

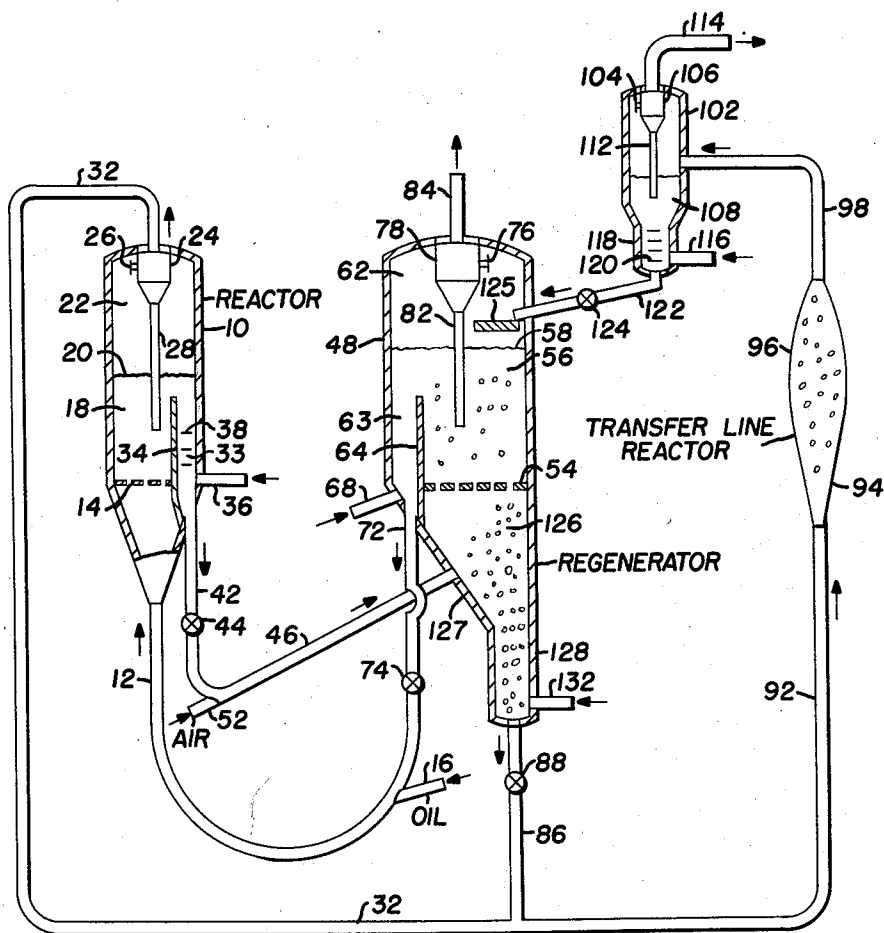
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CONVERSION OF HYDROCARBONS

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1

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CONVERSION OF HYDROCARBONS

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This invention relates to the conversion of higher boiling hydrocarbons to lower boiling hydrocarbons and more particularly relates to a process which includes a combination of catalytic cracking and thermal cracking to obtain a high ratio of gasoline to coke.

With conventional catalytic cracking processes, high octane number gasoline is produced but these processes are often limited by the catalyst regeneration facilities.

There is considerable flexibility inherent in the cracking process, particularly in the fluid process, due to the inter-relationship of process variables. For example, a refiner with a cracking unit can increase conversion while holding coke yield constant by increasing reactor temperature. Other things being constant (such as catalyst quality, feed stock), if the reactor temperature were increased from 900° to 950° F. this would have the effect of reducing coke yield by about 18 wt. percent of the coke yield at 900° F. If then at 900° F. the "430° F. + conversion" had been 51%, then cracking severity could be increased by cracking now at 950° F. and the appropriate catalyst to oil ratio and w./hr./w. to give the same coke yield as was originally made at the 900° F. reactor temperature. Under such conditions, the total catalytic conversion would be 54% or a 3% increase in conversion to gasoline and lighter products. In turn, the ability to do this is limited by heat balance considerations which may be limiting.

In other words, with a fixed design unit, there is some flexibility, the units are normally limited by carbon burning capacity and heat balance limitations. Large increases in conversion usually require a very large reduction in feed rate to the unit, which may be unprofitable. In turn, large increases in conversion (even up to 30%) may be obtained by thermal aftercracking with no increase in coke yield. Also, considerable thermal conversion may be added to the catalytic conversion step without decreasing the high octane of the gasoline produced which is typical of catalytic conversion.

According to the present invention a high conversion of gas oil or the like to gasoline is obtained while at the same time the amount of coke formed on the catalyst is minimized.

According to the present invention the total catalytically cracked products after separation of catalyst (reactor overhead taken to the catalytic fractionator) are thermally aftercracked in the absence of added catalyst by passing them through a contacting device whereby the products are contacted with catalytically-inert shot particles which supply heat and increase the temperature whereby short time-high temperature thermal cracking takes place. The shot particles which have been cooled in this process are separated from the vaporous products and are passed to the catalyst regenerator where they pick

2

up the required heat for the thermal cracking step. Thus heat is supplied by the combustion reaction wherein carbon is burnt from the "spent cracking catalyst."

The additional thermal cracking converts gas oil to lighter products without forming coke. The lighter products include gasoline and light gases. Improved yields of gasoline can be obtained by polymerization of the C₃'s and C₄'s. Directionally, thermal aftercracking produces somewhat more C₃ and lighter gases, some butylenes, slightly less butane, more gasoline than equivalent increment of conversion obtained catalytically over a base catalytic conversion.

There is usually some aftercracking present in the dilute phase and transfer overhead line of reactors and the amount can be as great as 3-4% of the total conversion. However, the preferred amount of thermal aftercracking is between about 7 and 15% and the beneficial effects in this region were unexpected. For new cracking units, it is attractive to build less carbon burning capacity into the unit and substitute some thermal conversion.

In existing catalytic cracking units, thermal aftercracking is a cheap means of expansion when carbon burning is limited. Cracking feed stock to the unit can be increased. The attractiveness of thermal aftercracking increases as feed stock quality becomes poorer. Attractiveness of thermal conversion improves at high overall conversion levels due to very high yield of catalytic coke at high conversion, illustrated below for average gas oil feed.

Conversion change, percent.....	0-49	49-54	54-64
Carbon, wt. percent on increment.....	1.71	0.88	2.16
Selectivity to carbon, percent for increment....	3.5	17.6	21.6

Within the scope of this invention the thermal aftercracking can be applied in various ways. For example, one can keep constant the catalytic intensity, which increases total conversion, and one can keep constant the final conversion and decrease catalytic conversion and add thermal conversion.

Thermal aftercracking severity is controlled primarily by control of temperature rather than control of contact time in a fixed installation. However, contact time could be increased or decreased within the scope of this invention by design changes. For example, thermal aftercracking contact devices could be placed in series and sections used or by-passed as desired by varying point of introduction of the catalytic vapors to be thermally cracked.

Various contacting devices are possible. A reaction vessel is described wherein contact time is provided for the hot shot to raise the temperature of the catalytic reaction products and to cause desired thermal reactions to occur. It is desired that the contacting be conducted in a reaction vessel. This can be designed so that the reactor is of the transfer line type having a moderate hold-up of inert shot or of the type where a dense bed is provided. Since heat conductivity is rapid in the system, long holding times of shot are not usually desired and a transfer line type reactor is preferred.

More particularly, according to the present invention a higher boiling hydrocarbon oil, such as gas oil (which may consist of fresh gas oil or recycle of cycle gas oil boiling within the boiling range of the fresh gas oil feed), is contacted with finely divided cracking catalyst at a temperature between about 850° F. and 1000 F. so that between about 35-70% by volume of the hydrocarbon

feed oil is converted to products boiling below 430° F. (gasoline and other lighter constituents). Normally, no more than about 15% coke (by weight on the oil feed), is formed, although this will vary with cracking quality of the feed stock and may be between 8 and 15%. The total catalytically cracked products which are vaporous (this excludes coke on catalyst) are separated from the finely divided catalyst particles containing coke or carbonaceous material deposited thereon. The concentration of catalyst particles in the total separated vaporous catalytically cracked products is less than about 0.1 lb. of catalyst per 1000 cubic feet and may be between about 0.05 and 0.15 lb. of catalyst per 1000 cubic feet of vaporous product.

The separated catalyst-free catalytically cracked products are then heated to a temperature higher than that of the catalytic reactor in order to promote thermal reaction. Normally the temperature shall be raised at least 50° F. higher than that existing in the reactor and at least 50° F. less than that existing in the catalytic regenerator. Usually, the temperature in the transfer line reactor will be between about 1000° F. and 1150° F. Higher temperatures are employed to crack more refractory stocks or where larger increments of thermal aftercracking are required, contacting time being constant. Higher temperatures are maintained by circulating a greater amount of inert shot per unit of oil vapors, i.e. increased w./w. The vapors are maintained or soaked at selected temperatures between about 1.0 and 20 seconds. The table below indicates relative rates of thermal reaction as a function of temperature.

Temp., ° F.	Thermal Reaction Rate Factor
950.....	0.318
1,000.....	1.000
1,050.....	3.040

An example for a specific catalytic reaction product is:

To supply 12% thermal conversion over a base of 30% catalytic conversion would require 11 seconds contact at 1000° F. or 1.3 seconds at 1100° F. Similarly to supply 12% thermal conversion over a base of 50% catalytic conversion would require 15 seconds at 1000° F. or 1.7 seconds at 1100° F.

During this thermal cracking or soaking step, additional gasoline and dry gas (C₃ and lighter gases) are formed but substantially no coke is formed. At most, less than about 0.5% by weight of the original feed to the catalytic cracking reactor will be formed as coke. In the thermal aftercracking or soaking step, heat is supplied by shot which was passed through the catalyst regeneration zone to be heated by direct contact with the catalyst particles undergoing regeneration. The shot particles are selected to be larger and/or of higher density so that they may be separated from the smaller less dense catalyst particles in the regeneration zone by settling or elutriation.

The regeneration zone is maintained at a temperature between about 1050° and 1200° F. so that the shot particles are heated to a temperature higher than that in the catalytic cracking zone. The hot shot particles and the vaporous cracked products are passed through a pipe or line to a reactor, preferably, through a transfer line reactor providing concurrent flow of the shot particles and vaporous cracking products in contrast to the turbulent fluid catalytic beds in the cracking or conversion zone and the regeneration zone. The transfer line reactor is preferably an upflow reactor and there is only a small amount of backmixing. The superficial velocity of the vaporous cracked products passing through the transfer line reactor is between about 15 and 40 feet per second. While a transfer line reactor is preferred, a dense turbulent fluid bed may be used, if desired.

In the drawing, the figure represents one form of apparatus adapted for carrying out the process of this present invention.

Referring now to the drawing, the reference character 10 designates a vertically arranged elongated cylindrical vessel or reactor. Hot finely divided freshly regenerated catalyst is introduced into the bottom of vessel reactor 10 through line 12 below distribution grid 14 arranged in the bottom of the vessel or reactor 10. The catalyst may be an acid treated bentonitic clay or a synthetic silica alumina, silica magnesia catalyst or the like. The finely divided catalyst particles have a size distribution for the most part within the 10 to 100 micron range but normally some larger and smaller size particles will be present.

The oil feed to be cracked is introduced into line 12 through line 16 and generally this feed oil is a hydrocarbon gas oil but any other higher boiling or heavier hydrocarbon oils may be used for the conversion to gasoline or light motor fuels. The gas oil generally has a boiling range above about 400° to 500° F. Preferably the hydrocarbon gas oil is preheated to a temperature between about 500° and 700° F. by indirect heat exchange with high temperature product streams or by using a furnace (not shown). The catalyst to oil ratio to the vessel 10 may be between about 5 and 15 by weight. The use of thermal aftercracking to get a desired total conversion will result in less catalytic conversion. This can be accomplished by lowering the catalyst to oil ratio. This is desirable, since it results in improved selectivity in the catalytic cracking reaction.

The catalyst-oil mixture is introduced into the bottom of the reactor 10 at such a rate that the superficial velocity of the vapors and/or gases passing upwardly through the reactor 10 will be between about .5 and 5 feet per second, preferably in the range between about 2½ to 3 feet per second. If desired, superheated steam can also be introduced into the reactor 10 along with the gas oil and catalyst mixture. At these vapor velocities, the finely divided solid catalyst particles will form a dense dry fluidized turbulent bed 18 above the distribution grid 14 and the fluidized bed will have a density between about 25 and 40 lbs. per cubic foot when using a silica alumina catalyst containing about 13% alumina. Bed 18 has a level indicated at 20. Superimposed above the dense fluidized turbulent bed 18 is a dilute phase 22 which contains a small amount of entrained catalyst particles, normally about 1 to 10 lbs. of catalyst particles per cubic foot within a zone 1 to 3 feet above the bed level 20. The cracking temperature in vessel 10 is maintained between about 850° and 1000° F., preferably between about 875° to 950° F. and the pressure in the reactor 10 will normally be maintained at about 0 to 50 lbs. per square inch gauge (p.s.i.g.). The weight of oil per hour per weight of catalyst varies with catalyst activity, reactor temperature and cracking quality of the feed but normally is between about 2 and 20.

The hydrocarbon vapors are converted to lower boiling hydrocarbon products as they pass upwardly through the dense fluidized bed of solids 18. During the cracking operation, coke is formed which collects on the finely divided catalyst and thus reduces the activity of the catalyst. The cracked hydrocarbon vapors containing entrained catalyst particles are passed into a dust separating means 24 such as a cyclone separator by passing through the inlet 26 of the cyclone separator. More than one cyclone separator may be used, if desired, especially where good catalyst separation and recovery are desired. The entrained solid catalyst particles are separated and returned to the dense fluidized bed 18 through dip leg 28. The total hot cracked vapors without intentional cooling pass overhead through line 32 and will be further treated as hereinafter described.

The reaction conditions in the reactor 10 are ad-

justed so that about 30 to 70% of the gas oil introduced into the reactor 10 is converted to products boiling below about 430° F. The conversion-feed rate relationship is maintained so as not to exceed the carbon burning capacity of the regenerator.

As pointed out above during the cracking operation the catalyst particles become spent by the deposition of coke thereon and they are passed to a stripping section 33 formed within the reactor 10 by vertical partition 34 which is formed on the chord of a circle. Other types of stripping sections may be used, such as a bottom well type of stripper or baffled annular strippers. In the form shown in the drawing, the top of the partition 34 is normally below the level 20 of the dense fluidized bed 18 so that spent catalyst from the dense fluidized bed overflows partition 34 into the stripping section 33. Stripping gas such as steam is introduced into the bottom of the stripping section through line 36 to flow upwardly countercurrent to the downflowing spent catalyst particles to strip or purge out volatile hydrocarbons. If desired, perforated baffles or disc and doughnuts 38 may be arranged within the stripping section to improve the action of the stripping gas.

The stripped spent catalyst is introduced into standpipe 42 provided with a control valve 44 and, if desired or necessary, fluidizing or aerating gas such as steam may be introduced at one or more points in the standpipe 42 to maintain the particles in a fluidized free flowing condition. The spent catalyst particles are then introduced into line 46 for passage to the regenerator 48. Air or other oxygen-containing gas is introduced into line 46 through line 52. The suspension of spent catalyst particles and air is introduced into the lower part of regenerator 48 below the distribution grid 54 therein. The superficial velocity of the gases passing upwardly through the regenerator 48 above the distribution grid 54 is between about .5 and 5 feet per second, preferably 2.5 to 3 feet per second and with a superficial velocity within this range the catalyst particles undergoing regeneration are maintained as a dense fluidized turbulent bed or mixture 56 having a level indicated at 58 and a dilute phase 62 superimposed thereabove.

The temperature during regeneration is maintained between about 1050° and 1200° F. The density of the fluidized mixture in the bed 56 is substantially the same as that of the fluid bed 18 in the reactor 10. A stripping section 63 may be formed in the regenerator by a vertical partition 64 and the top of this partition is preferably below the normal level 58 of the fluidized bed 56 so that during regeneration hot regenerated catalyst particles overflow the partition 64 into the stripping section. The stripping section 63 may be provided with baffles or disc and doughnuts, if desired. Stripping steam is introduced into the bottom of the stripping section 63 through line 68. Instead of steam, air or other gas may be used as the stripping gas in the stripping section 63. The stripping section 63 may be omitted, if desired, and any stripping that is necessary can be done in the overflow well in the regenerator.

The hot regenerated catalyst particles are then passed to the standpipe 72 having a control valve 74 for controlling the rate of withdrawal of hot regenerated particles from the regenerator 48.

If desired or if necessary, aerating or fluidizing gas may be introduced at one or more points into the standpipe 72 to maintain the catalyst particles in a fluidized free flowing condition. The hot regenerated catalyst particles from standpipe 72 are mixed with oil introduced through line 16 as previously described. Instead of the circulation system shown, the circulation of catalyst and control of catalyst flow from both regenerator and reactor by the U-bend principle shown in Packie Patent No. 2,589,124, granted March 11, 1952, may be used whereby aeration or blast steam controls density and

density differential in the two legs and thereby controls flow.

The hot combustion gases leaving the dilute phase 62 in the regenerator 48 contain entrained catalyst particles and the hot combustion gases pass through inlet 76 of dust separating means 78 which may be a cyclone separator or the like and the separated catalyst particles are returned to the dense bed 56 through dip leg 82. Hot combustion or flue gases pass overhead through line 84. More than one cyclone separator may be used, and the various cyclones may be staged in series for more effective catalyst separation.

Returning now to the total hot cracked vapors leaving reactor 10 through line 32, these vapors are mixed with a sufficient amount of hot inert solid particles introduced into line 32 from standpipe 86 having a control valve 88. These inert hot particles are of a larger size and higher density than the catalyst particles so that they are heavier than the cracking catalyst above described. The inert solid particles may be made of heat refractory material such as mullite, dense alumina or zirconia. Also inert metals can be used provided that these metals in either reduced or oxidized form are not catalyst contaminants. The metals must be inert themselves, and any erosion products on the catalyst must be inert and not introduce any catalytic effect such as for dehydrogenation type reactions. Also materials with high specific heat should be chosen.

The particle size range of the hot inert material is between about 400 and 1500 microns and the true density of the inert particles may be between about 3.0 and 4.0. When using mullite the true density is about 3.1.

The hot inert particles at a temperature between about 1050° and 1200° F. are mixed with the hot vaporous cracked products from line 32 at a temperature between about 850° and 975° F. so that the weight of cracked vapors per hour per weight of inert or shot particles is between about .05 and .5 and the resulting mixture of the hot vaporous cracked products and inert particles is at a temperature higher than the reactor temperature as previously described. Normally the temperature will be between about 1000 and 1100° F. in the transfer line reactor. The mixture is passed through line 92 and through transfer line reactor 94 which is shown as a vertically arranged vessel having a somewhat conical or cigar shape with the largest diameter being at the top or near the top as shown at 96. Other forms of transfer line reactors may be used.

By mixing the hot inert solid particles with the vaporous cracked products, the cracked vaporous products are rapidly heated to a higher thermal cracking temperature. The time of thermal aftercracking from the point of shot injection from standpipe 86 to the outlet from line 98 into separator 102 is between about 1.0 and 20 seconds, depending on temperature maintained and degree of thermal severity desired. With the temperature in excess of 1000° F. in the thermal cracking zone, the time of thermal aftercracking should be maintained between 0.5 and 10 seconds, and with the temperature between about 900° and 1000° F. in the thermal cracking zone the time of thermal cracking should be maintained between about 1 and 180 seconds.

The superficial vapor or gas velocity in the transfer line reactor 94 is in the range between about 15 and 40 feet per second, preferably between about 15 and 25 feet per second.

The temperature in the transfer line reactor is higher than that of the catalytic reaction zone (usually by at least 50° F.). Transfer line reactor temperature may be between about 900° and 1100° F., but a range of 1000°–1100° F. is preferred.

While the gas velocity in the transfer line is fairly high, there will be some solid slip in the transfer line reactor 94, that is, some of the inert particles will not pass

through the transfer line reactor 94 as fast as the gas or vapor. The transfer line reactor 94 is an upflow reactor so that all of the shot or inert solid particles are carried overhead from the reactor 94 with the thermally cracked vaporous products. The thermally cracked products and inert solid particles are taken overhead through line 98 and passed into an elongated vertical cylindrical stripping or separating vessel 102 at an intermediate portion thereof. By introducing the mixture into an intermediate portion of the vessel 102 and injecting the mixture tangentially to the inner wall, the gaseous cracked products are given a swirl and inert solids are thrown out by the centrifugal action to the wall of vessel 102 and in this way there is an initial separation of the inert solid particles from the thermally cracked vapors. The outlet from line 98 into vessel 102 is above the level of settled bed 108.

If desired, the thermally aftercracked products in vessel 102 above dense bed 108 may be quenched or rapidly cooled to cut down or eliminate undesired side reactions. The quench material may be water, steam, gas oil, naphtha etc. If a hydrocarbon stream is used it should be a high quality product recycled from the product fractionator so as to not lower the octane or quality of the products. The aftercracked products may have their temperature reduced from between 1000° and 1100° F. down to between 875° and 900° F. Normally no quench is needed, since the superheat in the product stream is used to supply heat for subsequent fractionation. Quench occurs in the product fractionator. The vessel 102 is sized to provide minimum soaking time at the elevated temperature.

The thermally cracked vaporous products containing entrained inert particles then pass through inlet 104 of the dust separating means 106 such as a cyclone separator or the like and the separated inert solids are returned to the bed 108 of inert solid particles through dip leg 112. More than one cyclone may be used if desired. The hot thermally cracked vaporous products substantially free of inert solids pass overhead through line 114 and are introduced into a fractionator (not shown) to recover desired products.

The inert solid particles separated from the thermally cracked products introduced into the stripping vessel 102 through line 98 settle into the bottom of the stripping vessel 102 and form the settled bed or mixture 108 above referred to. The shot or inert solid particles are stripped of any entrained hydrocarbons at the bottom portion of the stripping vessel 102 by means of an inert stripping gaseous medium such as steam introduced through line 116 into the bottom portion of the stripping vessel 102. Preferably as shown in the drawing, the bottom portion of the stripping vessel 102 has a reduced cylindrical section 118 of reduced horizontal cross section which may be provided with perforated baffle plates or disc and doughnut members 120 to increase the efficiency of the stripping. The settled particles form a downflowing bed 108.

The shot or other inert solid particles lose heat during the thermal aftercracking step and the particles at a lower temperature are withdrawn from the bottom of the cylindrical section 118 of the stripping vessel 102 and passed through line 122, provided with a control valve 124, into the dilute phase 62 above the dense fluidized bed 56 in the regenerator 48. If desired or necessary, fluidizing or aerating gas may be introduced into line 122 to maintain the inert solid particles in a free flowing aerated condition.

The shot or inert solid particles are now cooled below the temperature of the regenerator and they are introduced on to a horizontally arranged distribution plate 125 to distribute the shot particles in the dilute phase 62. This results in cooling of the flue gas in the dilute phase and preventing "afterburning" of catalyst in the

dilute phase. Afterburning occurs particularly at high regenerator temperatures and deteriorates the cracking quality of the catalyst, and, if uncontrolled, can damage the structure in the regenerator.

The distribution plate is supported in any suitable manner and extends from near the dip leg to near the inner wall of regenerator 48. The distribution plate is arranged at one side of the regenerator so as not to discharge inert solid particles into the stripping section 63 of the regenerator. The distribution plate 125 may be circular, oval, rectangular or any suitable shape. By discharging into the dilute phase, the inert solids are preheated before contacting the dense bed 56 in the regenerator. If desired, the line 122 may be arranged to discharge into the dense fluidized bed 56 in the regenerator 48 below the level 58 thereof, but this is not the preferred form of the invention.

By being introduced into the regeneration zone, the shot or inert solid particles are intimately mixed with the hot catalyst particles undergoing regeneration and they have their temperature rapidly raised to the regeneration temperature prevalent in vessel 48 and the inert particles are rapidly heated because of the intimate contact with hot catalyst in the dense fluidized bed.

As above pointed out, the shot or inert solid particles are of a larger size and are also heavier than the finely divided catalyst particles so that they settle in the regenerator and fall down through the openings in the grid 54. Of course, the openings in grid 54 must be larger than the largest shot particles to permit downward passage of the shot through grid 54. The lower portion of the regenerator below grid 54 has a partial conical portion 126 provided with a lower cylindrical extension 128 of reduced horizontal cross section.

The conical portion 126 has an inclined funnel-like wall 127 so that the large inert solid particles fall downwardly and are directed by the inclined wall 127 into the bottom smaller cylindrical section 128. The heated shot or inert solid particles are preferably maintained in a dense compact condition in the bottom cylindrical portion 128. The air or other gas is introduced at a low rate through line 132. The air introduced through line 132 may be preheated by indirect heat exchange with the hot combustion gases leaving the regenerator 48 through line 84. The heated air or other gas introduced into the bottom of the cylindrical portion 128 of the regenerator acts to strip out any adhering catalyst particles and the velocity of the gas is sufficient to return them to the dense fluidized bed 56 above the distribution grid 54.

The heated shot or inert material is withdrawn from the bottom of the cylindrical portion 128 of the regenerator and passed into the standpipe 86 above referred to. If desired, aerating gas may be introduced into the standpipe 86 at one or more points to maintain the shot particles in a freely flowing condition.

The control of the thermal aftercracking carried out in the transfer line reactor 94 is accomplished by controlling the rate of shot circulation between regeneration vessel 48 and the transfer line reactor 94. Increasing the circulation rate of shot will provide an increased temperature and increased thermal aftercracking and a decreased circulation rate will, of course, provide a decreased temperature and decreased thermal aftercracking.

The dimensions of the transfer line reactor 94 in which most of the thermal aftercracking is obtained can be selected to give the range of severity of thermal aftercracking desired by virtue of holding time. The control of the reaction is maintained by control of temperature in reactor 94. By increasing the circulation rate of the inert particles between vessels 48 and 94 the temperature in reactor 94 will be increased and increased thermal aftercracking will be obtained. By reducing the circulation rate a lower temperature in reactor 94 will be obtained.

In a specific example, wherein about 30,000 barrels per day of gas oil having the following characteristics:

Average West Texas feed	
Gravity, °API	23.3
Sulfur, wt. percent	1.5
Conradson carbon, wt. percent	0.5
Distillation:	
Percent at 430° F	1.7
Percent at 650° F	12.4
Percent 900° F	68.0
Percent 1000° F	88.0

are passed through line 12 into the reactor 10 which contains silica-alumina cracking catalyst having about 13% alumina. The operating conditions and major product yields are summarized below.

Operating conditions:		Average feed
Fresh feed, b./s.d		30,000
Reactor temp., °F		920
Catalyst to oil ratio		7
Steam, wt. percent on total feed		3
Percent recycle on fresh feed basis		100
Product yields, b./s.d.:		
Gasoline (including polymer)		20,000
Heating oil		8,650
Clarified oil		1,250
Heavy fuel oil		320
Carbon (wt. percent)		5.7
Catalytic conversion, percent		61

All of the products (except carbon) are withdrawn as cracked vaporous products through line 32 at a temperature of about 910° F. Some heat loss occurs, but this is minimized.

The regeneration zone 48 is maintained at a temperature of about 1200° F. The catalyst particles have a size between about 10 and 100 microns. The shot particles are made of mullite and have a particle size distribution between about 400 and 1500 microns and a true density of 3.1 compared to the apparent density of the catalyst particles of about 1.0. The mullite particles are heated to a temperature of 1200° F. in dense bed 56 in regenerator 48 and in this heated condition are passed to the bottom of the regenerator 48 into the cylindrical bottom portion 128 from which they are withdrawn and passed through line 86 for admixture with the total uncondensed hot cracked vapors leaving the reactor 10 through line 32. The weight of cracked products per hour per weight of hot mullite particles from line 86 is about 0.16 and this is sufficient to raise the temperature of the hot vaporous catalytically cracked products from a temperature of 910° F. to a temperature of 1050° F. and at this temperature the mixture of catalytically cracked products plus the hot mullite particles is passed through line 92, transfer line reactor 94 and line 98 and into the stripping vessel 102. The time of thermal aftercracking from the point of injection of the hot shot from line 86 to the separation of the hot shot in stripping vessel 102 is 6.0 seconds. This gives about 12% thermal conversion or a total conversion of 73%.

The hot shot particles collected in the bottom of the stripping vessel 102 are at a temperature of about 1045–1050° F. having lost a little heat through vessel walls, etc. They are returned to the regeneration zone 48 through line 122 to be reheated before they are again contacted with an additional amount of hot catalytically cracked vapors.

Following the thermal aftercracking step the amount of gasoline is increased without any substantial production of coke.

The following table is a comparison of the gasoline yield, coke yield and conversion obtained by catalytic cracking and condensing the cracked vaporous products from line 32 in the above example with the gasoline yield, coke yield and conversion obtained by thermal

aftercracking the total vaporous cracked products from line 32 in the above example.

TABLE

For cracking 30,000 b./s.d. "average" gas oil

	Conventional catalytic cracking	Present invention thermal aftercrack vaporous catalytically cracked products
Catalyst dense bed temp., ° F	920	920
Temp., ° F., thermal aftercracking	None	1,050
Oil residence in thermal aftercracking, seconds	15	6.0
Total Conversion, Vol. percent	65	73
Catalytic Conv., Vol. percent	61	61
Thermal Conv., Vol. percent	4	12
Coke, wt. percent of feed to catalytic cracking	5.7	5.7
Gasoline, b./s.d.	20,056	21,080
Coke yield at comparable conversion levels (73%)	11.2	5.7

* Contact time in dilute phase (22), cyclones, etc. This time at 920° F.

From the above data it will be seen that the total conversion obtained in accordance with the present invention was about 8% higher than that obtained with conventional catalytic cracking for comparable operating conditions. It will be further noted that this substantial increase in conversion was realized without any increase in the amount of coke or carbon produced. There was a 5.4% increase in the amount of gasoline produced and thus it will be seen that the gasoline to carbon or coke ratio for the present invention was substantially higher than that of the catalytic cracking process. The gasoline produced according to the present process has a high octane number, has good storage stability and acceptable gum.

In the above table, in the bottom line thereof the carbon yields of the two processes are compared at the same conversion level, namely 73%. In this comparison it is seen that the process of the present invention produces about 0.51 times as much coke as does the conventional catalytic cracking process.

What is claimed is:

1. A method for converting higher boiling hydrocarbons to lower boiling hydrocarbons which comprises contacting higher boiling hydrocarbons with finely divided solid catalyst particles in a contacting zone at a temperature of about 850°–1000° F. maintaining said hydrocarbons in contact with said catalyst in said contacting zone at said temperature to produce hydrocarbons boiling below 430° F. and coke, separating the total vaporous converting hydrocarbons from spent catalyst, mixing shot particles heated at a temperature between about 1050° and 1200° F. with said separated hot total vaporous converted hydrocarbons substantially free of spent catalyst, passing the resultant mixture through a soaking zone wherein said converted hydrocarbons are maintained at a higher temperature than in said contacting zone and between about 950° and 1150° F. until additional hydrocarbons are converted to components boiling below 430° F., separating cooled shot from the further converted vaporous hydrocarbons leaving said soaking zone and subsequently recovering motor fuel from the further converted hydrocarbons, withdrawing spent catalyst particles from said contacting zone and passing them to a regeneration zone wherein they are regenerated with an oxidizing gas and reheated before being returned to said contacting zone and utilizing some of the heat of regeneration to heat said separated shot before recycling it to said soaking zone.

2. A method according to claim 1 wherein said catalyst particles are maintained as a dense fluidized turbulent bed with a dilute phase thereabove and said cooled shot particles are introduced into the dilute phase of said regeneration zone for downward passage therethrough

to cool the dilute phase and minimize possibility of after burning occurring.

3. A process of converting higher boiling hydrocarbons to lower boiling hydrocarbons which comprises contacting higher boiling hydrocarbons with finely divided catalyst particles in a conversion zone maintained at a conversion temperature between about 875° and 975° F., separating the total hot vaporous converted products from spent catalyst particles containing carbonaceous material so that the vaporous products contain less than about 0.05 lb. of catalyst particles per 1000 cu. ft. of vapors, mixing shot particles heated to a temperature between about 1050° and 1250° F. with the total hot separated vaporous converted products, said shot particles being of a larger size and higher density than said catalyst particles, passing the resulting mixture through a soaking zone maintained at least 50° F. higher than said conversion zone but at a maximum temperature of 1150° F., and maintaining the resulting mixture at said elevated temperature for a time between about 0.5 and 10 seconds if the temperatures are in excess of 1000° F. and between 1 and 180 seconds if temperatures are in the range 900-1000° F. in the thermal soaking zone, separating shot particles from the total further converted vaporous products, recovering a desired motor fuel fraction from said further converted vaporous products, withdrawing spent catalyst particles from said conversion zone and passing them to a regeneration zone wherein the spent catalyst particles are regenerated by burning off carbonaceous material with air, and maintained as a dense fluidized turbulent bed, passing the separated shot particles to said regeneration zone for reheating said shot particles in said dense fluidized turbulent bed, separating reheated shot particles from the smaller catalyst particles undergoing regeneration by settling and withdrawing reheated shot particles from the lower portion of said regeneration zone for reuse in said soaking zone.

4. A process for converting higher boiling hydrocarbons to lower boiling hydrocarbons which comprises contacting higher boiling hydrocarbons with finely divided catalyst particles in a conversion zone maintained at a conversion temperature between about 875° and 975° F., separating the total vaporous converted products from spent catalyst particles containing carbonaceous material so that the vaporous products contain less than about 0.05 lb. per 1000 cu. ft. of catalyst particles, mixing shot particles heated to a temperature between about 1050° F. and 1250° F. with the total separated vaporous converted products, said shot particles being of a larger size and higher density than said catalyst particles, passing the resulting mixture through a soaking zone maintained at a temperature at least 50° F. higher than the reaction zone, and maintaining the resulting mixture at said elevated temperature for a time between about 0.5 and 180 seconds, separating shot particles from the total further converted vaporous products, recovering a desired motor fuel fraction from said further converted vaporous products, withdrawing spent catalyst particles from said conversion zone and passing them to a regeneration zone wherein the spent catalyst particles are regenerated by burning off carbonaceous material with air, and maintained as a dense fluidized turbulent bed, passing the separated shot particles into said dense fluidized turbulent bed in said regeneration zone for reheating said shot particles in said dense fluidized turbulent bed, separating reheated shot particles by settling, removing settled reheated shot from the lower portion of said regeneration zone for reuse in said soaking zone, and removing hot regenerated catalyst particles from said dense fluidized bed in said regeneration zone and returning them to said conversion zone.

5. A process of converting higher boiling hydrocarbons to lower boiling hydrocarbons which comprises contacting higher boiling hydrocarbons with a dense fluidized turbulent bed of finely divided catalyst particles in a conversion zone maintained at a conversion temperature between about 875° and 1000° F., separating the total hot vaporous converted products from spent catalyst particles containing carbonaceous material so that the vaporous products contain less than about 0.05 lb. per 1000 cu. ft. of catalyst, mixing shot particles heated to a temperature between about 1050° and 1250° F. with the total separated vaporous converted products, said shot particles being of a larger size and heavier than said catalyst particles, passing the resulting mixture through an upflow transfer line reaction zone at a velocity above about 15 feet per second maintained at a temperature higher than in said conversion zone and between about 925° and 1100° F. and maintaining the resulting mixture at said elevated temperature for a time between about 0.5 and 180 seconds to obtain additional conversion of said hydrocarbons, separating shot particles from the total further converted vaporous products leaving the top of said reaction zone and recovering a desired motor fuel fraction from said vaporous products, withdrawing spent catalyst particles from the dense fluidized bed in said conversion zone and passing them to a regeneration zone wherein the spent catalyst particles are regenerated by burning off carbonaceous material with air and maintained as a dense fluidized turbulent bed, passing the separated shot particles to region above the dense fluidized turbulent bed in said regeneration zone for downward passage therethrough and for reheating said shot particles in said dense fluidized turbulent bed, separating reheated shot particles by settling from the catalyst particles and removing settled shot from the lower portion of said regeneration zone and mixing the removed reheated shot with additional total vaporous converted products from said conversion zone and passing this mixture through said upflow transfer line reaction zone.

6. An apparatus of the character described including a reactor and a regenerator, means for circulating finely divided solids between said reactor and regenerator, gaseous outlets from the top of said reactor and regenerator, an upflow transfer line reactor, a pipe connecting said gaseous outlet from said first reactor with the bottom inlet to said transfer line reactor, a line leading directly from the bottom of said regenerator to said connecting pipe to directly conduct separated solids from the bottom of said regenerator to said transfer line reactor, a top outlet for said transfer line reactor, a separating vessel communicating with said transfer line reactor top outlet for separating solids from gaseous product, means for removing gaseous product from said separating vessel, a bottom withdrawal line leading directly from said separating vessel to the upper portion of said regenerator for passing separated solids from the bottom of said separating vessel to the top of said regenerator for admixture with finely divided solids undergoing regeneration therein.

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