Jan. 17, 1956

C. E. ADAMS ET AL

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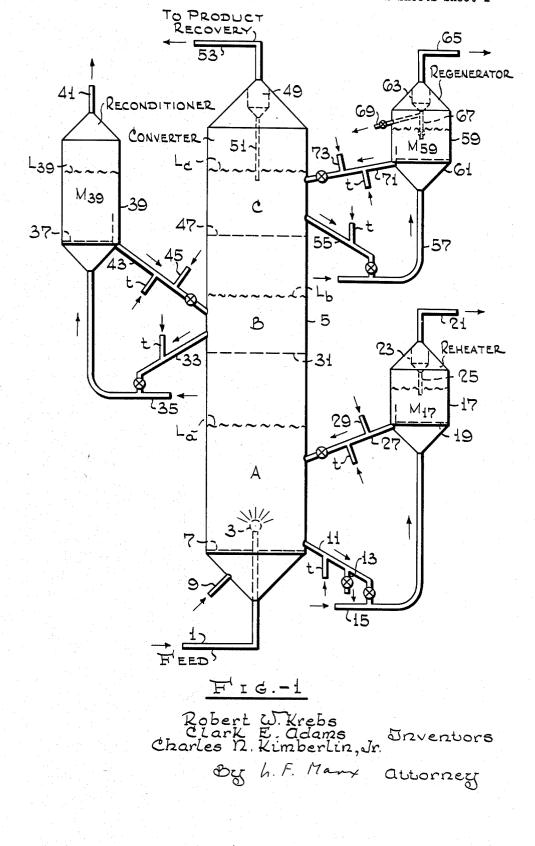
CONVERSION OF HEAVY HYDROCARBON OILS

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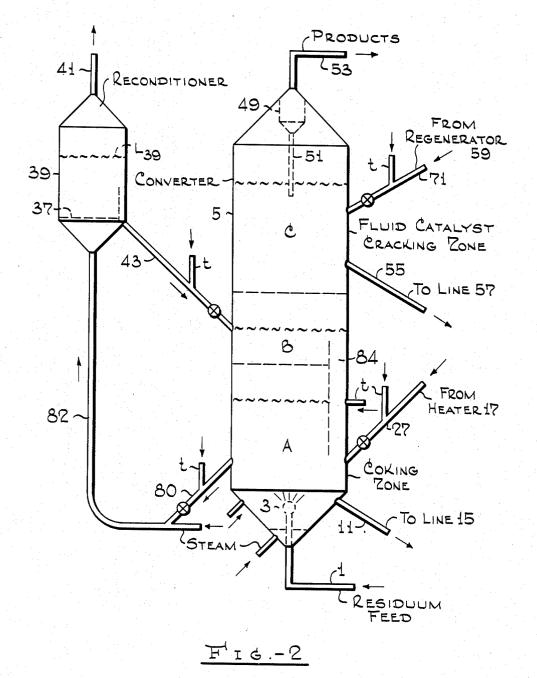
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Robert W. Krebs Clark E. Adams Inventors Charles N. Kimberlin, Jr. By h. F. Manx Attorney

United States Patent Office

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2,731,394 Patented Jan. 17, 1956

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CONVERSION OF HEAVY HYDROCARBON OILS

Clark E. Adams, Robert W. Krebs, and Charles N. Kimberlin, Jr., Baton Rouge, La., assignors to Esso Re-search and Engineering Company, a corporation of Delaware

Application May 25, 1951, Serial No. 228,234

6 Claims. (Cl. 196-49)

The present invention relates to a process of treating 15 hydrocarbons. More particularly, the invention pertains to a method of producing from relatively heavy or highboiling hydrocarbon oils of the type of topped or reduced crude or similar heavy residues increased quantities of motor fuel range fractions of improved quality as well 20 as higher boiling distillate fractions suitable for further cracking. Broadly, the invention involves the cracking of heavy residues of the type mentioned above wherein the feed is contacted successively with fluidized catalytically inert solids and cracking catalyst in such a manner 25 that the feed is heated to coking temperatures and freed of ash constituents in contact with inert solids while the cracking of the total volatile coking products takes place in contact with cracking catalyst, provisions being made for preventing coke fines, inorganic feed contaminants 30 and droplets of heavy liquid product to reach the catalyst by entrainment in the effluent from the coking stage.

In conventional petroleum refining the crude petroleum is first distilled to produce various distillate fractions and a residue boiling above about 700° F. or, in vacuum dis-35 tillation, even above 1050° F. Motor fuels are normally produced from the distillate fractions by suitable refining processes including thermal or catalytic cracking, reforming, isomerization, alkylation, etc., while the residue is worked up to yield marketable high-molecular weight 40 products such as lubricating oils, waxes, asphalt, fuel oils, etc. More recently, however, the demand for motor fuels has increased so greatly that it has become desirable to use the residues from the crude distillation extensively as an additional source of raw materials for motor fuels.

It has been known for a long time that motor fuels may be produced by coking crude residua, that is by subjecting the residues to cracking at severe conditions including relatively high temperatures and long holding times. The use of cracking catalysts in this reaction has likewise 50 been proposed. However, serious difficulties have been encountered in this type of operation chiefly as the result of the high ash content of the feed and the high rate of coke formation. Aside from the fact that the heavy coke deposits in the coking vessels and transfer lines require 55 frequent cleaning periods and plant shut-downs, catalyst contamination and deactivation by coke and difficultly removable ash constituents of the feed is so rapid that crude residua have been considered highly undesirable as feed stocks for conventional catalytic cracking processes.

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Some of these difficulties may be avoided in accordance with prior suggestions by coking residues in a dense turbulent bed of hot subdivided catalytically inert solids such as coke, pumice, kieselguhr, spent clay, sand, or the like fluidized by upwardly flowing gases or vapors. These solids serve primarily as a carrier for the coke formed and as a scouring agent preventing coke deposition on equipment walls. Also gasoline yields are somewhat higher as a result of the high surface area of the solids. The coke deposited on the solids may be burnt off in a separate fluid type heater vessel from which hot solids may be returned to supply heat required for coking. It

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is a matter of record that fluid operation affords greatest advantages with respect to heat transfer and economy, temperature control, ease and continuity of operation, etc.

While procedures of this type avoid catalyst contamination and heat supply by circulating catalyst, they are essentially thermal rather than catalytic in character and, therefore, result in the production of motor fuels of relatively low octane rating. The addition of a cracking catalyst in itself to the inert material is no complete solu-10 tion of the problem because there still remains the difficulty of catalyst contamination and deactivation by ash constituents of the feed, which cannot readily be removed by simple oxidative regeneration. In addition, large amounts of inert solids must be circulated together with the catalyst between reactor and regenerator.

It has also been suggested to pass the entire volatile effluent of a fluid type inert-solids coking zone without substantial heat loss directly to a separate fluid type catalytic cracking reactor. While this method affords important advantages with respect to heat economy, product quality, valuable product yields and continuity of operation, substantial proportions of coke fines, entrained heavy liquid and particularly of catalyst poisons which cannot be removed by conventional gas-solids separation means still reach the catalyst bed and accelerate irreversible catalyst deactivation. The present invention overcomes this difficulty and affords various additional advantages.

It is therefore the principal object of the present invention to provide improved means for producing motor fuels by coking heavy residua in contact with fluidized inert solids followed by catalytic cracking of the total volatile coking products. Other objects and advantages will appear from the description of the invention given below wherein reference will be made to the accompanying drawing in which

Fig. 1 is a semi-diagrammatical illustration of a system suitable to carry out a preferred embodiment of the invention; and

Fig. 2 is a similar illustration in simplified form of a desirable modification of the system shown in Fig. 1. In accordance with the present invention heavy residues of the type specified above are first contacted at coking conditions with a dense turbulent fluidized mass of catalytically substantially inert solids to convert the feed into lower boiling volatile products and coke depositing on the inert solids and to remove contaminat-ing ash constituents of the feed. The total volatile effluent of this coking stage together with entrained coke fines, ash dust and liquid droplets of unvaporized feed and/or product is passed without substantial heat loss directly into a separate dense turbulent fluidized guard bed of subdivided substantially inert solids. Liquid droplets are removed from the effluent through limited wetting of the guard solids. The entrained finely divided coke and ash dust is retained in the guard bed as a result of the wetting and the agglomerative tendency of fluidized beds, that is their tendency to retain particles which, according to Stokes' law, would be entrained if they were in disperse phase. The volatile effluent of the coking stage thus purified is then passed from the guard bed directly and without substantial heat loss through a separate dense turbulent bed of fluidized cracking catalyst to complete the conversion. The guard bed solids are continuously or intermittently reconditioned, i. e. treated to retain or regain those characteristics which are responsible for their purifying effect. This is accomplished by stripping and elutriation in a separate zone to remove hydrocarbon liquid, coke fines and inorganic ash dust by gas displacement and selective entrainment. The solids so treated are returned to the guard bed. If desired a limited combustion may be carried out in the reconditioning zone to aid in the removal of combustible

impurities and to maintain the guard solids at a desired high temperature. The solids thus reconditioned are returned to the guard bed.

In accordance with a specific embodiment of the invention solids from the fluidized coking bed may be used as guard solids. For this purpose, coked solids are continuously withdrawn from the fluidized coking bed, stripped and elutriated in a conditioning zone at the desired temperature to remove adhering liquid and solids fines including coke and ash, and the solids so conditioned 10 to act as guard solids are passed to the guard bed wherein they are fluidized by the volatile coking zone effluent passing through the guard bed to the fluid catalyst bed as described above. Guard solids are continuously removed from the guard bed and returned to the coking 15 bed at the rate at which they are withdrawn therefrom. This rate should be so controlled that the guard solids are retained in the guard bed for a time insufficient to allow a build-up of the undesirable materials on these solids or to allow the guard solids to collect sufficient 20 liquid to become sticky. The latter condition is particularly critical in many cases in which it is desirable to maintain the guard bed at a temperature below coking temperature to cause a reflux of heavy coker product undesirable for catalytic cracking or to cool the coker 25 effluent to a temperature more desirable for catalytic cracking.

While some of the inert solids previously suggested for the coking of residues in fluid operation, such as sand, pumice, spent clays, silica gel, etc. may be used in the 30 coking bed and/or the guard bed, coke affords greatest advantages in the process of the invention because product coke deposited on this material forms a valuable byproduct which may be recovered as a high B. t. u. fuel, as a raw material for activated carbon, and for other purposes, such as in the manufacture of carbon electrodes, etc. Any conventional cracking catalysts including activated clays, activated alumina, synthetic composites of silica gel with alumina, magnesia, and/or boria, etc., may be used in the catalytic cracking zone. 40

Fluidization conditions in all three beds may be maintained within conventional ranges. The particle sizes of the inert solids and catalyst depend, of course, to a certain extent on their relative densities. Assuming substantially equal densities of the order of that of conventional clay catalysts and coke, the particle size may be about 10-200 microns, preferably 50 to 150 microns. Linear superficial fluidizing velocities of the fluidizing medium in the three zones may vary from 0.3-5 ft. per sec., preferably from about 0.5-1.5 ft. per sec. to establish apparent densities in the beds of about 20 to 50 lbs. per cu ft.

Reaction conditions may include coking temperatures of about 800°-1200° F. and catalytic cracking temperatures of about 800°-1000° F. Pressures from atmos-55 pheric to about 100 p. s. i. g. may be employed throughout. The heat required by the coking and cracking reactions may be supplied in any conventional manner for example by indirect heating of the fluidized beds or by a limited combustion within the beds. The preferred 60 method of heat supply, however, is the circulation of catalyst and inert solids to separate catalyst regeneration and inert solids reheating zones, wherein these two types of solids are separately reheated by combustion of coke to temperatures above those of their respective 65 conversion zones, whereupon they are returned at these higher temperatures to their respective conversion zones for heat supply.

While the three fluid solids beds of the invention may be arranged in separate reactor vessels passed through 70in series by the hydrocarbon materials to be converted, the preferred embodiment of the invention provides for an arrangement of all three beds in a single substantially vertical reactor vessel subdivided by two spaced horizontal perforated plates into three superimposed sec- 75

tions. The lower-most section serves as the coking zone containing the fluidized coking bed. The intermediate zone contains the fluidized guard bed supported by a perforated plate, while the fluidized catalyst is located in the top zone above the upper perforated plate. The feed is supplied to the bottom zone, volatile products flowing upwardly through the guard zone into the catalyst zone to be withdrawn overhead from the catalyst zone. This arrangement affords substantial advantages with respect to control of coke deposition, heat economy, separation of the fluidized solids serving different purposes, as well as with respect to economies of construction and maintenance.

Having set forth its objects and general nature the invention will be best understood from the following description of the specific embodiments illustrated by the drawing.

Referring now in detail to Fig. 1 of the drawing, the system illustrated therein essentially comprises a converter 5, an inert solids reheater 17, a guard solids reconditioner 39 and a catalyst regenerator 59. The functions and coaction of these elements will be forthwith described using the conversion of crude distillation bottoms into motor fuels as an example. It should be understood, however, that the system may be employed for the conversion of other coke forming feed stocks into the same or different products in a substantially analogous manner.

In operation, reduced crude such as a 2.5 to 3.5% bottoms fraction having an API gravity of about 12° from the vacuum distillation of a South Louisiana crude or a similar heavy residue is supplied substantially in the liquid state at a temperature of about 500°-700° F. to line 1 which discharges through a spray nozzle 3 into lower zone A of converter 5 at a point above a suitable gas distributing means such as perforated plate or grid 7. Zone A contains a dense turbulent fluidized mass of solids having an upper interface La and maintained at about 850°-1100° F. A fluidizing gas such as steam, hydrocarbon gases or vapors is supplied through line 9 and grid 7 40 to establish a linear superficial gas velocity of about 0.3-3 ft. per second in zone A. Any of the inert solids mentioned above may make up the fluidized mass in zone A. However, coke having a particle size of about 20-150 microns is preferred. The oil feed rate to zone A may be about 0.1 to 4 weights of oil per hour per weight of fluidized solids in zone A (w./hr./w.), depending upon the temperature in zone A. At 800° to 950° F. the feed rate may be about 0.1 to 0.8 w./hr./w.; at 950-1050° F. the feed rate may be about 0.5 to 2.0 w./hr./w.; at temperatures above 1050° F. the feed rate may be about 1 to 4 w./hr./w. The temperature in zone A may be maintained at about 850°-1100° F. as follows.

Fluidized coke carrying freshly deposited coke may be withdrawn through a conventional standpipe 11 provided with one or more aerating and/or stripping taps t in a conventional manner. Product coke amounting to about 5 to 7 weight percent of the residuum feed may be recovered via branch pipe 13. This amount of coke is the excess over that required for heat supply and applies in the case of the South Louisiana residuum, here specified; varying amounts of coke will be obtained from other feeds. The remainder of the coke discharges into air line 15 and may be passed suspended in air to the bottom of heater vessel 17 which it enters through a distributing grid 19 to form a dense turbulent fluidized mass M17 above grid 19. Combustion takes place in mass M₁₇ as a result of which the solids are heated to about 900°-1300° F. Flue gases are withdrawn overhead via line 21 preferably after fines separation and return in cyclone 23 provided with dip-pipe 25. Reheated solids are withdrawn from mass M17 through standpipe 27 aerated and/or stripped via taps t and supplied to zone A, substantially at the temperature of mass Mir. Fresh seed coke or the like may be supplied via line 29 as required. Since more coke is deposited on the solids in zone A than is required for heat generation in heater 17 the particle size of the solids may increase due to coke accumulation. To prevent this from reaching proportions detrimental to fluidization a grinding stage may be incorporated in the system of circulating solids. For example, a supersonic attriter may be combined with standpipe 11 or 27 in a manner known per se in the art of catalytic cracking.

Returning now to zone A of converter 5, the oil feed 10 may be converted therein to yield about 88 to 90 weight per cent of volatile products on feed. This yield applies to the South Louisiana residuum specified and differs with other feeds. Simultaneously, the ash contaminants of the feed which are present mostly in the form of sodium chlo- 15 ride, calcium chloride, magnesium chloride and other similar inorganic salts and metal soaps such as soaps of vanadium, iron, chromium and nickel and other organo-metallic compounds the nature of which is not well understood undergo changes as follows. The inorganic 20 salts remain essentially unchanged and are deposited on the solids in zone A. However, the metal soaps and other organo-metallic compounds are converted into a fine dust of the oxides and/or carbonates, usually of -10 microns particle size, which is readily entrainable at the prevail-25ing gas velocities. Volatile products containing entrained solids fines, ash dust and droplets of unconverted feed or heavy product pass overhead from level La through horizontal perforated plate or grid 31 arranged in an intermediate section of converter 5, substantially above level 30

The gases and vapors passing grid 31 enter zone B of converter 5, which contains a dense turbulent mass of inert solids having an interface L_b, fluidized by the upflowing gases and vapors. While the solids in zone B 35 serving as the guard bed may be the same as those used in zone A, sand having a particle size of about 50-100 microns will be referred to for the purpose of the present example. Quite generally, it may be desirable to use in zone B an inert solid of high attrition resistance to avoid losses in the subsequent reconditioning stage and excessive entrainment in the upflowing effluent of zone A. The gasiform effluent of coking zone A deposits in zone B its content of entrained coke fines, ash dust and liquid due to the agglomerative effect of fluidized masses, referred to 45 above. In order to maintain the purifying capacity of the fluidized mass in zone B the solids may be reconditioned as follows.

Fluidized solids may be withdrawn from zone B through a conventional aerated standpipe 33 and sus-50 pended in line 35 in an elutriating and stripping gas such as steam, flue gas, or the like. The suspension formed may be passed through grid 37 into the bottom portion of reconditioner 39, to form above grid 37 a fluidized mass M39 having an interface L39. The linear superficial 55 gas velocity in mass M₃₉ may be readily so controlled. say within about 1 and 3 ft. per second, that the solids fines and ash dust are preferentially entrained and the liquid is stripped off the sand, without substantial losses of sand particles. In order to maintain the temperature 60 of the sand at that desired for the guard bed in zone B and to aid in the removal of combustible liquid and solids fines it may be desirable to add small amounts of a combustion supporting gas such as air and/or oxygen to mass M39 via line 35. The temperature in zone B may be 65 somewhat lower than that of zone A and should preferably not exceed the temperature to be maintained in catalytic cracking zone C. Entrained solids and vaporized impurities are carried overhead from level L₃₉ by the elutriating and stripping gas and may be vented via 70 line 41. Reconditioned sand may be returned through conventional aerated standpipe 43 to zone B substantially at the rate at which solids are withdrawn from zone B. Make up stand may be added through line 45 as required.

Volatile effluent of zone B, now free of catalyst poisons passes overhead from level Lb through a horizontal perforated plate or grid 47 arranged in an upper section of converter 5 substantially above level Lb. Any entrained sand reaching grid 47 impinges on the imper-meable portions of grid 47 and is mostly thrown back into zone B. Volatile products pass grid 47 to enter zone C of converter 5 which contains a dense turbulent mass of subdivided cracking catalyst, such as a silicaalumina composite containing about 13% of Al2O3 and having a particle size of about 20-150 microns. The catalyst mass is fluidized by the gases and vapors to form an interface Le. The temperature of the catalyst mass may be maintained at about 800°-1000° F. in any conventional manner, providing for cracking times of about 3 to 20 seconds. At these conditions extensive cracking of the gas oil constituents of the coking products into motor fuels takes place in zone C. A mixture of gasiform products and fluidizing gases passes overhead from level Le preferably through a cyclone separator 49 provided with solids return pipe 51. The product stream may then be passed via line 53 to conventional product recovery equipment (not shown).

Since coke is deposited on the catalyst in the course of the cracking reaction the catalyst must be regenerated. This step may be combined with heat supply to zone C in the conventional manner as follows. Coked catalyst is continuously withdrawn through a conventional standpipe 55 provided with stripping and/or aerating taps tand passed to line 57 wherein it is picked up by air and conveyed to a lower portion of regenerator 59 via a suitable distributing grid 61. The catalyst forms a dense turbulent fluidized mass M59 wherein the catalyst is regenerated and reheated to about 900°-1200° F., but above cracking temperature. Combustion gases are withdrawn through cyclone 63 and line 65. Separated catalyst fines may be returned to mass M59 via dip-pipe 67 or discarded via line 69. Regenerated catalyst is returned to zone C substantially at the temperature of mass M59 via standpipe 71 provided with aerating and/or stripping taps t. The sensible heat of the regenerated catalyst serves to maintain the temperature of zone C at the desired level. Make-up catalyst may be added via line 73 as required. The system illustrated in Fig. 1 permits of various

modifications. For example, the reheated inert solids may be returned to zone A via fluidizing gas line 9 through grid 7 or via oil feed line 1. In the latter case, substantial portions of the feed are vaporized in line 1 and the feed is preferably supplied through grid 7 without the use of a spray nozzle. Other modifications within the spirit of the invention will appear to those skilled in the art.

In many cases it may be desirable to exclude not only catalyst poisons and entrained liquid from the catalyst zone but in addition the heaviest constituents of the vaporized coking product which have a particularly high coke-forming tendency in catalytic cracking. A system suitable for this purpose is illustrated in Fig. 2.

Referring now to Fig. 2, the system shown therein comprises the same major equipment elements as the system of Fig. 1, like elements being identified by like reference characters. The solids heater and catalyst regenerator have been omitted for the sake of simplicity. Operation of the system of Fig. 2 is substantially the same as that described with reference to Fig. 1 except for the operation of guard zone B, which may be as follows.

The volatile effluent of zone A is contacted in zone B with a fluidized mass of the same solids which are used in zone A. The guard bed is maintained at a high purifying capacity and at a temperature somewhat lower than that of zone A as follows, coke being preferably used as the fluidized contact solid in zones A and B. Fluidized coke is continuously withdrawn from zone A through a conventional standpipe 80 provided with stripping and/or aerating taps t. The withdrawn coke is suspended in 75 line 82 in a stripping and elutriating gas such as steam,

flue gas, etc. which may contain small proportions of a combustion-supporting gas such as air and/or oxygen. In general, however, the introduction of combustion-supporting gases into line 82 is not desired. On the contrary, it may even be desirable to provide a small amount of cooling in addition to that provided by the stripping This may be done by injection and elutriating gases. of water into line 82. The suspension formed is passed into reconditioner 39 and treated therein substantially as described with reference to Fig. 1, reconditioned coke 10 being passed to guard zone B via standpipe 43. Fluidized coke from guard zone B is continuously removed through a down-comer 84 or the like and returned to coking zone Operation of reconditioner 39 may be readily so Α. controlled that the coke in guard zone B is maintained 15 at a temperature about 50 to 250° F. lower than that of zone A to permit reflux of heavy coking products to the desired extent. The solids circulation rate from zone B to zone A, reconditioner 39 and back to zone B should be sufficiently high, for example 300 to 1500 lbs. per 20 barrel of residuum feed so that the time the coke is retained in zone B is insufficient to allow an excessive buildup thereon of materials undesirable in cracking zone C or to allow the coke in zone B to become so wet by condensed material that the coke becomes sticky.

The system of Fig. 2 may be modified as pointed out with reference to Fig. 1. In addition, heat may be withdrawn from the coke in reconditioner 39 or standpipe 43 in any conventional manner (not shown) to maintain the desired low temperature level in zone B. Other modi- 30 fications obvious to those skilled in the art are within the spirit of the invention.

When operating as described above with reference to Fig. 2 catalyst poisons are withheld from zone C and, in addition, the coke-formation rate in zone C is sub- 35 stantially reduced by excluding the heaviest coking products which are further thermally cracked by their return to zone A.

An additional reduction in the rate of coke formation and also of gas in zone C is realized as a result of better 40 maintenance of catalyst activity and selectivity that is obtained when avoiding contamination of the catalyst by the ash components of the residuum feed. This elimination of catalyst contamination by the metallic elements of the residuum feed also results in a substantial saving by reducing catalyst replacement rate; for example, when carefully avoiding catalyst contamination according to the present invention a catalyst replacement rate of only about 0.1 to 0.5 lb. of catalyst per barrel of residuum feed may suffice to maintain an advantageous level of 50 catalyst selectivity and activity, but in the absence of means for avoiding the contamination of the catalyst by the ash components of the feed a replacement rate of 0.5 to 5 lbs. per barrel of residuum feed may be required to maintain an equivalent degree of catalyst activity and selectivity. It will be appreciated, of course, by those skilled in the art, that the required catalyst replacement rate will depend somewhat upon the inherent stability and resistance to contamination of the particular catalyst employed in zone C, and upon the amount and nature of the ash constituents of the particular residuum feed. Crude residua vary widely in the nature and amount of their ash content. As an example, a vacuum residuum from a non-desalted South Louisiana crude may contain as much as 1600 lbs. per thousand barrels (PTB) of total ash comprising about 1200 PTB of sodium chloride, about 280 PTB of silica and salts such as calcium and magnesium chlorides and about 120 PTB of metals such as iron, nickel, vanadium, chromium, and the like measured as oxides. Desalting the crude results in re-70 moving most of the soluble ash components, but very little of the heavy metal components which are the most desirable of the ash constituents.

It will be appreciated that the yield and quality of the

(1) the quality of the feed stock, (2) the severity of the operations in both the thermal zone A and the catalytic zone C, and (3) with the catalyst replacement rate employed in zone C. The following are illustrative of the yields, exclusive of thermal coke already mentioned, that may be expected when feeding a typical South Louisiana vacuum residuum, employing a catalyst replacement rate of about 0.5 lb. per barrel of feed and operating according to the present invention at intermediate severities in both thermal and catalytic zones: (1) 3 to 10 weight per cent of coke, calculated on residuum feed, deposited on the catalyst in zone C; this coke must be burned for catalyst regeneration; (2) 8 to 20 weight per cent of gas (C3 and lighter) including about 4 to 11 weight per cent of propylene which may be polymerized to further increase the yield of gasoline; (3) 38 to 55 volume per cent of gasoline boiling up to about 430° F., and having an octane number by the Research Method of about 90 to 96; (4) 10-20 volume per cent of heating oil boiling in the range of about 430 to 650° F., and (5) 15 to 25 volume per cent of heavier products boiling above about 650° F., which may be recycled to the thermal conversion zone A.

On the other hand, failure to avoid contamination of the catalyst by ash and the heavy components of the 25feed results in a marked increase in catalyst coke deposits and of dry gas yields with a corresponding loss in yield of gasoline and other liquid products. The catalytic coke deposit may be as much as doubled and the gas yield increased by 50% by contamination of the catalyst even when employing a higher than desirable catalyst replacement rate. It is, of course, possible to alleviate these high coke and gas yields to some extent by employing excessive rates of catalyst replacement; but this is uneconomical as compared to the present method of protecting the catalyst from contamination.

The above description and exemplary operations have served to illustrate specific embodiments of the invention but are not intended to be limiting in scope.

What is claimed is:

1. In the process of producing lower boiling hydrocarbons from heavy hydrocarbonaceous residues which tend to produce finely divided contaminants for catalysts by coking said residues in contact with a dense, turbulent, fluidized mass of catalytically substantially inert solids 45 maintained at a coking temeperature in a coking zone and passing the volatile coking products including entrained particles of heavy liquid without intermediate condensation of constituents desirable for cracking through a dense fluidized mass of cracking catalyst maintained at a cracking temperature, the improvement which comprises maintaining in a vertical elongated contacting zone a lower dense fluidized mass catalytically inert solids at a coking temperature, an intermediate separate dense fluidized mass of catalytically inert solids which is maintained at a tem-55 perature not exceeding the coking temperature in the lower mass and sufficiently low to collect high boiling hydrocarbons from coked vapor products in sufficient quantities to separate catalyst contaminant materials from said vapor products by adhesion, and an upper separate dense fluidized mass of cracking catalyst maintained at said cracking temperature, feeding said residues to said lower mass, passing voltatile effluent of said lower mass in series upwardly through said intermediate and upper masses, separating the entrained liquid particles and finely 65 divided contaminants in said intermediate mass by adhesion as aforesaid, withdrawing catalytically cracked volatile products from said upper mass, passing solids from said intermediate mass to a separate reconditioning zone, removing constituents undesirable in catalytic cracking from said solids in said reconditioning zone and returning solids so reconditioned to said intermediate mass.

2. In the process of producing lower boiling hydrocarbons from heavy hydrocarbonaceous residues wherein products recovered via line 53 will vary somewhat with 75 finely divided solid contaminants for cracking catalyst

are produced, along with oil products, by coking said residues in contact with a dense, turbulent, fluidized mass of catalytically substantially inert solids maintained at a coking temperature in a coking zone and passing the volatile coking products without intermediate condensation of constituents desirable for cracking through a dense fluidized mass of cracking catalyst maintained at a cracking temperature, the improvement which comprises maintaining in a vertical elongated contacting zone a lower dense fluidized mass of catalytically inert solids at a cok- 10 ing temperature, an intermediate separate dense fluidized mass of catalytically inert solids at an elevated temperature not substantially exceeding said cracking temperature and such that high boiling hydrocarbons in the vapor stream are condensed on said inert solids and entrained 15 catalyst contaminants are caused to adhere thereto by reason of such condensation, and an upper separate dense fluidized mass of cracking catalyst maintained at said cracking temperature, feeding said residues to said lower mass containing particles of heavy entrained liquid and 20 catalyst contaminant particles, passing volatile effluent of said lower mass in series upwardly through said intermediate and upper masses so that the entrained liquid particles cause limited wetting of said intermediate mass and the catalyst contaminant particles adhere thereto, 25 withdrawing catalytically cracked volatile products from said upper mass, passing solids from said intermediate mass to a separate reconditioning zone, passing a gas upwardly through said solids in said reconditioning zone 30 at conditions conducive to remove said contaminants from said solids by elutriation, and returning solids so reconditioned from said reconditioning zone to said intermediate mass.

3. The process of claim 2 in which said gas contains 35sufficient free oxygen to support a combustion of combustible liquid constituents present in said reconditioning zone and to maintain in said reconditioning zone a solids temperature conducive to the maintenance of said elevated temperature. 40

4. In the process of producing lower boiling hydrocarbons from heavy hydrocarbonaceous residues which produce finely divided solid contaminants for cracking catalysts along with volatile products by coking said residues in contact with a dense, turbulent, fluidized mass of catalytically substantially inert solids maintained at a coking 45 temperature in a coking zone and passing the volatile coking products without intermediate condensation of constituents desirable for cracking through a dense fluidized mass of cracking catalyst maintained at a cracking 50 temperature, the improvement which comprises maintaining in a vertical elongated contacting zone a lower dense fluidized mass of coke at a coking temperature, an intermediate separate dense fluidized mass of coke at an elevated temperature substantially below said coking temperature, and an upper separate dense fluidized mass of 55

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cracking catalyst maintained at said cracking temperature, feeding said residues to said lower mass, passing volatile effluent from said lower mass in series upwardly through said intermediate and upper masses, withdrawing catalytically cracked volatile products from said upper mass, entraining sufficient high boiling hydrocarbon from said lower mass to adhere to said intermediate mass and help separate said solid contaminants from the effluent by adhesion passing coke including condensed heavy coking products and deposited solids fines from said intermediate mass to said lower mass, passing coke and solids fines from said lower mass to a separate reconditioning zone, passing a gas upwardly through said reconditioning zone at conditions conducive to remove solids fines from said coke by elutriation, and returning coke so reconditioned to said intermediate mass at a temperature and rate conducive to the maintenance of said elevated temperature in said intermediate mass.

5. The process of claim 4 in which said coke passed to said reconditioning zone is cooled by direct contact with water.

6. The process of producing lower boiling hydrocarbons, suitable for catalytic cracking, from heavy hydrocarbon oil which contains potent metal-containing contaminants for cracking catalysts, which comprises contacting said oil with a mass of preheated essentially noncatalytic particles suspended or fluidized in a gasiform stream at a coking temperature between about 850° and 1150° F. for a period of time sufficient to vaporize and crack thermally a substantial part of said oil with concomitant production of droplets of high boiling oil and metal-containing contaminants suspended in said gasiform stream and in the vapor products of conversion, establishing a cooler mass of the essentially non-catalytic solid particles aforesaid in the form of a fluidized bed, passing said gasiform stream and said vapor products upwardly through said cooler mass at such a rate as to strip out said droplets and contaminants onto said solid particles, and continuously cycling solids between said cooler mass and a fluidized solids reconditioning zone operated at a temperature 50 to 250° F. lower than said coking temperature whereby the temperature within said cooler mass is continuously maintained at the level required for effective separation of said metal-containing contaminants from said vapor products.

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