

April 17, 1956

E. W. S. NICHOLSON ET AL  
CRACKING OF REDUCED CRUDE WITH THE USE  
OF INERT AND CATALYST PARTICLES

2,742,403

Filed April 12, 1951

2 Sheets-Sheet 1

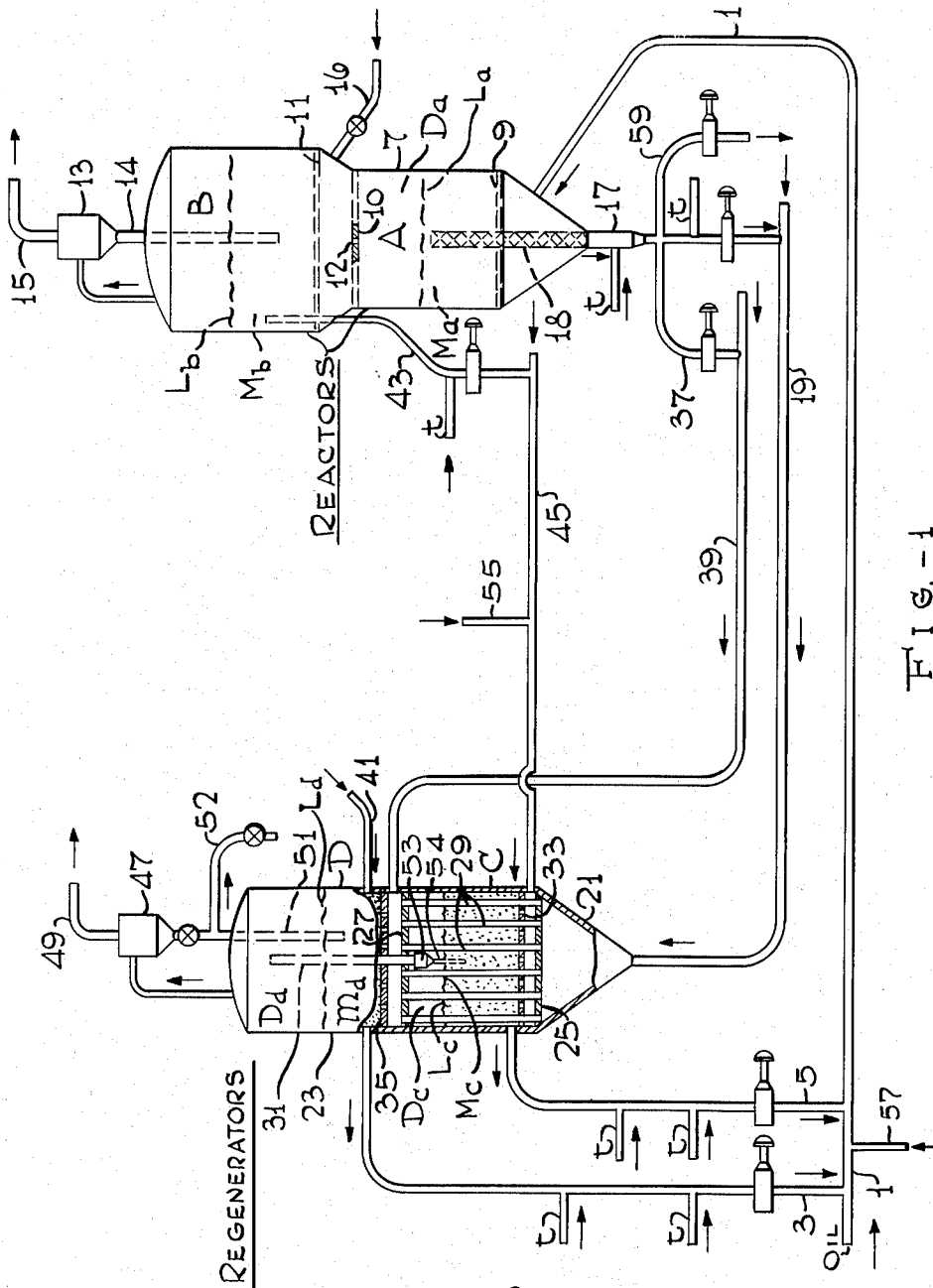


FIG. 1

Edward W. S. Nicholson  
Sumner B. Sweetser

Inventors

By *L. F. Marx* Attorney

April 17, 1956

E. W. S. NICHOLSON ET AL  
CRACKING OF REDUCED CRUDE WITH THE USE  
OF INERT AND CATALYST PARTICLES

2,742,403

Filed April 12, 1951

2 Sheets-Sheet 2

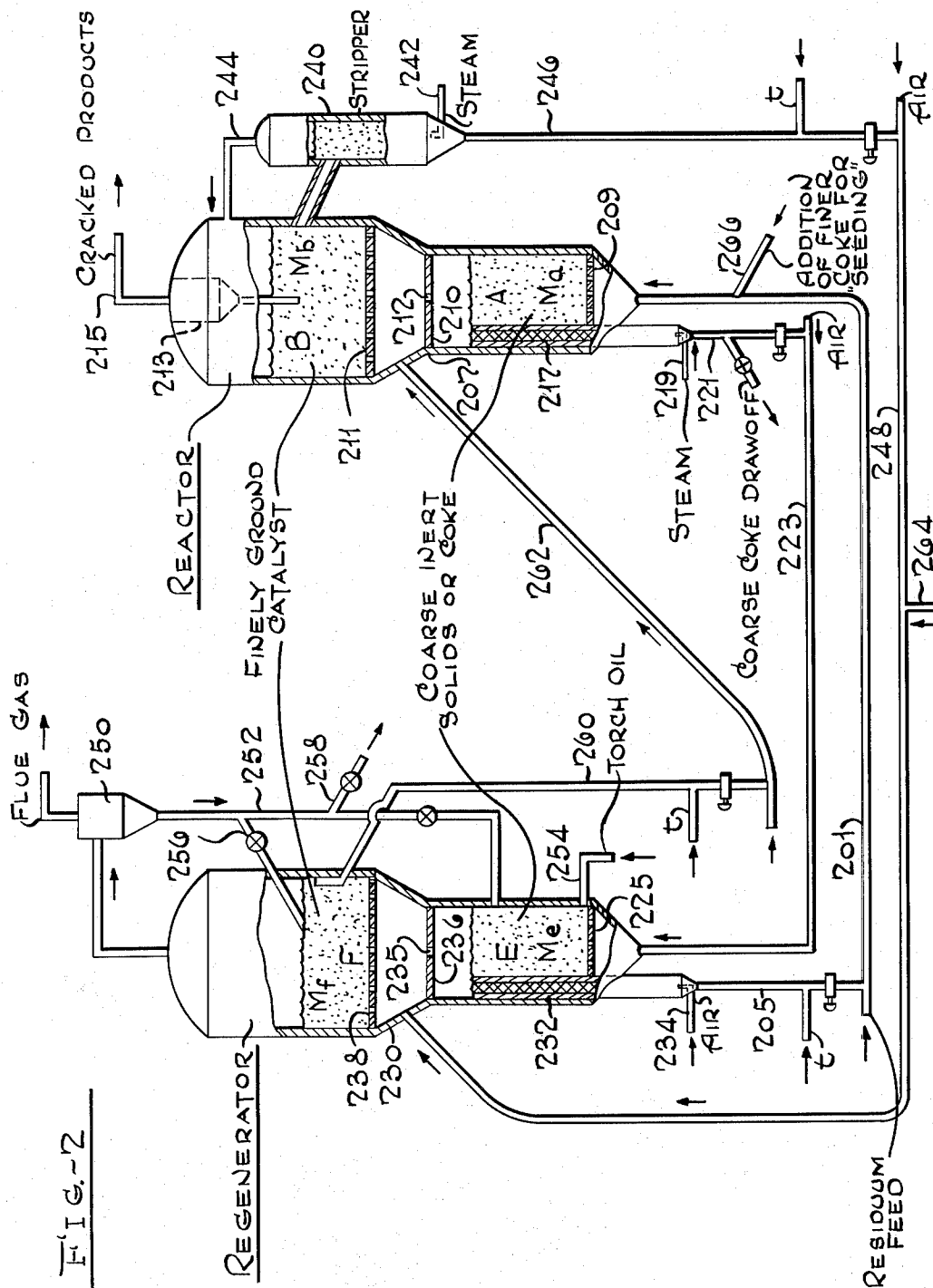


FIG. 2

Edward W. S. Nicholson Inventors  
Sumner B. Sweetser

By *L. F. Marx* Attorney

1

2,742,403

## CRACKING OF REDUCED CRUDE WITH THE USE OF INERT AND CATALYST PARTICLES

Edward W. S. Nicholson, Baton Rouge, La., and Sumner B. Sweetser, Cranford, N. J., assignors to Esso Research and Engineering Company, a corporation of Delaware

Application April 12, 1951, Serial No. 220,554

5 Claims. (Cl. 196-49)

The present invention relates to a process of treating hydrocarbons. More particularly, the invention pertains to a method of producing from relatively heavy or high-boiling 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 as higher boiling distillate fractions suitable for further cracking. Broadly, the invention involves the catalytic cracking of heavy residues of the type mentioned above wherein the feed is contacted with fluidized catalytically inert solids and cracking catalyst in such a manner that the feed is heated to coking temperatures and deashed in contact with predominantly inert solids while most of the cracking takes place in contact with solids consisting at least predominantly of cracking catalyst, heat required for coking and cracking being supplied by burning coke formed in the process from the solids.

In conventional petroleum refining, the crude petroleum is first distilled to produce various distillate fractions and a residue boiling above about 700° 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 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 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 which are formed in the coking vessels and transfer lines require frequent cleaning periods and plant shut-downs, catalyst contamination and deactivation by coke and difficultly removable ash constituents of the feed are so rapid that crude residua have been considered highly undesirable as feed stocks for conventional catalytic cracking processes.

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

2

which hot solids may be returned to supply heat required for coking. It 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 supply heat 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 solution 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. Prior suggestions of separating inert solids from catalyst by elutriation prior to coke combustion have been unsuccessful either because of insufficient separation between the catalyst particles and the inert solids particles or because of poor fluidization of the coarser (or denser) of these two different types of solids. The present invention overcomes these difficulties.

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

In accordance with the present invention, heavy residues of the type specified above are coked by contacting the feed at coking conditions first exclusively with hot relatively coarse inert solids and then passing the pre-cooked feed upwardly through a fluidized mass consisting predominantly of relatively coarse inert solids and containing small amounts of relatively fine cracking catalyst in such a manner that substantial upward elutriation of relatively fine catalyst from relatively coarse inert solids takes place with the effect that the feed is maintained at cracking conditions in contact first with a catalytically substantially inert mass of solids and immediately thereafter with cracking catalyst. In addition to being of smaller particle size the catalyst may be of lower density to permit or enhance this type of separation. Classification by particle size and/or density in this manner is accomplished in accordance with this invention in dense phase operation involving bottom withdrawal of solids by providing a place for the more readily entrainable particles to which they may escape from the fluidized mass. Experimental data have shown that this is an indispensable condition for efficiently elutriating relatively more entrainable particles from a fluidized mass composed of both particles of high and of low gas settling rates, particularly if it is desired to form a second fluidized mass of entrained particles above the mass from which the particles were entrained. In these experiments a bed of relatively fine and readily entrainable solids was superimposed over a bed of relatively coarse solids of higher settling rate. At low fluidizing gas velocities, below those required to fluidize the coarse bed the bed of fine solids was fluidized and remained in the form of a clearly separated, superimposed bed. When the velocity was increased to the range necessary to fluidize the coarse bed, the two beds were intimately mixed and it was impossible to distinguish two beds. However, when a separating grid was provided in the contacting zone a very sharp separation between the coarse lower bed and the fine upper bed could be maintained even when circulating solids entrained from the upper bed back to the lower bed. It has also been

observed that the relative entrainment rate of the smaller or lighter particles is substantially increased when coke is preferentially deposited thereon. This preferential deposition takes place in the case of the present invention because of the higher cracking activity of the catalyst particles as compared with that of the inert material.

In accordance with an embodiment of this invention, a mixture of reduced crude precoked as indicated above, highly entrainable (e. g. small sized) catalyst and less entrainable (e. g. coarser) inert solids may be injected at coking conditions into the lower portion of a dense phase fluid type reactor at fluidization conditions conducive to the formation of a dense fluidized phase separated by an interface from an upper disperse phase within the reactor. By reason of the smaller size of the catalyst particles as well as of their relatively high carbon content, most of the catalyst is entrained in the fluidizing gas while the larger inert particles may be collected and withdrawn from the dense turbulent fluidized phase. This effect is enhanced and the formation of a second fluidized bed consisting essentially of catalyst above the dense fluidized phase of coarse inerts is made possible by providing a perforated grid above the fluidized bed of inerts through which the fine catalyst may escape to form a fluidized bed above this grid. Catalyst particles carried overhead with the products of reaction may be separated by any suitable means such as cyclone separators or settling chambers. The coked catalyst may then be regenerated under controlled conditions which keep the temperature below the level which would decrease the activity of the catalyst. Because of the high concentration of coke on the catalyst it may be regenerated at a high rate, and especially at a more rapid rate than if it were diluted with a large amount of inert material. Regenerator capacity is thereby saved and less catalyst is held up in the system.

Substantial coke deposits also form on the inert material and it may be regenerated in a separate coke combustion stage. No precautions are necessary in keeping the temperature of regeneration of the inert material at a low level. Therefore, one modification of the invention provides for removal of the coke from this material at a considerably higher temperature than is allowable for, and actually employed in, the regeneration of the catalyst. If such higher temperature cannot be obtained from combustion of product coke alone, natural gas, gas oil or other combustible materials may be added with the inert diluent so that it can be heated to a higher temperature. The hot regenerated or heated inert material and the hot regenerated catalyst are preferably added to the liquid feed in separate streams in a manner adapted to raise the feed temperature to the level desired for coking.

When operating in accordance with the invention, the reduced crude feed may be heated to the desired coking temperature without having to heat the catalyst to an excessively high temperature or to circulate large amounts of inert material with the catalyst. In other words, a small amount of inert material heated to a high temperature may take the place of a large amount of catalytic and inert material heated to a lower temperature. Moreover, because the inert material and the catalyst may be handled separately, it is possible to cause the salts and other contaminants in the liquid feed to be deposited almost entirely on the inert material, thus preventing rapid deactivation of the catalyst. This is accomplished by adding the hot, regenerated inert material to the liquid oil stream ahead of the point of introduction of the catalyst, so that substantial vaporization and all salt deposition occurs before the bulk of the catalyst is added. The inert material may also be separately removed for desalting and then returned to the system. Elutriation of the catalyst may be substantially enhanced by providing in the reactor a packing of solids of non-fluidizable size having irregular interstices through which the fluidized mass of solids may percolate. It may be desirable to

prevent any contact between catalyst and unvaporized feed in the coking zone. This may be accomplished by returning regenerated catalyst from the regenerator directly to the catalyst bed contacted exclusively by the effluent vapors of the coking zone.

Fluidization conditions may be maintained within conventional ranges. The relative particle sizes of the catalyst and inert solids depend, of course, to a certain extent on the relative densities. Assuming substantially equal densities of the order of that of coke and conventional natural or synthetic clay catalysts, the inert solids may have a particle size of about 100-500 microns and the catalyst a particle size of about 80 microns and less. Linear superficial velocities of the fluidizing medium in the cracking zone may vary from about 0.5-10 ft. per second to establish apparent densities in the dense solids phase of about 10-50 lbs. per cu. ft. and about 0.001-1 lb. per cu. ft. in the disperse phase.

Reaction conditions may include oil preheating temperatures of about 300°-700° F., coking temperatures of about 800°-1200° F., catalytic cracking temperatures of about 850°-1000° F., catalyst regeneration temperatures of about 950°-1250° F. and inert solids regeneration or heating temperatures of about 1050°-1500° F. or higher. In this operation, the ratio of total solids to oil may be from about 1:1 to about 20:1 by weight. The proportion of inert material to catalyst may be from about 1:1 to about 40:1.

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, coke affords greatest advantages in the process of the invention because product coke deposited on this material forms a valuable by-product which may be recovered as a high B. t. u. fuel, as a raw material for activated carbon, and for other purposes. Extraneous coke from petroleum or coal may be used to start up the process while thereafter product coke may serve as the inert solid. The product coke may be withdrawn and at least a part of it ground to provide fresh seed coke. An alternative method for continuously providing seed coke without withdrawing product coke from the unit is the inclusion of a supersonic attriter in the coke cycle as it is known in the art of fluid catalytic cracking. Any conventional cracking catalyst including activated clays, activated alumina, synthetic composites of silica with alumina, magnesia and/or boria, etc., may be used.

Having set forth its objects and general nature, the invention will be best understood from the more specific description hereinafter read with reference to the drawing in which:

Figure 1 is a semi-diagrammatical illustration of a system suitable to carry out an embodiment of the invention in a multi-bed reactor and regenerator; and

Figure 2 shows a system similar to that of Figure 1 wherein inert solids and catalyst are maintained substantially in separate circulation circuits.

Referring now in detail to Figure 1 of the drawing, reduced crude such as an 8% bottoms fraction from the vacuum distillation of a West Texas crude or a similar heavy residue is supplied in the liquid state at a temperature of about 300°-700° F. to line 1 wherein it is admixed with hot fluidizable inert solids supplied by standpipe 3 and subsequently with hot fluidizable cracking catalyst supplied by standpipe 5 as will appear more clearly hereinafter. The inert solid may be petroleum coke, for example, having a particle size of about 100-500 microns and a temperature of about 1200°-1500° F. The catalyst may be any of those listed above, for example, a silica-alumina composite containing about 13% alumina and having a particle size of up to 80 microns; it may be supplied at a temperature of about 1000°-1150° F. The feed ratio of coke/oil and catalyst/oil may be about 0.5-19 and 1-10 by weight, respectively. An oil residence time of about 0.1-5 seconds is provided between the feed

points of standpipes 3 and 5 to permit vaporization of the feed and salt deposition prior to the entry of the catalyst into line 1. With reduced crudes having Conradson carbon contents above about 5, substantial coke deposition on the inert solids likewise takes place in this interval.

The mixture of solids and substantially completely vaporized feed may enter the lower portion of coking reactor 7 at a temperature of about 800°–1200° F. through a grid plate or other distributing device 9. Reactor 7 may have a lower section A separated from an upper wider diameter section B by a grid 11. If desired, sections A and B may be further separated by a suitable flow restriction formed by a partition 10 having an opening 12, to prevent materials introduced through line 16 between partition 10 and grid 11 from entering section A of reactor 7. Sections A and B are so designed that at the prevailing feed conditions the linear superficial vapor velocities therein are about 2–10 ft. per second and 1–3 ft. per second, respectively. When so operating, section A contains a dense, turbulent, fluidized mass  $M_a$  having an interface  $L_a$  from which catalyst is continuously elutriated to form a disperse phase  $D_a$  above level  $L_a$ . Mass  $M_a$  may have an apparent density of about 20–50 lbs. per cu. ft. and may contain about 1–20% of catalyst. It may be maintained substantially at the temperature of the entering feed. Oil contact time in mass  $M_a$  may be about 1–10 seconds. At these conditions, a limited catalytic reaction and extensive thermal cracking normally take place in mass  $M_a$  whereby carbon is deposited on inerts and catalyst. In addition, section A serves as an elutriation section for separating catalyst from inert solids.

The elutriated catalyst suspended in the partially reacted oil vapors passes upwardly through disperse phase  $D_a$  and grid 11 into section B to form therein a second dense, turbulent, fluidized mass  $M_b$  having an interface  $L_b$ . Mass  $M_b$  may have an apparent density of about 10–40 lbs. per cu. ft. It consists practically exclusively of catalyst containing only insignificant proportions, say about 1–5% of disintegrated inert solids fines entrained together with the catalyst from section A. Mass  $M_b$  may have a temperature of about 800°–1100° F. and provide a vapor contact time of about 3–15 seconds. At these conditions, the cracking reaction is substantially completed in mass  $M_b$ , so as to form about 0.5–6% of coke on the catalyst. Cracked product vapors containing some entrained catalyst may be withdrawn overhead from level  $L_b$  and passed through suitable gas-solids separation means such as cyclone 13 via line 15 to conventional product recovery equipment (not shown). Separated catalyst may be returned to mass  $M_b$  via line 14.

Regeneration of the solids and generation of the heat required for feed vaporization and cracking, in addition to preheat of the feed, may be carried out as follows. Inert solids which may contain up to about 5% of freshly deposited coke may be withdrawn in downward flow from mass  $M_a$  through a conventional standpipe 17 substantially at the rate at which solids flow through line 3. The solids in standpipe 17 are stripped and/or aerated through one or more taps  $t$  with small amounts of a suitable gas such as air, flue gas, steam, etc. Standpipe 17 may be provided in its upper portion with a packed elutriating section 18 wherein fine catalyst carried into standpipe 17 is elutriated upwardly by the gas introduced through taps  $t$ . The withdrawn inert solids may be passed wholly or in part, say a proportion of about 30–100% thereof, into air supply line 19 wherein they form a dilute suspension of solids in air which may be passed to the conical bottom portion 21 of regenerator 23.

Regenerator 23 may be of substantially cylindrical design and divided by horizontal solid plates 25 and 27 into two sections C and D and conical bottom 21. A plurality of vertical tubes 29 open at top and bottom may traverse section C and penetrate plates 25 and 27. A similar verti-

cal tube 31 may penetrate plate 27 and terminate in an upper portion of section D. Horizontal grid plates 33 and 35 may be arranged closely above, but in spaced relationship to plates 25 and 27, respectively.

The suspension of inert solids and air supplied to bottom cone 21 via line 19 passes upwardly through tubes 29 and grid 35 into section D wherein it forms a dense, turbulent, fluidized mass  $M_c$  separated by an interface  $L_c$  from a disperse phase  $D_c$ . That portion of the inert solids withdrawn from mass  $M_c$  which is not supplied to line 19 may be passed through standpipe 37 and suspended in an additional amount of air in line 39. This suspension may be passed to the space between plate 27 and grid 35 and thence into mass  $M_c$ . Combustion of coke deposited on the inert solids takes place in mass  $M_c$  whereby the solids are reheated. When operating in accordance with the present example, the amount of coke on the inert solids may be insufficient to establish a desirable temperature of about 1200°–1500° F. in mass  $M_c$ . Additional fuels such as torch oil, natural gas, petroleum coke or the like may be supplied through line 41 to make up for this deficiency. The linear superficial gas velocity in mass  $M_c$  is preferably maintained at about 2–10 ft. per second to establish the desired dense phase of the character described.

Returning now to reactor 7, spent and coked catalyst may be downwardly withdrawn from mass  $M_b$  through conventional standpipe 43 substantially at the rate of solids flow through line 5. Solids in standpipe 43 may be aerated and/or stripped through taps  $t$  and fed into air supply line 45. The suspension formed may be passed into the space between plate 25 and grid 33 and thence into section C to form therein a dense, turbulent, fluidized mass  $M_e$  separated by an interface  $L_e$  from a disperse phase  $D_e$  so that tubes 29 are imbedded in mass  $M_e$ . The air supply to mass  $M_e$  is preferably so controlled that a temperature of about 1000°–1150° F. is maintained therein by combustion of carbon and a linear superficial gas velocity of about 1–3 ft. per second suitable for dense phase operation is established. A portion of the heat generated in mass  $M_e$  is transferred to the inert solids passing through tubes 29 imbedded in mass  $M_e$  so as to preheat the inert solids and simultaneously to assist in controlling the temperature of mass  $M_e$  at the desired level whereby substantial quantities of heat are removed from the catalyst regeneration zone (mass  $M_e$ ), thus permitting operation of this zone at a lower temperature while still removing carbon. Flue gases containing small amounts of entrained catalyst are withdrawn from phase  $D_e$  and may be passed through cyclone 53 to tube 31 directly into phase  $D_a$ . From there, combined flue gases from sections C and D and entrained solids may be passed via cyclone or other separator 47 and line 49 to any desired use. Separated solids may be returned to mass  $M_a$  via line 51 or discarded via line 52. Small amounts of catalyst not recovered in cyclone 53 will enter phase  $D_a$ . Catalyst separated in cyclone 53 is returned via line 54 to mass  $M_c$  to avoid accumulation of catalyst in mass  $M_a$ .

Hot inert solids may be withdrawn from mass  $M_a$  via conventional standpipe 3, stripped and/or aerated therein through taps  $t$  with a suitable gas such as steam, flue gas, air, etc., and returned substantially at the temperature of mass  $M_a$  to oil feed line 1 at the rate and for the purpose indicated above. Similarly, hot regenerated catalyst may be withdrawn from mass  $M_c$  and supplied via standpipe 5 to oil feed line 1 as described above to complete the solids cycle. Make-up catalyst may be supplied through line 55 and make-up inert solids through line 57, as required.

Any desired portion of the inert solids withdrawn from mass  $M_a$  via standpipe 17 may be branched off through standpipe 59 to be passed to a desalting unit for the removal of deposited ash constituents of the oil by leaching with water or dilute acids or in any other conventional manner. Inert solids so purified may be returned to the

system via line 57, if necessary after a suitable adjustment of their particle size by crushing, grinding, etc. When coke is used as the inert solid, the withdrawn coke may be ground to a smaller particle size for seeding. Also, a supersonic type attriter may be arranged in mass  $M_a$  or in line 1 between the feed points of standpipes 3 and 5, in any manner known per se. Excess coke may be recovered. If desired, some reaction space, in the form of a high velocity coil type reactor (not shown), may be provided on line 1 just ahead of reactor 7 so that the catalyst entering section A will have a higher carbon concentration conducive to its enhanced elutriation from the inert solids in mass  $M_a$ .

The system described with reference to Figure 1 may also be used to crack a combination of feeds consisting of a reduced crude and a lighter, overhead stock. The reduced crude may be introduced as a liquid and may be vaporized by addition of hot inert solids and catalyst as described above. The lighter, vaporizable stock may be separately vaporized in a conventional furnace and introduced directly into the upper section B of reactor 7. Gasoline (the entire gasoline fraction, aviation gasoline, or the fraction above aviation gasoline) can be recycled to this upper section, maintained at a lower temperature than the lower section for refining of aviation gasoline to lower acid heat and the production of additional aviation gasoline. A process can also be used wherein cycle oil is recycled to the lower section A, maintained at a high temperature, and gasoline recycled to the upper section B with the resultant production of ultimate yields of low acid heat aviation gasoline. Other modifications and uses of the system of Figure 1 may appear to those skilled in the art without deviating from the spirit of the present invention.

A system having many of the characteristics of that shown in Figure 1, but designed for a substantially independent circulation of separate streams of inert solids and catalyst is illustrated in Figure 2. Reaction and operating conditions are substantially those described with reference to Figure 1 unless otherwise stated.

In operation, each pound of reduced crude feed is contacted in line 201 with about 0.5-30 lbs. of hot coarse inert solids such as coke supplied from standpipe 205 at a temperature of about 1100°-1500° F. substantially free of catalyst as will appear hereinafter. Feed coking and vaporization begin in feed transfer line 201 and are completed in section A of reactor 207 provided with feed distributing grid 209, in dense phase operation at a temperature of about 850°-1200° F. Product vapors containing insignificant amounts of entrained solids pass overhead through opening 212 of partition 210 and grid 211 into section B wherein they are contacted with a dense fluidized mass  $M_b$  of fine cracking catalyst at a temperature of about 800°-1100° F. to cause cracking and further coke deposition, cracked products being recovered via separator 213 and line 215, all substantially as described with reference to corresponding elements of Figure 1.

Coarse inert solids are withdrawn from dense phase  $M_a$  preferably via a packed stripping and elutriation well 217 supplied with a suitable stripping and elutriating gas, such as steam, via line 219 to remove adhering hydrocarbon vapors and any fine catalyst carried into mass  $M_a$  from regenerator 230. The withdrawn inert solids are passed via standpipe 221 to air line 223 and via grid 225 into the lower section E of regenerator 230 which may be of a design similar to that of reactor 207. Part of the coarse inerts may be withdrawn as product from line 221 as shown in Fig. 2. The reheated coarse inerts are withdrawn from dense phase  $M_e$  preferably via an elutriation and stripping well 232 supplied with stripping and elutriating gas, such as air, through line 234. The hot coarse solids then enter standpipe 205 and line 201 as above described. Flue gases pass upwardly through opening 235 of partition 236 and through grid 238 into section

F which contains dense fluidized phase  $M_f$  of fine catalyst undergoing regeneration as will appear hereinafter.

Returning now to section B of reactor 207, catalyst is continuously withdrawn downwardly from dense phase  $M_b$  preferably through a stripper 240 of essentially conventional design wherein the catalyst may be stripped with steam supplied through line 242. Stripped vapors may be returned via line 244 to the top of section B. Stripped catalyst is withdrawn from stripping vessel 240 through standpipe 246 and supplied to air line 248 through which the catalyst-in-air suspension is carried to section F of regenerator 230 at a point below grid 238. Coke is burned off the catalyst in fluidized mass  $M_f$  at a temperature of about 1000°-1150° F. The combined flue gases from beds  $M_e$  and  $M_f$  are passed to separator 250 from which separated hot fine catalyst may be returned to mass  $M_e$  via line 252 to supply thereto additional carbon for heat generation by combustion, provided the inert solids regeneration is carried out at a temperature not substantially exceeding that of the catalyst regeneration, in which case the catalyst fines may also supply sensible heat to the inert solids bed. If the amount of carbon so provided in mass  $M_e$  is insufficient for maintaining therein the desired high temperature, torch oil or fuel gas may be supplied to mass  $M_e$  via line 254. Catalyst separated in separator 250 may also be returned to mass  $M_f$  via line 256 and/or discarded via line 258, particularly if the inert solids are regenerated at substantially higher temperatures than the catalyst and catalyst returned to the inert solids bed would be deactivated by exposure to excessively high temperatures.

Hot regenerated catalyst is withdrawn downwardly from dense phase  $M_f$  via standpipe 260 and suspended in line 262 in a carrier gas, such as steam, product tail gas, or vapors of cycle gas oil or distilled virgin gas oil. The suspension formed enters section B of reactor 207 at a point below grid 211 to complete the catalyst cycle and to maintain mass  $M_b$  at the desired temperature. A catalyst circulation rate of about 1-20 lbs. per pound of oil feed is suitable at the conditions here specified. Lines 264 and 266 may be used to supply make-up catalyst and inert solids, respectively, as described with reference to lines 55 and 57 of Figure 1.

The systems illustrated in the drawing permit of various modifications. Whenever air is referred to this term is intended to comprise any free oxygen containing gas reacting exothermically with carbon to a degree adequate to generate the heat required. Thus, gases richer or poorer in oxygen than air may be used if desirable for the maintenance of proper fluidization conditions at the rate of combustion required. Fluidization on the reactor side may be facilitated by injecting suitable amounts of steam or gaseous hydrocarbons or vaporized naphtha fractions together with, or separately from, the oil feed into the reactor bottom. Whenever the particle size of the inert solids grows too large as a result of excessive coke deposition, a suitable grinding step may be included in the purification treatment designed to remove deposited feed contaminants.

While in the above examples reference has been made to the use of catalyst in a form more readily entrainable than the inert solids and this is the preferred embodiment of the invention, it is noted that some of the advantages of the invention may be secured when the inert solids are used in a more readily entrainable form than the catalyst. If desired, the systems illustrated may be readily adapted to this type of operation in a manner obvious to those skilled in the art.

The foregoing 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. A heavy residual petroleum oil conversion process which comprises combining a preheated residual oil with a stream of catalytically inert particles at a coking tem-

perature in a transfer line in the substantial absence of catalyst particles, to vaporize said oil and to deposit ash-forming and catalyst contaminating constituents of said oil on said inert particles; thereafter adding to the resulting suspension a stream of catalyst particles of sufficiently smaller particle size than said inert particles to give a basis for separation of the particles by elutriation, then introducing the suspension of oil vapors, catalyst particles and inert particles into a fluidized coking bed maintained at a coking temperature in the lower portion of a reaction zone, said coking bed comprising from 1 to 20% of said catalyst particles, elutriating catalyst particles from said coking bed by entrainment in oil vapors to an upper fluidized cracking bed maintained at a cracking temperature in said reaction zone to complete the conversion of the oil, said cracking bed comprising from 95 to 99% catalyst particles, recovering overhead from said cracking bed vaporous conversion products, regenerating catalyst particles withdrawn from said cracking bed and separately reheating inert particles withdrawn from said coking bed.

2. A heavy oil conversion process which comprises the steps of maintaining in a reaction zone at a coking temperature and a cracking temperature, respectively, a lower coking bed of fluidized solids comprising particulate inert solids and from 1 to 20% particulate catalytic solids, and an upper cracking bed of fluidized solids comprising particulate catalytic solids and from 1 to 5% particulate inert solids; said beds being fluidized at superficial gas velocities in the range of 0.5 to 10 feet/sec., said inert solids having a size in the range of about 100 to 500 microns, and said catalytic solids having a size below about 80 microns and being more entrainable than said inert solids; said beds being separated by a gas distributing device to permit separation of catalytic solids from the inert solids of said coking bed by elutriation; stripping and circulating catalytic solids containing from 0.5 to 6% coke from said cracking bed to an external regeneration zone, regenerating said catalytic solids in said regeneration zone by contact with a free oxygen-containing gas at a temperature in the range of 950° to 1250° F.; stripping and circulating inert solids from said coking zone to an external heating zone and back through a transfer line to maintain said coking temperature; contacting a heavy oil containing ash, catalyst contaminating and coke-forming constituents with freshly heated inert solids from said heating zone in the substantial absence of catalytic solids in said transfer line to vaporize said oil and to deposit said constituents on the inert solids; introducing freshly regenerated catalytic solids from said regeneration zone into said transfer line after a time in the range of 0.1 to 5 seconds from the contacting of said heavy oil and freshly heated inert solids; discharging the resulting suspension of oil vapors, inert and catalytic solids into said coking bed; elutriating catalytic solids by

entrainment in oil vapors from said coking bed to said cracking bed; and recovering vaporous conversion products overhead from said cracking bed.

3. The process of claim 2 wherein said inert solids comprise coke produced by the process, and wherein a portion of said coke is withdrawn as product.

4. A fluidized solids residual oil conversion process which comprises the steps of maintaining in a reaction zone at a coking temperature and a cracking temperature, respectively, a lower fluidized coking bed comprising particulate inert solids and from 1 to 20% of particulate catalytic solids, and an upper cracking bed of fluidized particulate catalytic solids, said catalytic solids being more readily entrainable in gases than said inert solids; maintaining in a burning zone in superposed relation, a regenerating bed of fluidized particulate catalytic solids at a regeneration temperature in the range of 950° to 1250° F., and a heating bed of fluidized particulate inert solids at a higher temperature in the range of 1050° to 1500° F.; introducing a free oxygen-containing gas into the lower portion of said burning zone to fluidize and burn the carbon on the solids therein; circulating inert solids from said coking bed to said heating bed and back to maintain said coking temperature in the range of 800° to 1200° F.; circulating catalytic solids containing from 0.5 to 6% coke from said cracking bed to said regenerating bed and back to maintain said cracking temperature in the range of 850° to 1000° F.; contacting a residual oil with freshly heated inert solids from said heating bed in a transfer line in the substantial absence of catalytic solids, to vaporize said oil and to deposit catalyst contaminants and coke on the inert solids; discharging the resulting suspension into said coking bed; elutriating catalytic solids by entrainment in oil vapors from said coking bed to said cracking bed; and recovering vaporous conversion products comprising a substantial proportion of gasoline boiling range constituents of high octane overhead from said cracking bed.

5. The process of claim 4 wherein said regenerating bed is disposed below said heating bed in said burning zone, wherein said inert solids are circulated from said coking bed to said heating bed through said regenerating bed in indirect heat transfer relation therewith.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

2,355,016	Stein	Aug. 1, 1944
2,364,145	Huppke et al.	Dec. 5, 1944
2,378,531	Becker	June 19, 1945
2,388,055	Hemminger	Oct. 30, 1945
2,393,636	Johnson	Jan. 29, 1946
2,436,160	Blanding	Feb. 17, 1948
2,436,486	Scheineman	Feb. 24, 1948
2,446,247	Scheineman	Aug. 3, 1948