Dec. 19, 1972 M. C. BRYSON ET AL 3,706,654

FLUID CATALYTIC CRACKING PROCESSES AND MEANS

Filed Nov. 12, 1969 2 Sheets-Sheet 1

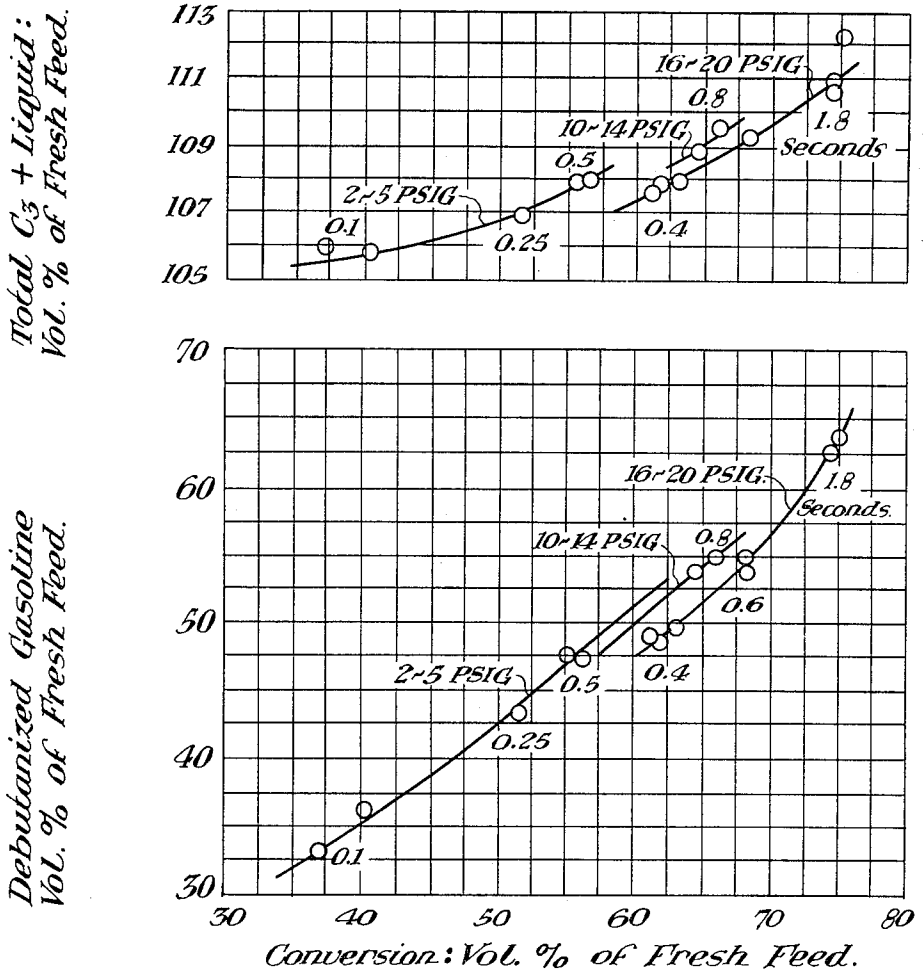


Fig. 2.

Effect of Hydrocarbon Partial Pressure (PSIG) at Various Contact Times (Seconds)

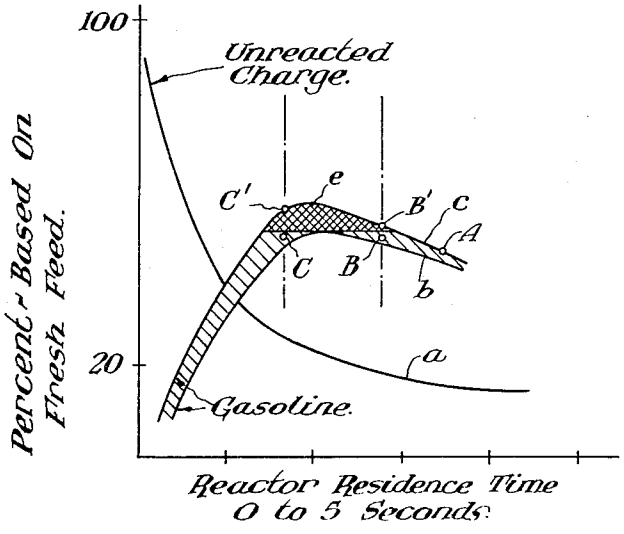


Fig. 1.

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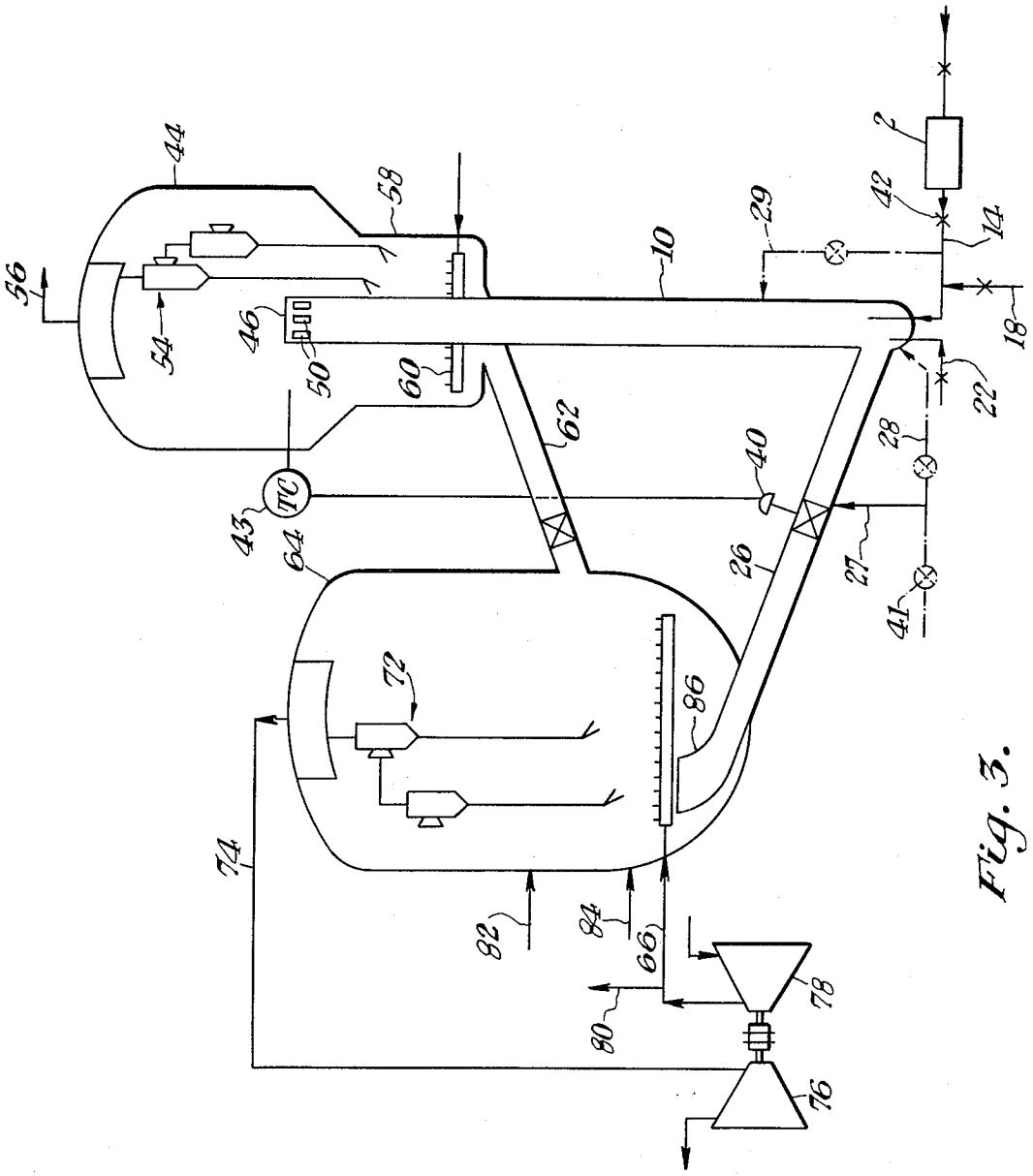


Fig. 3.

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3,706,654

FLUID CATALYTIC CRACKING PROCESSES AND MEANS

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U.S. Cl. 208—74 25 Claims

ABSTRACT OF THE DISCLOSURE

A process for cracking a principal hydrocarbon charge (such as a furnace oil or gas oil) capable of being cracked to gasoline in the presence of a fluidized cracking catalyst, said process comprising the steps of maintaining a predetermined range of temperatures within said catalyst stream, adding a naphtha diluent (gasoline type hydrocarbon) to said catalyst stream, controlling the partial pressure of said charge in said stream by maintaining a given ratio of said diluent to said charge, and adding said diluent to said catalyst stream at a point having a higher temperature than that at which said charge is added so that a significant proportion of each of said naphtha and said charge is cracked by said catalyst. An exemplary cracking plant is provided for effecting the process as outlined. Methods are provided for the upgrading of virgin and cracked naphthas and for enhancing the olefinic yields therefrom.

The present invention relates to the cracking of petroleum hydrocarbon feed stocks to gasoline in the presence of a highly active fluid cracking catalyst and to the unexpected upgrading and cracking of certain components added with the feed stock.

In the aforementioned application, S.N. 836,383, a method is presented for improving the operation of a fluidized, catalytic cracking process without lowering the pressure in the reaction zone or in the catalyst disengaging or stripping vessel. An unexpected advantage results from charging a diluent gas to the inlet of the cracking reaction zone to lower the partial pressure of the charge hydrocarbon in the system. Any diluent which is a vapor or becomes a vapor under the conditions of the reaction zone can be used. An inert gas such as steam or nitrogen is a suitable diluent. A mixture of gases can be employed. If the diluent is a hydrocarbon, it should desirably have a boiling point below about 430° F., i.e., it should be a gasoline range hydrocarbon or lighter. If it boils above the gasoline range, it will, of course, itself be a portion of the cracking feed. Recycle methane or ethylene could be employed. In further accordance with the aforementioned application it was found that a lower hydrocarbon feed partial pressure at any given reaction zone total pressure produces the unexpected effect of increasing the selectivity to gasoline production at a given conversion level of fresh feed or, conversely, requiring a lower conversion of total feed to produce a given gasoline yield.

In accordance with the aforementioned previous invention, it was further discovered that the gasoline selectivity advantage is transient and is lost if the cracking process is not terminated in a timely manner, as explained more fully in the first-mentioned previous application. Briefly, the amount of steam or other inert diluent must be sufficient to produce a significant reduction in partial pressure of the incoming hydrocarbon feed. In general, the greater the amount of steam or other diluent gas introduced relative to the hydrocarbon, the greater will be the effect upon selectivity, i.e., the greater the reduction in partial pressure, the greater the gasoline selectivity advantage.

In further accordance with the previous invention, it has been discovered that the gasoline selectivity advantage, owing to the presence of an inert diluent which is not itself capable of being cracked to gasoline, is most significant in the very early stages of the cracking reaction, which is also the period in which most of the cracking of fresh feed occurs. In point of fact, the productional curve of cracked hydrocarbon vapors from fresh feed with time is exponential, with the greatest rate of cracking occurring at the outset of the reaction so that the cracked vapors themselves quickly reduce the partial pressure of the unreacted feed. However, by the time these vapors are produced, most of the cracking has been completed. For example, after the hydrocarbon feed has been in the reaction zone for about 0.1 second, it is about 40% converted and after 1.0 second conversion has increased only to about 70 to 80%. In contrast to what was known before the first-mentioned Bryson and Murphy invention, reaction zone residence time is established not only by establishing the total charge rate, including both hydrocarbon and steam, but also by establishing the ratio of steam or other diluent to hydrocarbon in the charge. It was determined in accordance with the previous Bryson and Murphy invention that control of the ratio of diluent to hydrocarbon feed or charge and control of the total charge rate including both diluent and hydrocarbon are interdependent and interdependently exert a critical effect upon a gasoline yield. The residence time of fresh hydrocarbon feed in the reactor is controlled such that the maximum selectivity of the process for gasoline yield is not impaired by the phenomenon known as "aftercracking." Avoidance of aftercracking and also of the phenomenon known as "backmixing" are explained hereinafter with reference to FIGS. 1 and 3, and is further detailed in the aforementioned copending application.

In any particular cracking process the gasoline yield and residence time values which encompass the gasoline selectivity advantage of the present invention will depend upon many variables peculiar to a given process. Examples of these variables are the particular catalyst which is employed, the level of carbon on the regenerated catalyst, catalyst activity and/or selectivity, reaction temperature, and the refractory characteristics of the feed. The extent of the selectivity advantage of our present invention might be as low as one-half percent to one percent or as high as three to five percent depending upon the desired ratio of diluent vapor to hydrocarbon feed at the reactor inlet. Considering that gasoline is the most economically desirable product of the cracking operation, the economic value of a selectivity advantage of even one-half or one percent actually recovered as product effluent is considerable in a commercial reactor unit which can process 100,000 to 150,000 barrels per day of hydrocarbon feed.

The present invention relates to a method for unexpectedly improving the selectivity to gasoline production

in cracking processes utilizing a fluidized zeolitic cracking catalyst or a catalyst of comparable activity and/or selectivity. The present invention also provides methods and means for unexpectedly upgrading existing naphtha or gasoline stock through the cracking or analogous reaction. In this connection a surprising result is thereby evident from our invention, as the cracking reaction conventionally is used to produce gasoline stocks in the first instance, but not for the upgrading of existing gasolines.

The present invention, as in the case of the previous Bryson and Murphy inventions, is particularly useful in connection with cracking processes utilizing fluidized catalysts. Natural or synthetic zeolite aluminosilicate cracking catalysts exhibit high activity in the cracking of hydrocarbon oils both in terms of total conversion of feed stock and in terms of selectivity towards gasoline production.

Although zeolitic aluminosilicates are especially useful catalysts for the purposes of the present invention, any silica alumina or other cracking catalyst which is sufficiently active and/or selective to be capable of producing a transient maximum or peak gasoline yield from the total fresh hydrocarbon feed capable of being cracked to gasoline at residence times of 5 seconds or less are within the purview of our present invention. The maximum gasoline yield obtained at residence times within 5 seconds is transient and rapidly diminishes. After a residence time of one second, most of the fresh hydrocarbon feed is converted, and there is a sharp drop in rate of conversion of fresh feed. However, if the hydrocarbon continues to remain in contact with the catalyst, products of the earlier cracking operation themselves in turn undergo cracking. This occurrence is termed "after-cracking." Since there is a greater abundance of cracked material than uncracked material after only about one-half to one second of reaction zone residence time the situation rapidly arises wherein considerably more cracking of cracked than uncracked material can occur. When this situation prevails, the desired gasoline product initially produced at a high selectivity in accordance with the present invention becomes depleted owing to aftercracking at a faster rate than it is replenished from cracking of remaining uncracked feed so that the selectivity advantage initially achieved is subsequently lost at a significant rate. If timely disengagement of hydrocarbon and catalyst does not occur prior to the occurrence of a significant amount of aftercracking the very existence of the earlier advantageous selectivity effect can be entirely masked.

In fluid catalytic cracking operations it is generally advantageous to operate the cracking reactor at pressures in the range of about 20 to 30 pounds per square inch gauge and it is undesirable in terms of the integrated operation, including catalyst regeneration and power recovery from regenerator flue gases, for reactor pressures to fall significantly below this level. For example, catalyst regeneration is generally favorably influenced by elevated temperatures and pressures. Furthermore, in systems where regenerator flue gas is utilized to drive a turbine to compress combustion air to be supplied to the regenerator, it is important to maintain an elevated pressure in the regenerator in order to obtain efficient turbine operation. Since spent catalyst must flow from the reactor zone to the regenerator, a correspondingly high pressure is consequently required in the reactor in order to urge catalyst towards the regenerator. However, as noted previously and described more fully below, relatively high reactor hydrocarbon feed pressures are less favorable to gasoline selectivity in the cracking operation than are relatively low pressures.

It has been known, even before the advent of the previous Bryson and Murphy invention, that the use of an inert diluent such as steam at the hydrocarbon feed zone accomplishes certain advantageous effects in a fluidized catalytic cracking operation, such as assisting in fluidization of the catalyst, vaporization of liquid feed, dispersal

of catalyst into the hydrocarbon feed, and increasing the reaction rate. However, such prior art provides no teaching of the proper control of diluent quantity and feed rate vis-a-vis the hydrocarbon feed in order to obtain the aforementioned improvement in gasoline selectivity. It was previously considered that the amount of steam to be employed in a fluid catalytic cracking process should not be great in order to avoid a reduction in residence time and thereby a loss in conversion rate. This is, of course, contrary to the findings of the previous Bryson and Murphy invention and also of our present invention. In the control methods for fluidized catalytic cracking operations, as they existed prior to our aforementioned co-invention, a vapor such as steam was added to the inlet of the reaction zone, which may comprise an elongated riser tube, to assist dispersal of the catalyst into the hydrocarbon feed. The amount of steam was not considered particularly critical. Reaction residence time (space velocity) was then adjusted to control gasoline yield in the reactor effluent. If analysis of reactor effluent indicated that an adjustment of the residence time was required, the hydrocarbon flow rate was adjusted. However, no criticality was attached to the fact that this adjustment also varied the ratio of steam to hydrocarbon at the reaction zone inlet. In short, the partial pressure of the hydrocarbon feed within the reaction zone was left largely to chance.

The invention disclosed in the first-mentioned copending application offers, then, a significant improvement over the prior art, in these respects, as briefly described above. The previous Bryson and Murphy invention teaches the proper control of hydrocarbon partial pressure and residence time within the reactional zone in order to maximize gasoline yield and selectivity. Control of partial pressure and residence times are further elaborated upon below with reference to FIGS. 1 and 2, which provide also a basis for our present invention. The improvement in gasoline yield as a result of the previous Bryson and Murphy invention is significant and should not be minimized. However, this previous invention contemplates the addition of a diluent material which is a gas or vapor at the reactor conditions attendant upon its entrance, but which is largely inert under such conditions. That is to say, the diluent does not itself significantly enter into the reaction but provides only the primary function of reducing the partial pressure of the hydrocarbon feed. This remains the case whether steam, nitrogen, methane, ethylene, naphtha, or other hydrocarbon having a boiling point below about 430° F. is utilized as the diluent and is added concurrently with the hydrocarbon feed. Even if naphtha or similar lower boiling hydrocarbon were used pursuant to the teachings of the previous Bryson and Murphy inventions, the diluent thus comprised is essentially inert at the temperature and reaction conditions attaining in the reactional zone downstream from its point of entry. Under these conditions, naphtha (boiling between 100° and 430° F.) is sufficiently refractory to avoid any conversion of the naphtha. Although the previous inventions contemplate a further lowering of the hydrocarbon feed partial pressure while in the reaction zone by virtue of cracking of the gas oil, a significant lowering of the partial pressure from this source is delayed until after that residence time corresponding to the maximum selectivity range.

The present invention contemplates an unexpected further lowering of the vapor pressure of the gas oil or similar hydrocarbon feed by providing unique methods and means for the prior cracking of a naphtha diluent before admixture with the principal hydrocarbon feed.

Present trends in the petroleum industry have caused concern over possible shortages of light olefins. Although the aforementioned zeolitic aluminosilicates have demonstrated substantial increases in gasoline conversion, they tend to yield less light olefins and other light ends than the previously used amorphous silica-alumina catalysts. This applies with equal force to the aforedescribed, as

well as other prior catalytic cracking processes which employ zeolitic cracking catalysts. Concurrently with the present day downward trend in the production of light olefins, light olefins are experiencing an increased demand throughout the petroleum industry. The light olefinic ends find a most important use as sources of high octane alkylate for gasoline blending stocks, as well as for general petrochemical usage.

Our invention, therefore, further contemplates cracking of a naphtha stock in conjunction with the usual hydrocarbon feed in a catalytic cracking unit to obtain, unexpectedly, a higher yield of light olefinic ends. In this connection we have further discovered that the unconverted portion of the naphtha feed is unexpectedly upgraded from lower octane gasoline constituents to constituents having a significantly higher octane rating.

It is known, of course, that either a virgin or pyrolytic naphtha fraction can be cracked to obtain light olefins and for other purposes. The process, however, heretofore has been generally unrewarding as the naphtha fraction itself includes gasoline constituents, and, previously, there has existed no motivation for the charging of naphtha as feed stock into a catalytic cracking unit. In the usual or known cracking operation gasoline constituents are, of course, produced by the cracking of larger molecules. No process is known to us for the upgrading of existing gasoline constituents either alone or in conjunction with the usual hydrocarbon feed stocks to improve the octane rating of the naphthas. In point of fact, feeding of gasoline constituents into a conventional catalytic cracking unit has been carefully avoided in the past whenever possible. Further, the cracking of naphtha alone not only does not result in a significant upgrading of the gasoline rating, but is difficult to sustain on a continuous basis as the cracked naphtha deposits very little coke or residual carbon upon the fluidized catalyst. Although our present invention takes advantage of this fact, naphtha cracking by any of the known processes leaves an insufficient deposit of carbon on the catalyst to supply the heat required for reheating and regenerating the catalyst in the regenerating vessel.

We overcome these disadvantages of the prior art and accomplish the aforementioned desirable results by providing a fluidized catalytic cracking process wherein a hydrocarbon feed and diluent naphtha are added separately to adjacent reaction zones or at spaced locations within the same cracking reaction zone. The naphtha diluent, which is more refractory than the hydrocarbon feed at reaction temperatures of about 1000° F. and lower, preferably is added at a location of higher temperature so that it undergoes a significant cracking reaction prior to mixture with the hydrocarbon feed. Addition of the diluent naphtha is controlled such that the attendant temperature drop of the fluidized catalyst does not fall below that required for efficient vaporization and cracking of the gas oil charge. The respective points of introduction of the diluent naphtha and the hydrocarbon are sufficiently separated so that significant cracking and upgrading of the diluent naphtha occurs during the residence time of the flowing catalyst and diluent streams before the main hydrocarbon feed stream is encountered with attendant vaporization and cracking of the naphtha diluent leaves very little residual carbon upon the fluidized catalyst, and thus its efficacy for subsequent cracking of the hydrocarbon feed is substantially unimpaired. The vaporization and cracking of the diluent, moreover, affords additional mols of gas per unit weight of added diluent to provide a further and more advantageous lowering of the main hydrocarbon feed vapor pressure, with a given quantity of the diluent.

With our novel method, as briefly described above, we have been able unexpectedly to upgrade the quality of the unconverted naphtha derived from constituents of either a virgin or pyrolytic naphtha fraction, to increase the olefinic yield thereof, to lower advantageously the partial pressure of a hydrocarbon feed, to control the residence times of both the naphtha diluent and the hydrocarbon feed, and to increase the gasoline selectivity based upon a given hydrocarbon charge.

More specifically, in accordance with the present invention a preheated liquid hydrocarbon charge and a preheated fluidized zeolite or comparable cracking catalyst are added to a primary cracking reaction zone. The partial pressure of the hydrocarbon charge is established principally by the previous addition of diluent naphtha to the fluidized catalyst as described below. Further adjustment of the charge hydrocarbon partial pressure can be accomplished, if desired, by the concurrent addition of an inert diluent either directly to the primary reaction zone, to the charge inlet line, or to both. The character of the latter diluent, which can be steam, nitrogen, recycle methane or ethylene, etc., is such that, when used, it is gaseous under the conditions prevailing in the primary reaction zone.

In further accordance with the invention, a preheated diluent naphtha charge (boiling between about 100° F. and 430° F.) is added to the fluidized catalyst at a secondary cracking reaction zone, which, however, is disposed upstream of the primary reaction zone. At the point of its introduction into the secondary reaction zone, the fluidized catalyst stream is, therefore, at a substantially higher temperature. The naphtha diluent is substantially instantaneously vaporized and a substantial proportion thereof is almost immediately cracked and/or upgraded to low-boiling gasoline constituents, or cracked to the lighter olefins and other light ends. At the downstream end of the secondary reaction zone, the temperature of the combined fluidized catalyst and diluent stream has dropped to that which is appropriate for selectively cracking the principal hydrocarbon charge (usually a gas oil boiling between about 430° and 1100° F.) the principal hydrocarbon charge is likewise instantaneously vaporized upon its introduction into the aforementioned, primary reaction zone. The quantity of cracked naphtha diluent at the entrance to the primary reaction zone is sufficient to accomplish a substantial reduction of the partial pressure of the hydrocarbon charge. Cracking of the diluent in the preliminary or secondary reaction zone further lowers the partial pressure of the principal charge. As much as about 80% of the naphtha diluent can be cracked in the preliminary zone, which enhances the diluent function of the naphtha. Any required adjustment during the continuous cracking operation can be effected by varying the amount of naphtha diluent added to the upstream, secondary reaction zone, or alternatively, or in conjunction therewith, by adding or varying an inert gaseous diluent, which can be supplied at the inlet of or upstream from the downstream or primary reaction zone as noted above.

Owing to the reactive conditions to which the diluent naphtha is subjected by our novel process, a very wide range of naphtha compositions or gasoline fractions can be employed. Because our novel process exhibits increased selectivity to olefin production, particularly among the lighter ends, a naphtha having a preponderance of paraffins and other hydrocarbon saturates can be used. For this reason, a naphtha constituted of at least 70% by volume of saturates, and preferably higher, is a desirable diluent, as such compositions are less desirable for other purposes and yield an increased olefinic production. For the same reasons, a naphtha composed of 10% by volume or less, and preferably 5% or less, of olefins is desirable.

The selectivity to gasoline production of the cracking process is enhanced owing to the lower partial pressure of the principal hydrocarbon feed at the entrance of the primary reaction zone, wrought by the cracked naphtha diluent from the upstream or secondary reaction zone either alone or in combination with an inert diluent added at the inlet of or upstream from the downstream or primary reaction zone. To prevent subsequent loss of the selectivity advantage, both the diluent charge and the

principal hydrocarbon charge are permitted to remain in the presence of the catalyst only as long as further conversion of uncracked hydrocarbon produces a significant increase in gasoline yield. The system is controlled so that substantially at the time when further conversion of uncracked hydrocarbon produces no significant increase in gasoline yield or at the time when some decrease in gasoline yield ensues, the catalyst and hydrocarbon are substantially instantaneously disengaged from each other to prevent aftercracking of gasoline product (derived primarily from the hydrocarbon feed but also and to a limited extent from the uncracked portion of the naphtha diluent) from negating the selectivity advantage initially achieved owing to the partial pressure effect.

Analysis of the product to measure total conversion of both feed and diluent, or gasoline yield or both will aid in controlling the cracking reaction in accordance with this invention. These analyses will provide a measure of gasoline selectivity for controlling the reaction. Reaction time duration can be adjusted by regulation of cyclic catalyst rate, principal charge rate, diluent input rate, and the ratios therebetween, where the respective lengths of the primary and secondary reactor zones are fixed.

In accordance with this invention, the reactor is operated so that there is a continual increase in gasoline yield throughout substantially the entire length of the reactor coupled with a corresponding decrease in the unreacted proportion of the hydrocarbon feed. This permits the reaction to be terminated at or near the time of maximum gasoline yield. Significant backmixing in the primary and secondary reaction zones is avoided, as this would lead to aftercracking. Backmixing can result from an excessive linear velocity and attendant turbulence, or by the formation of a dense catalyst bed which induces turbulence in the flowing vapors. The principal hydrocarbon charge and the diluent remain in the primary reaction zone only until a decrease in the proportion of unreacted feed is not accompanied by any substantial net increase in gasoline yield. Maximum gasoline yield is accompanied by maximum gasoline selectivity.

The overall time of contact between principal hydrocarbon charge and catalyst can be as low as about 0.5 second or less but not greater than about 5 seconds and will depend upon many variables in a particular process such as the boiling range of the charge, the particular catalyst, the amount of carbon on the regenerated catalyst, the catalyst activity, the reaction zone temperature, and quantity of polynuclear aromatics. The reaction should be permitted to proceed long enough to crack any mono- or di-aromatics or naphthenes because their reaction products result in relatively high gasoline yields and are the most readily crackable aromatics, but the reaction should be terminated before significant cracking of other polynuclear aromatics occurs, as cracking of these latter compounds occurs at a slower rate and results in excessive deposition of carbon on the catalyst. It is clear that no fixed cracking time duration can be set forth but the time will have to be chosen within the aforesaid range depending upon the particular system. In one system, even slightly exceeding a 1.0 second residence time might result in such severe aftercracking that the selectivity advantage would be lost, while in another system unless a 1.0 second residence time is appreciably exceeded there might not be sufficient cracking of charge hydrocarbon to render the process economically advantageous. Generally, the residence time will not exceed 2.5 or 3 seconds and 4 second residence times will be rare.

We accomplish these desirable results by providing a process for cracking a principal hydrocarbon charge capable of being cracked to gasoline in the presence of a fluidized cracking catalyst, said process comprising the steps of maintaining a predetermined range of temperatures within said catalyst stream, adding a naphtha diluent to said catalyst stream, controlling the partial pressure of said charge in said stream by maintaining a given ratio of said diluent to said charge, and adding said diluent to said catalyst stream at a point having a higher temperature than that at which said charge is added so that a significant proportion of each of said naphtha and said charge is cracked by said catalyst.

We also desirably provide a similar process including the additional steps of establishing a ratio of said naphtha diluent and the conversion products thereof to said principal charge and of establishing a residence time of said principal charge such that a greater percentage yield of gasoline based on total hydrocarbon feed is recovered from said process in the presence of said naphtha diluent and its conversion products than could be recovered from said process in the absence of said naphtha diluent.

We also desirably provide a similar process including the additional step of establishing the ratio of said naphtha diluent and its conversion products to said principal charge such that a greater percentage yield of lighter olefins based on total hydrocarbon feed is recovered from said process in the presence of said naphtha diluent than could be recovered from said process in the absence of said diluent.

We also desirably provide a similar process including the additional step of establishing the ratio of said naphtha diluent to said principal charge and a predetermined temperature and residence time of said diluent in said catalyst stream prior to engagement with said principal charge such that the octane rating (quality) of the unconverted proportion of said naphtha diluent is upgraded.

We also desirably provide a similar process including the modified step of adding said naphtha diluent in the range of about 5 percent to about 45 percent by volume of the total hydrocarbon feed.

We also desirably provide in a catalytic cracking plant, the combination comprising conduit means for defining a primary reaction zone and for adding a principal hydrocarbon feed thereto, additional conduit means for defining a secondary reaction zone upstream of said primary zone and for adding a diluent hydrocarbon feed thereto, and catalyst conduit means connecting said zones for circulating a catalyst stream successively through said secondary and said primary zones.

During the foregoing discussion, various objects, features and advantages of the invention have been set forth. These and other objects, features and advantages of the invention together with structural details thereof will be elaborated upon during the forthcoming detailed description of certain presently preferred embodiments of the invention and presently preferred methods of practicing the same.

In the accompanying drawings we have shown certain presently preferred embodiments of the invention and have illustrated certain presently preferred methods of practicing the same, wherein:

FIG. 1 is a graphical representation of the variation in unreacted charge and gasoline yield versus reactor residence time, pursuant to one aspect of my invention;

FIG. 2 is another graphical representation illustrating the effect of variation in partial pressure of hydrocarbon feed upon debutanized gasoline yield and total conversion rate; and

FIG. 3 is a schematic apparatus and fluid flow diagram of an exemplary catalytic cracking operation arranged according to my invention.

A reference to FIGS. 1 and 2 will illustrate the significant improvement wrought by the present invention.

FIG. 1 contains curves semi-quantitatively relating the amounts of unreacted charge and gasoline, as a percentage of fresh feed, to reaction zone residence time. Curve *a* of a unreacted principal charge, typical of most fluid cracking charge stocks, shows that the amount of unreacted charge (curve *a*) asymptotically approaches a value somewhat less than 20 percent of fresh feed within the residence times contemplated by our novel process. The

gasoline curves show that the quantity of gasoline produced rapidly reaches a somewhat rounded maximum or peak which generally coincides with the time at which the cracking rate of unreacted charge becomes substantially diminished. The gasoline yield at the peak for a given charge will be determined primarily by reactor temperature, to an extent by the level of carbon on the catalyst, and to an extent by the catalyst-to-oil ratio. After reaching a peak the gasoline level diminishes because the aftercracking of gasoline predominates over production of gasoline from the unreacted feed. The lower gasoline curve *b* shown in FIG. 1 indicates that level of gasoline which would attain in the reaction zone, assuming substantially no diluent naphtha is introduced. The upper gasoline curve *c* shows the higher gasoline level achieved by adding the naphtha diluent to the cracking process to lower the principal hydrocarbon charge partial pressure and thereby to increase selectivity to gasoline. A still larger gasoline yield, attainable with our present invention results when the increase in light olefin yield, also provided by this invention, is converted into gasoline by alkylation.

To illustrate the advantages of controlling residence time and principal charge partial pressure, it will be assumed that a fluid cracking process is opertaing with addition of diluent naphtha to the secondary reaction zone (with or without direct diluent addition to the primary reaction zone) and the gasoline yield is at point A shown in FIG. 1 where significant aftercracking has occurred. In order to reduce the extent of aftercracking, it is decided to increase the charge rate of hydrocarbon into the primary reaction zone, thereby reducing the hydrocarbon residence time. In conventional processes, residence time is usually adjusted by changing the hydrocarbon charge rate rather than diluent charge rate since for any given percentage increase or decrease in charge rate of diluent or hydrocarbon, the effect upon reaction residence time will usually be much greater in the case of the hydrocarbon adjustment because the total amount of hydrocarbon charged is usually much greater than the total amount of diluent charged. Owing to the shorter residence time and concomitant reduction in aftercracking, a higher gasoline yield B is achieved. However, because the hydrocarbon partial pressure at the primary reaction zone inlet has been increased by an increase in hydrocarbon flow rate, the point B is removed from the upper gasoline curve *c* in the direction of the lower gasoline curve *b* and is outside the cross-hatched zone *e* (FIG. 1) which denotes a range of improvement proffered by this aspect of the invention. The cross-hatched zone *e* denotes the transient elevated gasoline yields which can be recovered by the use of diluent vapor or combination of vapors but which could not be recovered in the absence of such vapor or vapors. On the other hand, if the same decrease in hydrocarbon residence time were achieved by increasing both the principal hydrocarbon and diluent flow rates in the same ratio so that the partial pressure of the principal hydrocarbon charge at the reaction zone inlet remained unchanged at the new residence time, the new operating point would be at B′, instead of B, which is within the aforementioned range of diluent improvement. On the other hand, if the same total flow rate were achieved by increasing the ratio of the naphtha and naphtha conversion products (by prior cracking of naphtha diluent) to principal hydrocarbon charge the new operating point would be above *b′*, and of course the area covered by the cross-hatched zone E of FIG. 1 would be enlarged. Now, if the hydrocarbon charge rate is again increased in a conventional cracking operation, to further reduce residence time, a point C is reached which is still further removed from the middle gasoline curve C in the direction of the lowest gasoline curve B than is point B because the hydrocarbon partial pressure has been further and disadvantageously increased in going from point B to point C. Again, because of the increase in hydrocarbon partial pressure, point C is outside the optimum selectivity range of my novel process. On the other hand, if the same residence time indicated at point C is achieved by increasing the flow rates of both diluent and hydrocarbon, rather than hydrocarbon alone, so that the hydrocarbon partial pressure at the new residence time is the same as it was at point A, the point C′ is achieved which is within the optimum selectivity range. Again, the prior cracking of naphtha diluent according to the present invention, results in a further lowering of partial pressure and attendently higher gasoline selectivity.

It is seen from FIG. 1, that the operating points B and C, provided by conventional processes, represent essentially similar gasoline conversion levels occurring at different residence times, and one might readily make the erroneous assumption that these points define a flat maximum gasoline yield, however, points B and C lie outside the range of the present invention whereas operating points B′ and C′ fall within the optimized selectivity range of this invention. Thus points B′ and C′ lie at higher gasoline yield levels than points B and C, even though points B and B′ and points C and C′ represent the same residence times, respectively. Starting from point A, point B′ is reached by the method of lowering residence time via a change in both diluent flow rate and principal hydrocarbon flow rate while, also starting from point A, point B is reached by the method of changing the hydrocarbon flow rate only to achieve the same residence time as point B′. Starting from point B′, point C′ is reached by changing both diluent flow rate and hydrocarbon flow range to lower the residence time, while point C is reached by the simpler and conventional method of changing the hydrocarbon flow rate only to achieve the same residence time as at point C′. It is apparent that to achieve the aforementioned gasoline selectivity advantage the residence time and the apportioning of diluent and hydrocarbon flow rates to achieve said residence time are interdependent and represent a critical combination for purposes of process control.

In making the aforementioned changes in diluent flow rate to maintain a constant partial pressure of the hydrocarbon charge or to reduce the partial pressure thereof, it is within the scope of the present invention to vary the flow rate of the diluent naphtha which supplied to the inlet of the secondary reaction zone for subsequent mixing of both unreacted naphtha and cracked naphtha product with the hydrocarbon charge at the entrance to the primary reaction zone, i.e., where the effluent from the secondary zone enters the primary reaction zone. It is also contemplated that the total diluent added to the process can comprise the aforementioned naphtha diluent plus a minor quantity of an inert diluent or additional naphtha diluent added directly to the entrance of the primary reaction zone or alternatively or in combination therewith added directly to the hydrocarbon feed stream prior to its delivery to the primary reaction zone. Thus, in accordance wtih my invention, the diluent to hydrocarbon ratio can be modified by adjusting the feed rate of naphtha diluent to the secondary reaction zone, by adjusting diluents (if used) supplied directly to the primary reaction zone, by adjusting diluents (if used) supplied directly to the hydrocarbon feed stream, or by a combination of two or more of these.

The reaction temperature in the primary reaction zone, in accordance with this invention can range between about 900° F. and about 1100° F. Desirably, the temperature range is maintained between 950° F. and 1000° F. The total pressure in the primary reaction zone can vary widely and can be for example 5–50 p.s.i.g. or preferably 20–30 p.s.i.g. The total pressure in the preliminary or secondary reaction zone (where the naphtha diluent is cracked in the absence of principal hydrocarbon charge) desirably is maintained within the range of 5 to 50 p.s.i.g. The maximum residence time in the primary reaction zone is 5 seconds and for most charge-stocks, the residence time will be about 1.5–2.5 seconds in most

cases or, less commonly, 3–4 seconds. For high molecular weight charge stocks which are rich in aromatics, a 0.5–1.5 second residence time is suitable in most cases in order to crack mono- and di-aromatics and naphthenes which are the aromatics which crack most easily and which produce the highest gasoline yield, but to terminate the operation before appreciable cracking of polyaromatics occurs because these materials produce high yields of coke, C_2 and lighter gases.

In order to minimize the deposition of coke on the catalyst in the preliminary or secondary reaction zone, the maximum residence time of the combined catalyst and diluent stream therein, is limited to a range of about 2 seconds to about 20 seconds and preferably to 2–10 seconds. Limitation of the residence time in the secondary reaction zone in this manner maximizes the conversion of the naphtha diluent but minimizes the reduction in catalytic effect of the zeolitic material when subsequently engaged to the principal hydrocarbon charge at the entrance to the primary reaction zone. Limiting the residence time in the secondary reaction zone also avoids aftercracking of the naphtha diluent and attendant production of C_2 and lighter gases, and coke. The quantity of naphtha diluent, added to the entrance of the secondary reaction zone can vary between about 5 and about 45 percent by volume (with about 5–20% being preferred) based on the total hydrocarbon (gas oil plus naphtha) charge. The ratio of diluent naphtha to primary hydrocarbon charge can be varied depending upon the desired extent of partial pressure depression of the primary charge. Preferably, the quantity of diluent naphtha added to the secondary reaction zone is limited to about 45 percent by volume in order to provide an adequate residence time in the secondary reaction zone and to limit the yields of coke and C_2 and lighter gases. In accordance with the invention additional diluents, where desirable, can be added by injecting either a naphtha diluent or an inert such as one of those mentioned previously at the entrance of the primary reaction zone or preliminarily into the hydrocarbon feed stream.

The length to diameter ratio of the primary reaction zone can vary widely, but the reactor should be elongated to provide a high linear velocity, such as 25–75 feet per second, and to this end a length to diameter ratio above 20 or 25 is suitable. The primary reaction zone can have a uniform diameter or can be provided with a continuous taper or a step-wise increase in diameter along the reaction path to maintain a nearly constant velocity along the flow path. The amount of diluent supplied to the secondary reaction zone or concurrently to both reaction zones can vary depending upon the ratio of primary hydrocarbon to diluent desired for control purposes.

In accordance with the invention, the temperature of the initially admixed catalytic and naphtha diluent stream at the entrance to the secondary reaction zone is maintained in the neighborhood of about 250° F. higher than the fluid stream temperature adjacent the entrance of the primary reaction zone. A desirable temperature range at this point in the secondary reaction zone is 1200–1250° F. although the secondary reaction zone can be operated with a substantial degree of success in the temperature range of about 1100°–1300° F. The higher temperature range in the secondary reaction zone is desirable to promote cracking of either virgin or pyrolytic diluent naphtha.

Cracking of the more refractory naphtha, which is occasioned by the higher temperature range in the secondary zone, results in increased mols of gases from a unit weight of naphtha diluent which further lowers the partial pressure of the subsequently added, principal hydrocarbon feed in the primary reaction zone, while minimizing the quantity of naphtha diluent initially added to the secondary reaction zone. The higher temperature maintained in the initial stages of the secondary reaction zone also increase the selectivity of the cracking reaction in the secondary zone to light olefins. As noted previously, an increased olefinic production is extremely advantageous in maximizing the ultimate gasoline production from cracking and attendant alkylation operations. Notwithstanding the higher cracking temperature in the secondary reaction zone, the deposition of coke from the naphtha diluent upon the catalyst is extremely low so that the efficacy of the catalyst for subsequently cracking the principal feed is substantially unimpaired. In the primary reaction zone, at least half of the heat of the catalyst is immediately taken up by vaporization of the hydrocarbon feed and the remainder is applied to cracking the feed. The heat of vaporization of gas oil for example is about the same as the heat of the cracking reaction or about 80 B.t.u. per pound for cracking in comparison with about 90 B.t.u. per pound for vaporization. Thus, little heat is available for cracking or aftercracking of the naphtha diluent, when the latter enters the primary reaction zone. The desirability of adding the naphtha and gas oil at spaced locations in the reactional system is thereby apparent.

The boiling point of the naphtha diluent can vary characteristically between about 100° F. and about 430° F. It follows that the naphtha diluent itself is in the gasoline boiling range. As a practical matter that portion of the naphtha fraction having a lower octane rating or which is otherwise unsuitable for various reasons as a gasoline constituent is preferably used as a diluent. For example, a lighter naphtha fraction (e.g., one boiling between 100° F. and 290° F.) can be employed where the ultimate gasoline blend is destined for warmer climates or seasons, in which blend the lighter naphtha fraction is not ordinarily desirable. Conversely, in the production of gasolines which are blended for use in colder climates or seasons, the heavier naphtha fraction (e.g., boiling between 290° F. and 430° F.) is more desirable for diluent purposes, as the aforementioned lighter fraction then becomes more suitable as a gasoline constituent.

The use of the naphtha dilutent in the aforedescribed manner, i.e., by cracking the naphtha diluent in a secondary or preliminary reaction zone, is desirable from other standpoints in addition to the beneficial lowering of the hydrocarbon feed partial pressure. Up to about 80 percent of the diluent naphtha can be cracked selectively in the secondary reaction zone without impairing the reaction in the primary cracking zone. In our novel cracking operation there is an unexpected and significant upgrading of a portion of the naphtha or gasoline material to more desirable gasoline constituents, which unexpectedly raises the octane rating of that portion of the gasoline product. We deem this to be a surprising result as conventional cracking operations heretofore have produced gasoline from larger non-gasoline molecules rather than an upgrading of existing gasoline constituents. A significant and increased production of C_3, C_4 and C_5 olefins results from the cracking operation, according to my present invention, which can be subsequently alkylated to provide a further quantity of desirable gasoline constituents. Although a lesser quantity of naphtha diluent desirably is used, we have successfully employed as much as about 45 percent by volume of diluent naphtha, based on the combined initial liquid charge to the primary and secondary reaction zones, and have achieved unexpectedly advantageous conversion rates, gasoline yield, octane rating, and olefin production. On the other hand, the amount of coke deposited upon the fluidized catalyst by cracking of the diluent naphtha in the preliminary or secondary reaction zone was less than 0.1 percent by weight with a diluent naphtha proportion as high as about 45 percent.

A zeolite catalyst is a highly suitable catalytic material for use with this invention. A mixture of natural and synthetic zeolites can be employed. Also a mixture of crystalline zeolitic organosilicates with non-zeolitic amorphous

silica alumina is suitable as a catalytic entity. Any catalyst containing zeolitic material or otherwise which provides a transient maximum gasoline yield within a 5 second residence time is suitable. The catalyst particle size must render it capable of fluidization as a disperse phase in the reactor. Typical and non-limiting fluid catalyst particle size characteristics are as follows:

Size (microns):	Wt. percent
0–20	0–5
20–45	20–30
45–75	35–55
>75	20–40

These particle sizes are usual and have not been preselected for this invention. A suitable weight ratio of catalyst to primary charge is about 4:1 to about 12:1 or 15:1 or even 25:1, generally; or 6:1 to 10:1, preferably. On the other hand the weight ratio of catalyst to naphtha diluent can vary between about 15:1 and about 100:1. The fresh hydrocarbon feed is generally preheated to a temperature of about 600° F. to 700° F. but is generally not vaporized during preheat, and the additional heat required to achieve the desired reactor temperature is imparted by the still hot, regenerated catalyst and added diluent, issuing from the seconary reaction zone.

The weight ratio of catalyst to hydrocarbon charge is varied to affect variations in reactor temperature. Furthermore, the higher the temperature of the regenerated catalyst the less catalyst is required to achieve a given reaction temperature. Therefore, a high regenerated catalyst temperature will permit the very low reactor density level set forth below and thereby help to avoid backmixing in the reactor. Generally, catalyst regeneration can occur at an elevated temperature of about 1240° F. or 1250° F. or more to reduce the level of carbon on the regenerated catalyst from about 0.6 to 1.5 to about 0.05 to 0.3 percent by weight. At usual catalyst to oil (naphtha and gas oil) ratios the quantity of catalyst is more than ample to achieve the desired catalytic effect, in both the primary and secondary reaction zones, and therefore if the temperature of the catalyst is high, the ratio can be safely decreased without impairing conversion. Since zeolitic catalysts are particularly sensitive to the quantity of carbon deposited thereon, regeneration advantageously occurrs at elevated temperatures in order to lower the carbon level on the catalyst to the stated range or lower. Moreover, since an important function of the catalyst is to contribute heat to the reactor, for any given desired series of reaction zone temperatures the higher the temperature of the catalyst charge the less catalyst is required, the lower the catalyst charge rate, and the lower the density of the material in the reaction zones. As stated, low reaction zone densities help to avoid backmixing.

The reactor linear velocity, while not being so high that it induces turbulence and excessive backmixing, must be sufficiently high that substantially no catalyst accumulation or build-up occurs in either reaction zone because such accumulation itself leads to backmixing. Therefore, the catalyst to hydrocarbon weight ratio at any position throughout each of the reaction zones desirably is maintained about the same. Stated another way, catalyst and hydrocarbon at any linear position along the reaction path in each cracking zone both flow concurrently at about the same linear velocity, thereby avoiding significant slippage of catalyst relative to the hydrocarbon component. A build-up of catalyst in either reaction zone leads to a dense bed and backmixing which in turn increases the residence time in that zone for at least a portion of the charge and induces aftercracking. Avoiding a catalyst build-up in the reaction zones results in a minimal catalyst inventory in the reactor, which in turn results in a high space velocity. Therefore, a space velocity of over 100 or 120 weight of primary hydrocarbon feed per hour per weight of catalyst inventory and about 200 to 2000 (normally around 1000) weight of diluent naphtha feed per hour per weight of catalyst inventory, is highly desirable. In the primary reaction zone the space velocity should not be below 35 and can be as high as 500 with reference to the combined gas oil and naphtha diluent. Owing to the low catalyst inventory and low charge ratio of catalyst to total hydrocarbon, the density of the material at the inlet of the primary reaction zone where the feed is charged can be as low as about 1 to less than 5 pounds per cubic foot, although these ranges are non-limiting. An inlet density in the secondary zone, where the diluent naphtha and catalyst is charge, below 4 or 4.5 pounds per cubic foot is desirable since this density range is too low to encompass dense bed systems, which induce backmixing. Although conversion falls off with a decrease in inlet density to very low levels, the extent of aftercracking is a more limiting feature than total conversion of fresh feed, even at an inlet density of less than 4 pounds per cubic foot. At the outlet of either reaction zone the density of the corresponding fluid stream will be about half the density at the inlet because the cracking operation in either the naphtha diluent or the gas oil charge produces about a fourfold increase in mols of gaseous hydrocarbons. The decrease in density through either reaction zone can be a measure of the related conversion.

A wide variety of hydrocarbon oil charge stocks can be employed. A suitable primary charge is a gas oil boiling in the range of 430° F. to 1100° F. As much as 5 to 20 percent of the fresh charge can boil above this range. Some residual oil can be charged. A zero to 5 percent recycle rate can be employed. Generally, the recycle will comprise at least 650° F. oil from the product distillation zone which contains catalyst slurry. If there is no catalyst entrainment, recycle can be omitted.

Tests have been conducted, as set forth in detail in the aforementioned copending application, to illustrate the advantage of the crystalline zeolite aluminosilicate catalyst over an amorphous silica-alumina catalyst in a fluid catalytic cracking system. The zeolite catalyst system exhibited a higher conversion rate (85.5 percent compared to 75.5 percent) and a higher gasoline yield (61.0 percent to 47.5 percent). However, while the total yield of C_3 and C_4 hydrocarbons is about the same for the zeolite and the amorphous catalyst systems, the proportion of C_3 and C_4 hydrocarbons which are olefinic is lower when utilizing a zeolite catalyst. As noted previously, this represents a disadvantageous feature of the zeolite catalyst because C_3 and C_4 olefins are useful for the production of alkylate which can be blended with the gasoline produced directly by cracking to improve its octane rating. As mentioned previously, the disadvantageous lessening of olefin production with zeolite catalyst systems is more than counterbalanced by light olefinic yields from cracking of the naphtha diluent.

A series of tests have been conducted which illustrate the effect of hydrocarbon partial pressure (reduced with an inert diluent) upon selectivity to debutanized gasoline and to C_3 plus liquid yields. The charge stock inspections and other test conditions are detailed in the aforementioned copending application.

The results of the tests are illustrated in FIG. 2 in which debutanized gasoline yield and total C_3 plus liquid yield, both recorded as percent by volume of fresh feed, are plotted against total conversion at various partial pressures of hydrocarbon in the system and at various residence times. The pressure ranges given on the face of the graphs indicate the partial pressure in the system of all primary hydrocarbon vapors, cracked and uncracked. For each partial pressure, conversion data is indicated for one or more residence times.

As shown in FIG. 2, at any given conversion level the selectivity to gasoline as well as to total C_3 plus liquid increases with decreasing hydrocarbon partial

pressure. Taking a 60 percent conversion level for purposes of example, when the hydrocarbon partial pressure is 16–20 p.s.i.g., the gasoline yield is 47.5 percent; when the hydrocarbon partial pressure is 10–14 p.s.i.g. the gasoline yield increases to almost 50 percent; and when the hydrocarbon partial pressure is 2–5 p.s.i.g. the gasoline yield increases still further to about 51.5 percent. Advantageously, a greater improvement in gasoline selectivity occurred in reducing hydrocarbon partial pressure from 16–20 p.s.i.g. to 10–14 p.s.i.g. than occurred in reducing the hydrocarbon partial pressure from 10–14 p.s.i.g. to the very low partial pressure of 2–5 p.s.i.g.

Example I

To demonstrate the efficacy of our invention in upgrading "unconverted" naphtha, in increasing gasoline yield and increasing olefinic production, we have run tests utilizing a virgin, paraffinic naphtha as diluent material and a full range gas oil as primary hydrocarbon charge. The naphtha was charged in sufficient quantity to evaluate yields and was for test purposes 44.4 volume percent of the total charge. The naphtha was preliminarily cracked at 1200° F. for 2 seconds in the lower portion of the transfer line of the apparatus described below in connection with FIG. 3, which corresponds to the aforementioned preliminary or secondary reaction zone. The gas oil was cracked at 1000° F. for 0.5 in the riser portion of the apparatus, i.e., the primary reaction zone. The cracked naphtha was, of course, added to the gas oil at the entrance of the primary reaction zone to reduce the partial pressure of the gas oil. The aforementioned pilot plant run was compared with a similar run using gas oil only, and the complete results of the two runs are set forth in the following table.

TABLE I

Run Number	Combined feeds I	Gas oil only II
Charge stock:		
Naphtha charge rate, gm./hr.	360	636
Gas oil charge rate, gm./hr.	450	----------
Catalyst; cracking conditions:		
Transfer line temperature, ° F.:		
Top	1,000	1,000
Bottom	1,200	1,000
Contact time, seconds:		
Gas oil charge	0.5	2.5
Naphtha charge	2.5	----------
Cat/oil ratio, wt./wt.:		
On fresh feed	8.2	8.7
On total feed	8.2	8.7
Total charge rate, g./hr.	810	636
Dispersion steam, lb./1,000 lb. catalyst	6.0	3.6
Stripping steam, lb./1,000 lb. catalyst	6.1	7.3
Stripping N^2 as steam, lb./1,000 lb. catalyst	5.1	6.1
Catalyst circulation rates, gm./hr.:		
Calculated catalyst circulation	5,584	4,587
Measured catalyst and coke circulation	6,648	5,568
Coke-free measured catalyst circulation	6,615	5,530
Carbon on spent catalyst, weight percent percent on catalyst	0.501	0.689
Carbon on regeneration catalyst, weight percent on catalyst	0.183	0.219
Operating conditions, regeneration:		
Average temperature, ° F.	1,149	1,149
Average pressure, p.s.i.g.	29.6	29.6
Miscellaneous data:		
Uncorrected weight balance	99.1	97.1
Stabilized gasoline, weight percent of fresh feed	56.0	53.0
Hydrocarbon gas, weight percent of fresh feed	27.1	20.4
Total stabilizer gas, s.c.f.	201.45	131.19
HC gas gravity	1.423	1.370
C_4 in actual 10 RVP gasoline, volume percent	3.84	4.32
C_4 in actual 10 RVP gasoline, weight percent	2.79	2.81
10 RVP gasoline, weight percent	61.2	56.0
Knock rating [adjusted to 10 Reid Vapor Pressure (RVP)]:		
Motor octane numbers:		
Clear	79.7	83.9
+3 cc. TEL	86.0	87.5
Research octane numbers:		
Clear	87.6	95.6
+3 cc. TEL	94.6	99.7
Conversion, volume percent of fresh feed (100-gas oil)	88.1	80.1

TABLE I—Continued

Run Number	Combined feeds I	Gas oil only II
Yields, volume percent of fresh feed (corrected to 100 weight percent balance):		
Debutanized gasoline distribution	65.9	64.2
Isopentane	6.6	7.4
n-Pentane	4.1	0.7
Pentenes-Pentenes	4.5	3.9
Hexanes and heavier	50.9	52.1
Butane-Butene	16.9	16.3
Isobutane	5.6	7.1
n-Butane	2.1	2.1
Butenes	9.2	7.2
Propane-propylene	13.8	11.5
Propane	4.6	2.7
Light catalyst gas oil	3.2	13.6
Heavy catalyst gas oil	0.0	0.0
Decanted oil	8.7	6.3
Total volume percent received	108.4	112.0
10 RVP gasoline distribution	69.7	68.5
Excess butane-butene	13.1	12.0
Gas (C_4 and lighter), weight percent	24.7	20.2
Gas (C_2 and lighter), weight percent	3.6	3.2
Hydrogen, weight percent	0.06	0.06
Carbon, weight percent	2.6	4.1
Coke (0.9 carbon, 0.1 H_2), weight percent	2.9	4.5
H_2S, weight percent; Unit Efficiency (volume percent of conversion):		
Debutanized distribution	74.8	80.2
Depropanized distribution	93.9	100.6
Yield data; percent on fresh feed:		
Debutanized gasoline distribution	58.45	53.19
Isopentane	5.05	5.10
n-Pentane	3.22	0.49
Pentenes	3.42	2.79
Hexanes and heavier	46.76	44.82
Butane-butene	12.31	10.50
Isobutane	3.87	4.36
n-Butane	1.50	1.33
Butenes	6.94	4.81
Gas (C_3 and lighter)	12.38	9.72
Methane	1.76	1.43
Ethane	0.71	0.86
Ethylene	1.08	0.85
Propane	2.88	1.48
Propylene	5.88	5.04
Light catalyst gas oil	3.67	14.62
Heavy catalyst gas oil	0.00	0.00
Decanted oil	10.30	7.42
Product inspections:		
Debutanized gasoline, gravity: °API	63.5	55.5
Hydrocarbon type analysis, volume percent:		
Aromatics	20.5	32.5
Olefins	19.0	14.0
Saturates	60.5	53.5
Reid vapor pressure, p.s.i.	5.9	6.6
Micro octane number:		
Motor +0.5 g.p.b./gal	79.0	83.6
Motor +3.0 g.p.b./gal	85.1	86.8
Research +0.5 g.p.b./.gal	86.7	95.3
Research +3.0 g.p.b./.gal	93.3	99.0
Distillation, D 86:		
Over point, ° F.	116	955
End point, ° F.	379	412
10% at, ° F.	145	133
50%	192	226
90%	304	368
Recovery, percent	99.0	97.3
Residue, percent	0.6	0.8
Loss, percent	0.4	1.9
Light catalytic gas oil:		
Gravity, ° API	20.2	13.0
Sulfur, weight percent	0.73	0.92
Viscosity, SUS at 100 F.	33.8	38.5
Carbon residue, D 524 10% Btms., weight percent		0.51
Pour point, ° F.	−35	−10
Distillation, D 86:		
Over point, ° F.		
End point, ° F.		720
10% at, ° F.		486
50% at, ° F.		536
90% at, ° F.		649
Decanted oil:		
Gravity, °API	14.8	0.5
Sulfur, weight percent	0.97	1.46
Carbon residue, Rams. bottom, weight percent	0.55	5.50
Distillation, vacuum corrected to 760 mm. Hg.):		
10% at, ° F.	615	640
30% at, ° F.	673	699
50% at, ° F.	716	747
70% at, ° F.	776	815
90% at, ° F.	869	944

The results of these tests can be summarized as follows:

(1) The conversion of the naphtha diluent to C_3 and C_4 gases was estimated at 32 volume percent.

(2) Selectivity to C_3 and C_4 olefinic production is estimated to be 62.5 percent based on the naphtha charge.

(3) Improvement in quality or upgrading of the unconverted naphtha was obtained.

(4) Improvement in the cracking of the gas oil charge was obtained owing to the reduced partial pressure in the primary reaction zone or riser.

The charge to the transfer line or secondary reaction zone of the fluidized catalyst cracking plant consisted for the purpose of the test run of 44.4 volume percent virgin Kuwait naphtha (105–290° F.) and 55.6 volume percent South Louisiana full-range gas oil.

Inspections of the naphtha charge stock are shown in the following table:

TABLE II.—NAPHTHA CHARGE STOCK INSPECTIONS

Run Number	I
Charge stock	Naphtha
Characterization factor	12.54
Gravity, ° API	73.4
Hydrocarbon Analysis, D 1319, vol percent:	
Aromatics	3.5
Olefins	0.5
Saturates	96.0
Hydrocarbon analysis, ASTM D 2427, wt. percent:	
Propane	0.01
i-Butane	0.15
n-Butane	1.50
i-Pentane	5.54
n-Pentane	3.60
C_6 and heavier	89.20
Hydrocarbon analysis, ASTM 1956, vol percent:	
Paraffins	77.4
Cycloparaffins	18.6
Bicycloparaffins	0.0
Alkylbenzenes	4.0
Benzene	0.8
Toluene	3.0
C_8 Alkylbenzenes	0.3
Total	100.0
Distillation, D 86, F:	
Over point	105
End point	293
Over at:	
10%	143
30%	162
50%	180
70%	198
90%	222

The inspections of the gas oil charge stock are set forth in the following table:

TABLE III.—GAS OIL CHARGE STOCK INSPECTIONS

Run Number:	I	II
Charge stock (Southern Louisiana gas oil):		
		Same as Run No. 1.
Characterization factor	11.81	Do.
Gravity, °API	23.5	Do.
Sulfur, GRM 1156, wt. percent	0.58	Do.
Viscosity, SUS at, F.:		
130		
150	91.0	Do.
210 210	48.9	Do.
Carbon residue, Rams., ASTM D 524, wt. percent	0.19	Do.
Aniline point, GRM 139, F	186	Do.
Bromine number, D 1159	3.31	Do.
Pour point, D 97, F	70	Do.
Refractive index, GRM 2413, nd at 20 C.	1.5095	Do.
Nitrogen, p.p.m.:		
Total, GRM 1121	640	Do.
Basic, GRM 1152	237	Do.
Metals, p.p.m.:		
Vanadium, GRM 803	<0.1	Do.
Nickel, GRM 803	<0.1	Do.
Distillation, vac. (corr. to 760 mm. Hg):		
Over point, F		Do.
Over at, F:		
10%	688	Do.
30%	745	Do.
50%	805	Do.
70%	873	Do.
90%	944	Do.
Catalyst		
Kellogg activity	53.5	Do.
Carbon factor (C)	0.53	Do.
Carbon factor (H)	0.62	Do.
Hydrogen factor	1.59	Do.

The naphtha stock was charged to the bottom injector of the transfer line, as shown in FIG. 3, and cracking occurred at 1200° F., utilizing in this case a 25:7 catalyst-oil ratio, and a two-second residence time. The gas oil, on the other hand, was charged to the bottom of the riser line 10 (as shown in FIG. 3), and cracking occurred in the gas oil and admixed effluent from the preliminary

reaction zone at 1000° F., with an 8:2 catalyst-oil ratio, and a 0.5 second residence time. The 0.5 second residence time was less than optimum and resulted primarily from the rather larger proportion of added diluent. In the control run, in which the charge consisted of gas oil only, cracking occurred at 1000° F., with an 8:7 catalyst-oil ratio and a residence time of 2.5 seconds.

A comparison of the results of the combined naphtha gas oil run and the gas-oil only run are summarized in the following table:

TABLE IV.—NAPHTHA-GAS OIL VERSUS GAS OIL CRACKING COMPARISON

	Naphtha-gas oil run	Gas oil run
Cracking conditions		
Charge stock	(1)	(2)
Percent of total charge	44.4	100.0
Temperature, F	1,200	1,000
Cat./oil ratio, wt./hr./wt	25.7	8.7
Contact time, seconds	2.0	2.5
Charge stock	(2)	
Percent of total charge	55.6	
Temperature, F	1,000	
Cat./oil ratio, wt./hr./wt	8.2	
Contact time, second	0.5	
Conversion, vol. percent:		
gas oil[3]	78.6	80.1
Naphtha	[4]32.0 [5](50.7)	
Total[3]	88.1	80.1
Product distribution, vol. percent:		
Total C_3	13.8	11.5
C_3=	9.1	8.8
Total C_4	16.9	16.4
C^4=	9.2	7.2
C^5+ gasoline	65.9	64.2
Total C_3+ volume	108.4	112.0
C_2 and lighter, wt. percent	3.6	3.2
Coke, wt. percent	2.9	4.5

[1] Kuwait light naphtha.
[2] Southern Louisiana gas oil.
[3] Conversion to 430° F. and lighter.
[4] Conversion to C_4 and lighter.
[5] Conversion to C_5 and lighter.

From the preceding table a significant increase in C_3 and C_4 olefins can be noted for the naphtha-gas oil run. It is noted also that the cracking of the gas oil charge in the experimental run was enhanced, in view of an estimated conversion of 78.6 percent at a 0.5 second residence time in the naphtha-gas oil run, which compares very favorably with an 80.1 percent conversion at a considerably longer and more nearly optimum residence time of 2.5 seconds in the control run.

In the following table the gasoline product quality of the experimental naphtha-gas oil run is compared to a typical gasoline quality obtained from the control run:

TABLE V.—NAPHTHA-GAS OIL VERSUS OIL CRACKING COMPARISON

	Naphtha-gas oil run	Gas oil run
Charge quality:		
FIA analysis, vol. percent:		
Aromatics	3.5	
Olefins	0.5	
Saturates	96.0	
Paraffins	77.0	
Estimated octane:		
Motor, clear	50–55	
Motor, +3	75	
Research, clear	50–55	
Research, +3	75	
Gasoline quality:		
Octane:		
Motor, +0.5	79.0	83.6
Motor, +3	85.1	86.8
Research, +0.5	86.7	95.3
Research, +3	93.3	99.0
FIA analysis, vol. percent:		
Aromatics	20.5	32.5
Olefins	19.0	14.0
Saturates	60.5	53.5

As noted from the preceding table, gasoline quality in the experimental run decreased somewhat. This was not unexpected, as a virgin naphtha fraction (50–75 octane) was employed in the experimental naphtha-gas oil run and moreover comprised nearly half of the total feed stock.

Most significantly, however, the gasoline octane ratings decreased only in the range of 2–8.5 octane numbers. It must be remembered that naphtha charge was predominately saturates (96 percent). It follows, then, that the gasoline composition resulting from the experimental run should have been drastically changed if the quality of the unconverted naphtha had not been improved. It was to be expected, for example in the case of the motor +3 and research +3 octane ratings, that the results of the experimental run should have about midway between the naphtha alone ratings (75 octane) and the cracked gas oil alone ratings, or about 81.0 and 87.0 respectively, assuming a maximum naphtha octane rating of 75. Instead, the actual ratings as seen from Table V were 85.1 and 93.3 respectively, which denote a most significant and marked upgrading of the unconverted portion of the naphtha charge. This considerable increase of at least 4 and 6 octane points in the motor +3 and research +3 ratings, would alone save respectively a minimum of 2 and 3 gms. of lead additives per gallon of gasoline. Further evidence of the beneficial results flowing from the use of naphtha as a diluent can be gleaned from Table V based upon a 5 percent increase in olefinic content, a decrease of 12 percent in aromatic content and in increased saturate content of only 7 percent in the gasoline product. These comparisons furnish a further indication of significant improvement or upgrading of the naphtha diluent.

Utilizing the yield data shown for the gas oil run (Tables I and IV) the following table presents the yield and quality estimates for the cracking of a virgin naphtha charge alone:

TABLE VI.—CRACKING OF LIGHT KUWAIT NAPHTHA, ESTIMATED YIELDS

Cracking conditions:	
Transfer line temperature, F	1,200
Cat-to-oil ratio	25.7
Contact time, seconds	2
Product distribution, vol. percent:	
Total C_4	17.6
C_4=	11.8
Total C_3	16.8
C_3=	9.7
Total C_3+	102.4
C_2 and lighter, wt. percent	4.3
C_2=	1.5
Coke, wt. percent	0.7
Selectivity to C_3 and C_4 olefins, percent	62.5
Conversion, vol. percent:	
To C_3 and C_4	32.0
To C_3, C_4, and C_5	50.7
Estimated unconverted naphtha quality:	
FIA analysis, vol. percent:	
Aromatics	6.7
Olefins	24.8
Saturates	68.5

Conversion of the naphtha charge to C_3 and C_4 light ends is calculated to be 32.0 volume percent. At this conversion rate, a 62.5 percent selectivity to C_3 and C_4 olefins was achieved. It is further estimated that a 50.7 percent conversion of the naphtha charge to C_3, C_4, and C_5 gases was obtained. The overall quality of the naphtha charge is therefore shown to be substantially improved even at this conversion level.

A suitable reactor-regenerator system for performing our invention is described with reference to FIG. 3. The cracking of the gas oil in the combined charge occurs in the primary reaction zone which includes an elongated reactor tube **10**, usually referred to as a riser. In this example, the riser has a length to diameter ratio of above 20 or 25. A full range hydrocarbon oil feed to be cracked is passed through preheater **2** to heat it to about 600° F. and is then charged into the bottom of the riser **10** through an inlet line **14**. Steam or other inert diluent, if desired, can be introduced into the oil inlet line **14** through inlet **18**. Similarly, steam or other inert diluent can be introduced independently and directly to the primary reaction zone, i.e. to the bottom of the riser **10** through line **22**, where desired for minor adjustments in partial pressure, residence time, catalyst fluidization, etc. Depending upon the amount of naphtha diluent added as described below, such inert diluent, for example, can aid in carrying upwardly into the riser **10** the regenerated catalyst stream which flows to the bottom of the riser **10** through transfer line **26**.

The preponderate proportion or all of the diluent for lowering the partial pressure of the gas oil is added, however, to the transfer line **26** through inlet line **27** at a predetermined distance from the junction between the transfer line **26** and the riser **10**, which defines the secondary or preliminary reaction zone. The amount of naphtha diluent added through the inlet **27** can vary from about 5 volume percent based on the gas oil charge to about 45 percent or more. The boiling range of the naphtha diluent can be selected as described previously, and the catalyst to oil ratio both in the transfer line **26** and in the riser **10** can be adjusted as required by means of valves **40**, **41** and **42**. It will be seen from FIG. 3 that the naphtha diluent is added sufficiently upstream of the riser **10**, in this example, to achieve a prescribed contact time or residence time of the naphtha and catalyst streams within the preliminary reaction zone. In this case, the residence time is about 2 seconds although considerable variation is possible depending upon a specific application of the invention. Up to about 80 percent of the naphtha can be converted in the secondary reaction zone, i.e. in the transfer line **26**, and as the naphtha is more refractory than the gas oil, substantially all of the naphtha conversion takes place in the transfer line. It will be understood, of course, that both the naphtha diluent and the gas oil can be added directly to the riser **10**, for example through alternative inlets **28**, **29** respectively. The distance between the entry points of the inlets **28**, **29** would determine the preliminary or secondary reaction zone.

The gas oil to be cracked in the riser **10** desirably has a boiling range of about 430° to 1100° F. The catalyst employed is a fluidized zeolitic aluminosilicate and is introduced into the riser **10** adjacent the bottom thereof where the riser is adjoined with the descending transfer line **26**. Depending upon the particular boiling range of a specific gas oil charge, the riser temperature is maintained within the range of about 900°–1100° F. and preferably within the range of 950°–1000°. The riser temperature is controlled by measuring the temperature of the product from the riser and then by adjusting the opening of valve **40** by means of temperature controller **43** to regulate the inflow of hot regenerated catalyst through transfer line **26**.

The temperature of the regenerated catalyst as it flows from the regenerator **64** into the transfer line **26** is considerably above the control temperature in the riser **10** or primary reaction zone so that the incoming catalyst contributes heat to the cracking reactions of the naphtha diluent in the lower portion of the transfer line **26** and as well as the gas oil in the riser **10**. The riser pressure desirably is in the range of about 10–35 p.s.i.g. Between about 0 and 5 percent of the oil charge to the riser **10** can be recycled (not shown). The residence time of the gas oil, converted naphtha and catalyst in the riser **10** is very small and ranges from about 0.5 to 5 seconds. The residence time in the primary reaction zone or riser **10** usually is shorter than in the secondary reaction zone or lower portion of the transfer line **26**. The velocity of the catalytic stream through the apparatus is about 35–55 ft. per second in order to minimize or prevent altogether any slippage between the hydrocarbon and catalyst, particularly in the riser **10**. Therefore, no bed of catalyst is permitted to build up throughout the apparatus, and in furtherance of this purpose, the density within the riser **10** is a very

low maximum of about four pounds per cubic foot at the bottom of the riser and decreases to about two pounds per cubic foot at the top of the riser. Since no dense bed of catalyst is permitted to build up within the transfer line **26** and riser **10**, the space velocity through the apparatus is unusually high and will have a range between 100 and 120 and 600 weight of hydrocarbon per hour per instantaneous weight of catalyst in the reactor. No significant catalyst build up within the reactor is permitted to occur and the instantaneous catalyst inventory within the lower portion of the transfer line **26** and in the riser **10** is due to a flowing catalyst to oil weight ratio in the range of about 4:1–15:1, the weight ratio corresponding to the feed ratio.

The hydrocarbon and catalyst exiting from the top of the riser **10** is passed into a disengaging vessel **44**. The top of the riser is capped at **46** so that discharge occurs through lateral slots **50** for proper dispersion. An instantaneous separation between hydrocarbon and catalyst occurs in the disengaging vessel, which terminates the cracking reaction. The hydrocarbon which separates from the catalyst is primarily gasoline together with some heavier components and some lighter gaseous components. The hydrocarbon effluent passes through a cyclone system **54** to separate catalyst fines contained therein and is discharged to a fractionator through line **56**. The catalyst separated from hydrocarbon in the disengager **44** immediately drops below the outlets of the riser so that there is no catalyst level in the disengager but only in a lower stripper section **58**. Steam is introduced into catalyst stripper section **58** through sparger **60** to remove any entrained hydrocarbon in the catalyst.

Catalyst leaving stripper **58** passes through transfer line **62** to a regenerator **64**. This portion of the catalyst contains carbon deposits which tend to lower its cracking efficacy and as much carbon as possible must be burned from the surface of the catalyst. As noted previously, virtually all of the carbon deposit is derived from the gas oil portion of the total hydrocarbon charge.

Burning is accomplished by introduction to the regenerator through line **66** of approximately the stoichiometrically required amount of air for combustion of the carbon deposits. The catalyst from the stripper enters the bottom section of the regenerator in a radial and downward direction through transfer line **62**. Flue gas leaving the dense catalyst bed in regenerator **64** flows through cyclones **72** wherein catalyst fines are separated from flue gas permitting the flue gas to leave the regenerator through line **74** and pass through a turbine **76** before leaving for a waste heat boiler wherein any carbon monoxide contained in the flue gas is burned to carbon dioxide to accomplish heat recovery. Turbine **76** compresses atmospheric air in air compressor **78** and this air is charged to the bottom of the regenerator through line **66**.

The temperature throughout the dense catalyst bed in the regenerator is in the neighborhood of 1250° F., and preferably is maintained about 250° F. above the control temperature in riser **10**. The temperature of the flue gas leaving the top of the catalyst bed in the regenerator can rise due to afterburning of carbon monoxide to carbon dioxide. Approximately a stoichiometric amount of oxygen is charged to the regenerator and the reason for this is to minimize afterburning of carbon monoxide to carbon dioxide above the catalyst bed to avoid injury to the equipment since at the temperature of the regenerator flue gas some afterburning does occur. In order to prevent excessively high temperatures in the regenerator flue gas due to afterburning, the temperature of the regenerator flue gas is controlled by measuring the temperature of the flue gas entering the cyclones and then venting some of the pressurized air otherwise destined to be charged to the bottom of the regenerator through vent **80** in response to this measurement. The regenerator reduces the carbon content of the catalyst from 1 ± 0.5 weight percent to 0.2 weight percent or less. If required, steam is available through line **82** for cooling the regenerator. Makeup catalyst is added to the bottom of the regenerator through line **84**. Hopper **86** is disposed at the bottom of the regenerator for receiving regenerated catalyst to be passed to the bottom of the reactor riser through transfer line **26**.

With cracking of the naphtha diluent and with a significant proportion of the gasoline product being derived from the naphtha diluent, it is evident that the partial pressure of the gas oil feed has been significantly and advantageously lowered. The advantages of such further lowering of the partial pressure of the gas oil feed is evident from FIG. 2 of the drawings, as noted previously.

From the foregoing it will be apparent that novel and efficient forms of a Fluid Catalytic Cracking Process have been described herein. While we have shown and described certain presently preferred embodiments of the invention and have illustrated presently preferred methods of practicing the same, it is to be distinctly understood that the invention is not limited thereto but may be otherwise variously embodied and practiced within the spirit and scope of the invention.

We claim:

1. A process for a lowered partial pressure cracking of a principal hydrocarbon charge in the presence of a stream of fluidized zeolite cracking catalyst to obtain a higher selectivity for and/or octane rating of gasoline constituents and increased production of C_3, C_4 and C_5 olefins, said process comprising the steps of maintaining a predetermined range of temperatures within said zeolite catalyst stream, adding to said catalyst stream a naphtha diluent boiling between about 100° F. and about 290° F. and having about 70–96% saturates, adding said principal charge to said catalyst stream, maintaining a lower partial pressure of said charge in said stream by maintaining a given ratio of said diluent to said charge, adding said naphtha diluent to said catalyst stream at a point having a higher temperature than that at which said charge is added so that a significant proportion of each of said naphtha and said charge can be cracked by said catalyst, locating said naphtha addition sufficiently upstream of the principal charge addition so that substantially all of the cracking and/or conversion of said naphtha takes place prior to said charge addition, thereafter admixing said diluent including the cracked products thereof with said charge to increase the effective volume of said diluent and to lower further the partial pressure of said charge, limiting the residence time of said principal charge in said zeolite catalyst stream to a maximum of about five seconds to avoid masking of said higher selectivity by aftercracking of said charge and of said naphtha, and limiting the total residence time of said naphtha in said zeolite catalyst stream to a maximum of about 20 seconds to avoid aftercracking and attendant polymerization of said constituents and said cracked products and to minimize coking of said catalyst and the production of C_2 and lighter gases.

2. The process according to claim **1** including the modified step of adding said naphtha diluent to said catalyst stream at a point having a temperature of the order of about 250° F. higher than that at which said principal charge is added.

3. The process according to claim **1** including the modified step of adding said naphtha diluent to said catalyst stream at a location upstream of said principal charge addition to define a preliminary cracking zone for said diluent and a primary cracking zone communicating therewith for receiving directly therefrom said catalyst, diluent and cracked diluent products, said principal charge being added directly to said primary zone.

4. The process according to claim **3** including the additional steps of maintaining a higher temperature and a given residence time in said preliminary cracking zone,

and maintaining a lower temperature and a different residence time in said primary cracking zone.

5. The process according to claim 3 including the additional step of adding a minor proportion of said naphtha diluent directly to the entrance of said primary zone.

6. The process according to claim 1 including the modified step of adding said naphtha diluent in the range of about 5 percent to about 45 percent by volume of the total hydrocarbon feed.

7. The process according to claim 1 including the additional step of establishing a ratio of said naphtha diluent and the conversion products thereof to said principal charge and establishing residence time of said principal charge such that a greater percentage yield of gasoline based on total hydrocarbon feed is recovered from said process in the presence of said naphtha diluent and its conversion products than could be recovered from said process in the absence of said naphtha diluent.

8. The process according to claim 1 including the additional step of establishing the ratio of said naphtha diluent and its conversion products to said principal charge such that a greater percentage yield of lighter olefins based on total hydrocarbon feed is recovered from said process in the presence of said naphtha diluent than could be recovered from said process in the absence of said diluent.

9. The process according to claim 1 including the additional step of establishing the ratio of said naphtha diluent to said principal charge and a predetermined temperature and residence time of said diluent in said catalyst stream prior to engagement with said principal charge such that the octane rating of the unconverted proportion of said naphtha diluent is upgraded.

10. The process according to claim 1 including the addition step of adding a minor quantity of said diluent directly to said principal charge prior to its introduction into said catalyst stream.

11. The process according to claim 1 including the modified step of establishing said naphtha residence time within the range of about 2 to 20 seconds.

12. The process according to claim 11 including the further modified step of limiting said residence time to about 2–10 seconds.

13. The process according to claim 1 including the additional step of maintaining a catalyst to naphtha ratio during said naphtha residence time of between about 15:1 and about 100:1.

14. The process according to claim 1 including the additional step of maintaining the density of the combined catalyst and naphtha stream below about 4.5 pounds per cubic feet.

15. The process according to claim 1 including the additional step of maintaining a space velocity relative to said naphtha residence time from about 200 to about 2000 weight of diluent naphtha feed per hour.

16. The process according to claim 15 including the modified step of establishing said space velocity in the neighborhood of 1000 weight of diluent naphtha feed per hour.

17. The process according to claim 1 including the modified step of adding said naphtha diluent having at least 70% by volume of saturates.

18. The process according to claim 1 including the modified step of adding said naphtha diluent having at most 10% by volume of olefins.

19. The process according to claim 1 including the modified steps of cracking said charge in a riser zone, and disengaging said charge and the cracked products thereof from said catalyst stream at the exit of said riser zone to avoid bed-cracking in a subsequent separation zone.

20. The method according to claim 1 including the modified step of limiting the residence time of said charge to a maximum of about 5 seconds.

21. The process according to claim 1 wherein said naphtha diluent includes that fraction thereof having the lowest octane rating.

22. The process according to claim 1 wherein the residence time of said principal charge is within about 0.5 to about 4 seconds, and the residence time of said diluent is within about 2 seconds to about 10 seconds.

23. The process according to claim 1 wherein the velocity of said primary charge in said zeolite catalyst stream is within about 25 to about 75 feet per second.

24. The process according to claim 1 wherein said principal charge is added adjacent the bottom of a riser cracker through which said catalyst stream is circulated, and said diluent is added to a transfer conduit coupling the bottom of said riser to a catalyst regenerator.

25. The combination according to claim 1 wherein said process is carried out in cracking apparatus including a riser tube and a transfer line connected thereto, said charge being added to said riser tube with at least a portion thereof added adjacent the junction thereof with said transfer line, and said naphtha is added to said transfer line at a point upstream of said junction.

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