across a mechanical barrier such as the wall of a pipe. It also may be directly cooled by contact with an inert gas or water injected into the stream. Combinations of direct and indirect cooling may be used.

It will be recognized by those skilled in the art that at least some direct cooling will perforce occur on contacting the side-stream of cracking catalyst with the solution of compound of combustion-promoter-metal, this cooling resulting from evaporation of solvent. Thus, a substantial portion if not all of the desired cooling may be achieved by simply diluting the solution of metal-promoter-compound with a substantial excess of solvent and injecting proportionally larger aliquots of solution into the contact zone.

Mixtures of solvents of different volatilities may be advantageously used, such as a minor amount of glycerol with a major fraction of water. In such instance, the water acts as co-solvent and a cooler, while the less volatile glycerol provides assurance that the metal-promoter-compound will maintain its integrity, undecomposed, until adequate contact with the catalyst has been achieved. The cooling effectiveness due to solvent volatilization may be enhanced by utilizing a solvent that endothermally decomposes in contact with hot cracking catalyst. Examples are alcohols such as tertiary butyl alcohol which dehydrates to isobutylene and water, or isopropyl alcohol which forms propylene and water. Such endothermally decomposing solvents may be used alone or in admixture with other solvents.

Mixtures of solvents that boil above 140°F but below 600°F are suitable. Mixtures, in general, will be characterized by a boiling range, and it is to be understood that when the expression "boiling range" is used herein it is intended to include both the range of temperatures applicable to mixtures, when such are used, and the single temperature boiling point applicable to a single solvent, when such is used, in which at least 95% of the solvent, i.e., substantially all of the solvent, distills. Furthermore, when reference is made herein to boiling or boiling range without reference to the prevailing pressure, it is to be understood that the prevailing pressure in the contact zone is to be applied, this pressure being most usually from 10 p.s.i. gage to 50 p.s.i. gage.

Although the side-stream of catalyst may be withdrawn from any part of the hot circulating inventory of cracking catalyst, it appears to be advantageous to utilize a side-stream of coked catalyst for the purpose of this invention. Therefore, it is preferred to withdraw the side-stream from the reactor or from the coked catalyst conduit. When from the reactor, it is preferred to withdraw catalyst from the stripper zone to avoid possible difficulties due to the presence of volatile hydrocarbons on the catalyst, i.e., the coked catalyst should be substantially free of gas oil or conversion products thereof when contacted with the solution of combustion-promoter-metal.

The withdrawn side-stream is conducted to a contact zone where it is contacted with the solution. The solution may be introduced by a spray nozzle or other suitable means promoting intimate contact. It is desirable to maintain the catalyst in the contact zone in a fluidized state, thereby promoting uniform temperature and good distribution of the metal compound on the catalyst. Volatilization of the solvent promotes fluidization. The side-stream, after impregnation, is conducted back and allowed to mix with the hot circulating inventory of catalyst. On return to high temperatures, the compound is believed to decompose, providing the active form of metal combustion promoter. Because of the extremely minute amounts of metal present, it is not possible to determine precisely the nature of the metal in its active form, i.e., whether it is present as elemental metal, as the sulfide, oxide, or in some other form.

The combustion-promoter-metal provided to the catalyst inventory by the method of this invention may be a component of all catalyst particles or only of some of the catalyst particles. In terms of its concentration in the entire system, it must be present in a large enough proportion to be able to effect the reaction of carbon monoxide with oxygen to carbon dioxide, provided the conditions in the regenerator are otherwise sufficient to support this combustion; e.g., sufficiently high temperature and sufficient air. Yet it must not be present in a proportion so large that it substantially adversely affects the operation of the cracking side of the process. This latter, upper limit on metal promoter content is to some extent a reflection of the design capacity of the cracking system including auxiliaries and downstream product resolution facilities compared to actual operating throughput. The upper level of platinum group metal content must be less than that which would cause this design capacity to be exceeded.

The concentration of the combustion-promoter metal may for example be from 0.01 to 50, more preferably 0.5 to 10 ppmw (parts per million by weight).

Figures 4 and 5 show two arrangements of side-stream and contact zones which exemplify the system of this invention. In both figures the catalyst section shown in Figure 1 is represented by a simple line drawing; the indicia not otherwise identified in the following paragraphs are repeated from Figure 1 and identify the same elements as in that figure.

In the side-stream and contacting arrangements shown in Figure 4, coked catalyst passes from coked catalyst conduit 36 into conduit 70 fitted with control valve 71. The control valve functions to regulate the rate of flow of the side-stream. Material passing the valve is conducted via conduit 72 through heat exchanger 73 which serves to cool the side-stream. The cooled catalyst passes via conduit 74 into vessel 75. Vessel 75 is fitted with a nozzle sprayhead, or other discharge means 78, which serves to discharge the solution of compound of combustion-promoter-metal fed to the discharge means via conduit 77. Conduit 79 passes into the vessel 75 and also connects with the discharge means 78. This conduit, which may be separate from conduit 77 or combined with it, serves to pass compressed air, steam, nitrogen, volatile solvent, or other inert dispersing medium into vessel 75 for the purpose of maintaining the catalyst in a fluidized state in the contact zone 75. The contacted cooled catalyst is passed via conduit 80 to the regenerator, thus being returned to the circulating inventory.

Although the illustration of Figure 4 shows the side-stream being taken from conduit 36, which originates in the stripping zone 24 shown in Figure 1, it may equally well be taken from the reactor vessel 81 directly or from the regenerator, or from regenerated catalyst conduit 6, or at any convenient point in the hot circulating inventory of catalyst. Although the side-stream in Figure 4 is shown returned to the circulating inventory via conduit 80, which returns the stream to the regenerator, it might equally well be returned to any convenient portion of the catalyst section such as to regenerated catalyst conduit 6, for example.

It is to be noted that vessel 75 is conveniently provided with temperature measuring means such as thermocouple means 76. Figure 5 illustrates another arrangement of the system of this invention. In this arrangement, a vessel 90 communicating with conduit 91 is attached to the stripping zone of the reactor vessel 81, with free communication of the contents of the stripping zone and vessel 90 via conduit 91. Conduits 77 and 79 and discharge means 78 refer to the same elements as shown in Figure 4. Conduits 77 and 79 pass into vessel 90, and discharge means 78 is located within said vessel. In this system, fluidized catalyst passes from the stripper zone 24 into vessel 90, is contacted with the solution of metal combustion promoter compound and is returned via the same conduit to the stripper zone. It is evident that the attachment of 91 may be made elsewhere than as shown, such as to the regenerator. It is preferred, however, that the attachment be to such points as will provide communication of the contents of vessel 90 and a fluidized bed of hot coked catalyst.

Whereas this invention has been illustrated by reference to a swirl regenerator as shown in Figure 1, for example, it is equally applicable to system in which other designs of regenerator are used, such as a riser regenerator designed for the complete combustion of carbon monoxide. By the method of this invention, a solution of a compound of a combustion-promoter-metal may be applied to virgin catalyst or to equilibrium catalyst. Furthermore, it may be used as the only method for providing said combustion-promoter-metal to said catalyst, or it may be used in conjunction with make-up catalyst that contains metal-combustion-promoter deposited thereon during its preparation. The method of this invention may be used to control the combustion of carbon monoxide in the regenerator, said control being achieved by suitable coupling means which control the flow rate of the sidestream or the pumping rate or the concentration of the solution of a compound of combustion promoter metal, in response to the composition of the flue gas, for example.

The following examples illustrate certain aspects of this invention and are not to be construed as limiting thereon. All parts or percentages given are by weight unless otherwise specified.

Example 1

In this example and those which follow, a continuous FCC pilot plant was used. The pilot plant consisted of a regenerator, a riser reactor corresponding to *4* of Fig. 1, communicating with a stripping zone corresponding to *24* of Fig. 1 and conduits corresponding to *6* and *36* of Fig. 1. Equilibrium catalyst was withdrawn from a commercial catalytic cracking plant and used in this and subsequent examples described herein. The catalyst was a typical commercial material of the rare earth exchanged faujasite type, with the faujasite dispersed in a silica alumina matrix. Its composition was found to be 61.3% SiO_2, 35.9% Al_2O_3, 2.77% Re_2O_3, 0.51% Na, 359 ppm Nickel and 404 ppm Vanadium.

For the purpose of this example, a vessel in the form of a tube, as illustrated in Fig. 5, was provided attached to and communicating with the dense bed in the regenerator. The tube had a volume of 25 cubic centimeters.

The vessel was provided with a nitrogen supply to maintain the catalyst as a fluid in the tube.

Prior to starting the contacting and impregnation of the catalyst with the combustion-promoter-metal compound, the pilot plant unit was started up with an inventory of 3500 grams of the hereinabove described catalyst and with wide-cut gas oil from a Mid-Continent crude as feed, and the operating conditions adjusted about as follows:

Reactor temperature, °F	1000
Stripper temperature, °F	1000
Regenerator temperature, °F	1250
Catalyst residence time in riser, seconds	7.0
Oil residence time in riser, seconds	4.5
Cat to oil wt. ratio	6.0

A solution of 6 milligrams of metallic platinum as tetra-ammine platinum dischloride in 250 ml of water was charged to a supply burette. The solution was pumped as a jet into above-described tube containing fluidized catalyst, the pumping rate being adjusted to give a contact zone temperature of about 350°F, as indicated by a skin-temperature measurement. Prior to introduction of the solution, the contact zone temperature measured about 900°F. The adjusted pumping rate was 66 ml/hr, and was terminated after 231 ml of solution had been pumped into the contact zone. Samples of catalyst were withdrawn from the stripper at half-hour intervals and evaluated for catalytic effectiveness in combustion of carbon monoxide.

The results are summarized in Table 1.

TABLE 1

Sample No.	Impregnation Time	ppm Pt	CO_2/CO Ratio
1	0 minutes	0	2.7
2	30 "	0.22	4.7
3	60 "	0.44	3.7
4	90 "	0.66	3.9
5	120 "	0.88	3.6
6	150 "	1.10	4.7

Example 2

The procedure of Example 1 was repeated with a fresh charge of equilibrium catalyst, except that heavy vacuum gas oil derived from a Sour West Texas Crude was used instead of the wide-cut gas oil. In this experiment, 6 milligrams of platinum as tetra-ammine platinum dichloride was dissolved in 180 ml of water. The solution was pumped at the rate of 119 ml per hour for one hour, at which time the temperature in contact zone was about room temperature. A catalyst sample withdrawn from the stripper at one hour showed no increased activity for promoting CO combustion. The impregnation was continued for a second hour, pumping 78 ml of the described solution, at the end of which period the temperature of the contact zone was about 350°F. A sample of catalyst, withdrawn after two hours of impregnation, gave a CO_2/CO ratio of 6.3 compared with a ratio of 2.7 for the catalyst before impregnation. The calculated promoter metal content of the sample was 1.9 ppm.

Example 3

For the purpose of this example, the tubular vessel used for contacting was attached to the stripping zone of the pilot plant. The system was charged with untreated equilibrium catalyst and adjusted as described in Example 1 but using the heavy vacuum gas oil used in Example 2.

A solution of 2 milligrams of platinum in 250 ml of water was pumped at a rate of 90 ml/hr to contact the catalyst until 135 ml of solution was consumed. The temperature in the contact zone varied from about 400°F initially, dropping to 220°F at which point the run was terminated and a sample of catalyst taken. The sample was calculated to contain 0.31 ppm platinum, and gave a CO_2/CO ratio of 410.

Example 4

Example 3 was repeated with a fresh charge of equilibrium catalyst but the flow rate of the contacting solution and the nitrogen flow rate were adjusted to keep the contact zone temperature in the range of from about 400°F to about 600°F. A sample of the final catalyst, calculated to contain 0.29 ppm platinum, gave complete combustion of carbon monoxide, i.e., a CO_2/CO ratio of infinity.

WHAT WE CLAIM IS:—

1. A cyclic, regenerative, catalytic cracking process of the known kind, in which catalyst, having contacted feed in a reactor under cracking conditions, in the absence of added hydrogen, traverses an external circuit which includes a regenerator and which returns the catalyst to the reactor in regenerated form, the moving mass of catalyst containing a concentration of a platinum group metal, or of rhenium, which is sufficient to catalyse oxidation of carbon monoxide in the regenerator but insufficient to act as a poison under said cracking conditions, characterized by the fact that the platinum group metal or rhenium is applied to the catalyst while (but not before) the catalyst is traversing said circuit.

2. A process according to Claim 1 wherein the platinum group metal, or rhenium, is applied to the catalyst as a compound which is decomposible under conditions encountered by the catalyst during the process.

3. A process according to Claim 1 wherein the platinum group metal, or rhenium, is applied to the catalyst as a colloidal suspension in a suitable medium or as a dispersion on a refractory oxide base of colloidal particle size.

4. A process according to Claim 1 or Claim 2 wherein the platinum group metal, or rhenium, is applied to the catalyst as an emulsion of a compound of the metal in a liquid or as a vapour of such a compound in a gaseous carrier.

5. A process according to any preceding claim wherein spent catalyst is periodically withdrawn from said moving mass and replaced by fresh catalyst in known manner, and wherein the metal is applied to catalyst at intervals so as to maintain said concentration substantially constant.

6. A process according to any preceding claim wherein said concentration is from 0.01 to 50 ppmw.

7. A process according to any preceding claim wherein said concentration is from 0.5 to 10 ppmw.

8. A process according to any preceding claim wherein the metal is applied to the catalyst in the regenerator.

9. A process according to any of Claims 1 to 7 wherein the metal is applied to the catalyst while the catalyst is passing from the reactor to the regenerator.

10. A process according to Claim 9 wherein the catalyst is unstripped.

11. A process according to any of Claims 1 to 7 wherein the metal is applied to catalyst passing from regenerator to reactor.

12. A process according to any preceding claim wherein the metal is applied to the catalyst while the catalyst is in a sidestream.

13. A process according to Claim 12 wherein the side stream is withdrawn from a catalyst stripping zone.

14. A process according to Claim 12 wherein the side stream is withdrawn from a coked catalyst conduit.

15. A process according to any of Claims 12 to 14 wherein said side stream is confined to a single vessel which is closed apart from its communication with said circuit.

16. A process according to Claim 15 wherein said vessel opens into the reactor, regenerator, coked catalyst conduit is regenerated catalyst standpipe.

17. A process according to any of Claims 12 to 16 wherein the catalyst in the side stream is fluidized.

18. A process according to any of Claims 12 to 17 wherein the metal is applied in the form of a solution of a compound in a solvent which boils between 140 and 600°F at the prevailing pressure.

19. A process according to Claim 18 wherein the catalyst in the side stream is at a temperature below 600°F.

20. A process according to Claim 18 or Claim 19 wherein the solvent is water.

21. A process according to any of Claims 18 to 20 wherein the amount of solution employed is sufficient to cool the side stream to the boiling range of the solvent at the prevailing pressure.

22. A process according to any of Claims 18 to 21 wherein the solvent comprises an organic compound endothermically decomposable on contact with hot cracking catalyst.

23. A process according to any preceding claim wherein the application of metal to catalyst comprises mixing with the catalyst a composite of said metal and a refractory support.

24. A process according to Claim 23 where-

in said support comprises an inorganic oxide such as alumina, silica-alumina or clay.

25. A process according to Claim 23 or Claim 24 wherein said support is particulate and of substantially the same dimensions as said catalyst.

26. A regenerative catalytic process according to Claim 1 substantially as described with reference to the accompanying drawings.

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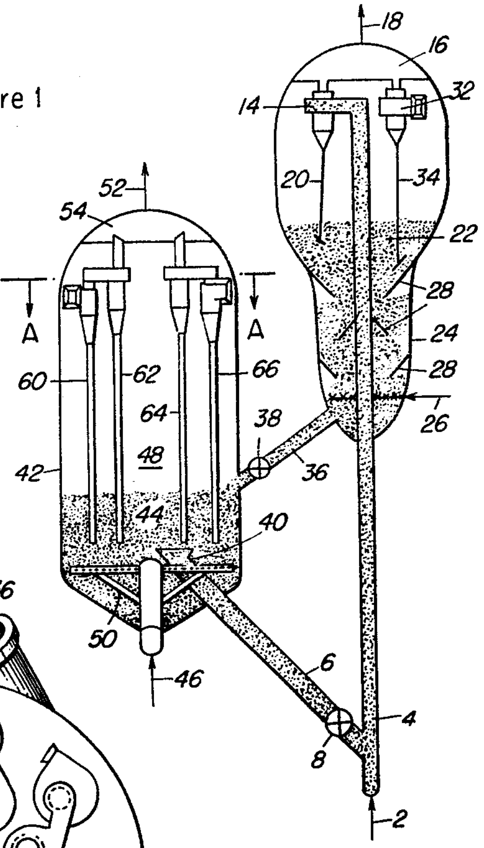
Figure 1



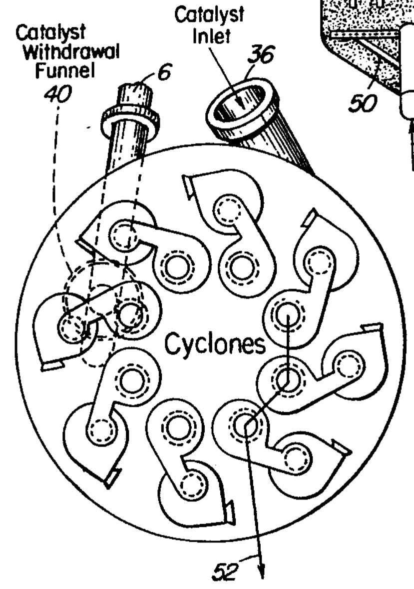
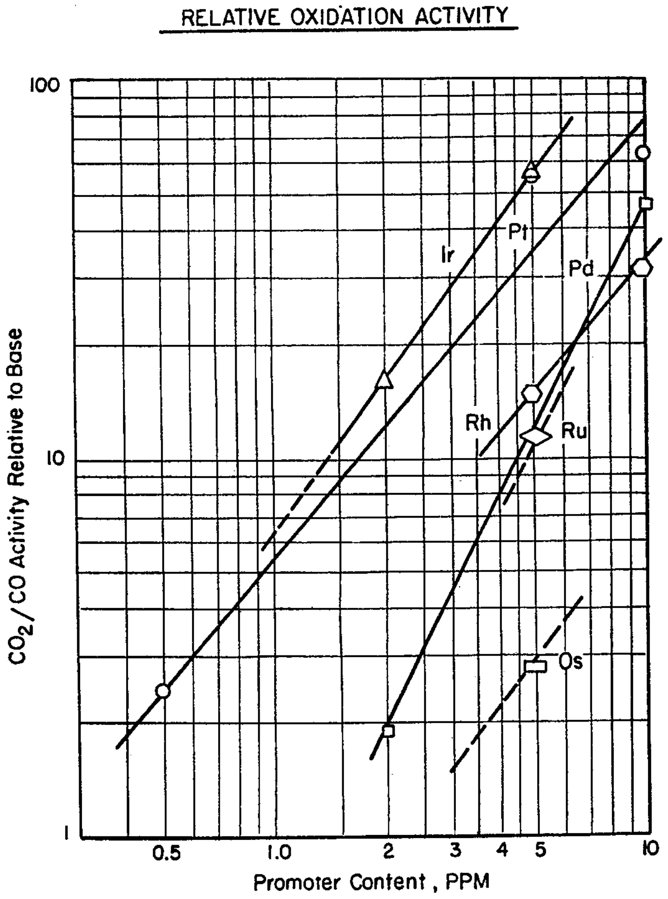


Figure 2

FIGURE 3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1
CO₂/CO Activity Relative to Base
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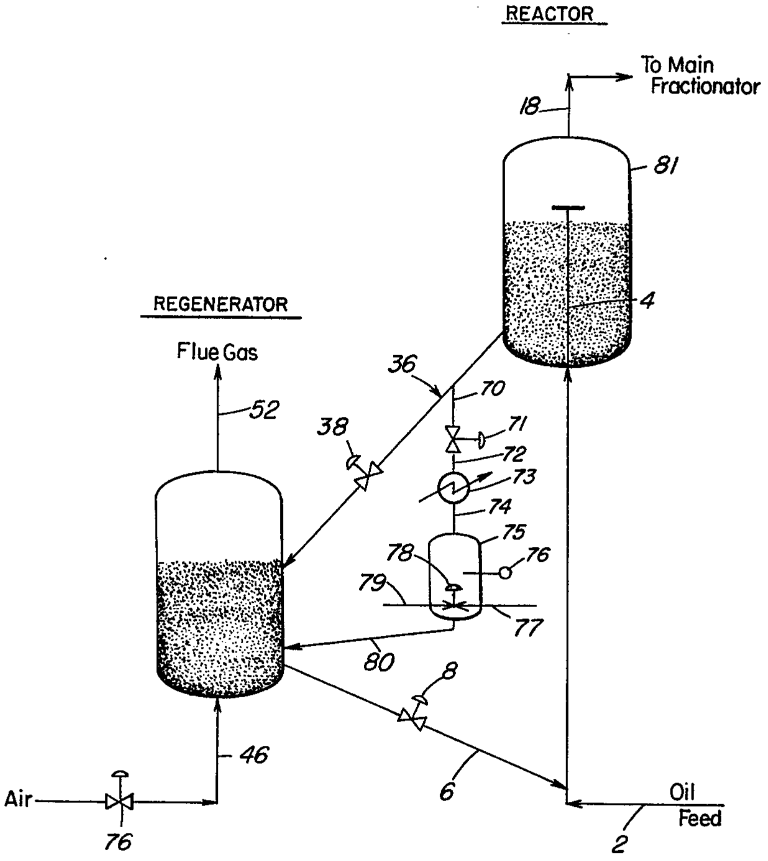
1.0
2
3
4
5
10
Promoter Content, PPM
Ir
Pt
Pd
Rh
Ru
Os

Figure 4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REGENERATOR
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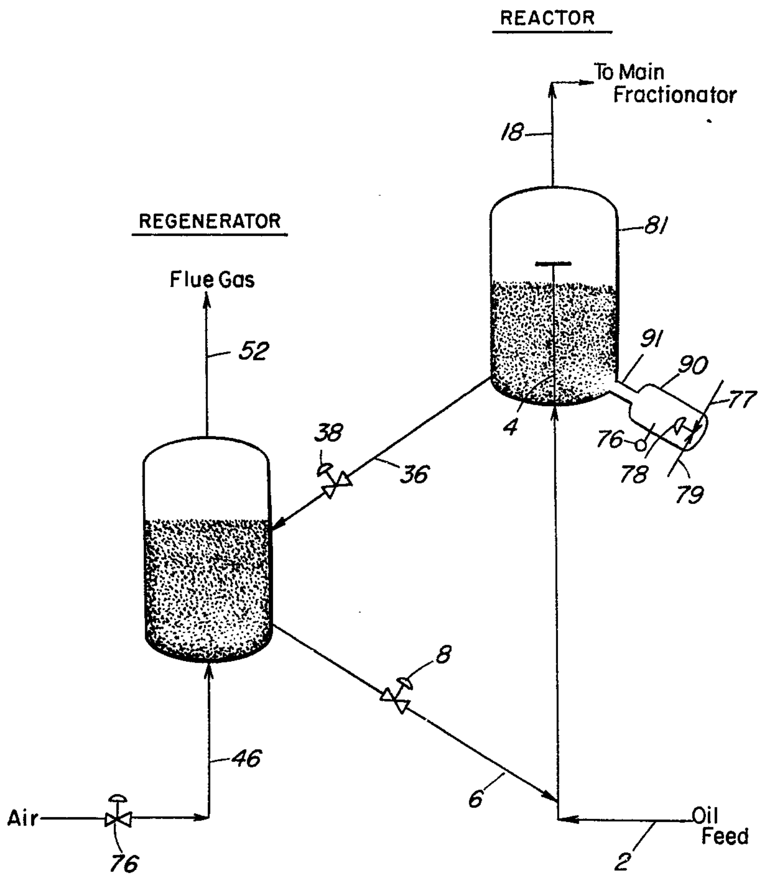
Air
76
6
Oil Feed
2

Figure 5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6
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