(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 490 886 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **92200692.9**

(51) Int. Cl.⁵: **C10G 11/18**

(22) Date of filing: **08.02.89**

This application was filed on 11 - 03 - 1992 as a divisional application to the application mentioned under INID code 60.

(43) Date of publication of application:
17.06.92 Bulletin 92/25

(60) Publication number of the earlier application in accordance with Art.76 EPC: **0 381 870**

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: **STONE & WEBSTER ENGINEERING CORPORATION**
245 Summer Street
Boston Massachusetts 02107(US)

(72) Inventor: **Gartside, Robert J.**
47 Weston Road
Wellesley, Massachusetts 02181(US)

(74) Representative: **Roggero, Sergio**
Ing. Barzanò & Zanardo Milano S.p.A. Via Borgonuovo 10
I-20121 Milano(IT)

(54) Process for selectively producing ethylene and aromatics by catalytic cracking.

(57) Ethylene and aromatics are selectively produced by catalytically cracking a hydrocarbon feedstock in a fluidized catalyst bed at very short kinetic residence times and employing a deactivated, or low-activity catalyst of the zeolite type.

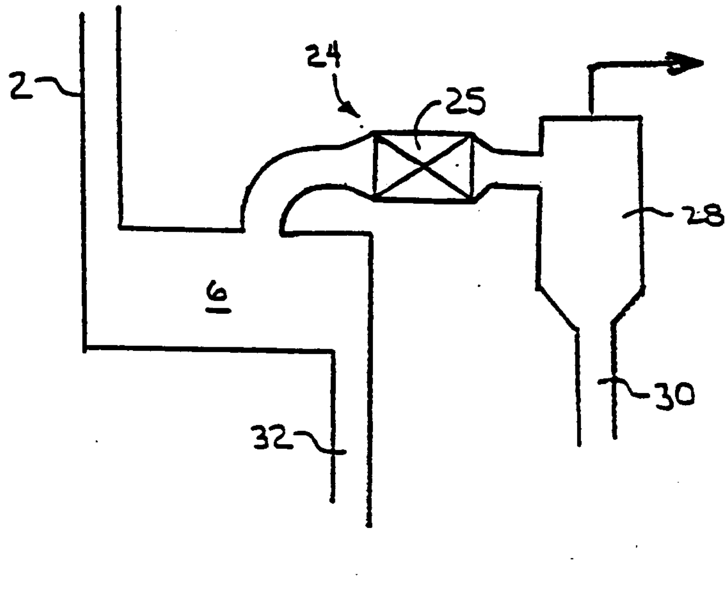

FIG 5

EP 0 490 886 A2

This application is a divisional of EP 89 200 285.8, published as EP-A1-0 381 870.

The parent application aforesaid relates to a process for catalytically cracking a hydrocarbon feedstock to selectively produce C_3 to C_6 olefins with the aid of a high activity acidic cracking catalyst, that is, a zeolitic catalyst associated with a dehydrogenation catalyst consisting of a metal oxide selected from the oxides of iron, chromium, tin or platinum on an inert carrier.

In the process according to the parent application aforementioned, the production of aromatics is reduced to a few percentage units when using a high activity catalyst, and to nil when mere pyrolysis is adopted. The present invention, instead, relates to a process for catalytically cracking a hydrocarbon feedstock to selectively produce ethylene and aromatics.

More particularly, this invention relates to a process for cracking hydrocarbons in the presence of an entrained stream of deactivated, or a low-activity, heat-carrying solids at short residence times with a view to selectively producing ethylene and aromatics, specifically benzene.

It has been known long since to crack naturally occurring hydrocarbons in order to produce valuable olefinic materials, such as ethylene and propylene.

One well known non-catalytic cracking process is pyrolysis, which typically takes place in the presence of steam at high temperatures, pyrolysis to olefins being generally explained in terms of a free-radical mechanism.

At high temperatures, radical initiation takes place by homolysis of a C-C bond, and, once initiated, the free radicals undergo two principale reactions, namely:

(1) scission at the beta position of the radical, and

(2) abstraction of a hydrogen, resulting in the termination of the reaction.

The prior art tenders several examples of high-temperature, short time hydrocarbon conversion processes.

US-A-2 906 695 discloses a process for the kind referred to above, in which the hydrocarbon feedstock is contacted with fluidized particulate solids at a tempertuare of from 538 ° C to 649 ° C, in the initial section of a reactor, the resultant reaction mixture is caused to flow rapidly trough the reaction zone and and receives a strong rotational motion about the axis of the flow, additional highly heated particulate solids being introduced immediately thereafter in the central portion of the fluid mixture so as to heat the mixture to a temperature of from 677 ° C to 982 ° C (1250 ° F-1800 ° F).

GB-A-2 048 299 discloses a catalytic cracking process in which hydrocarbons having a boiling point above 220 ° C are converted into lower boiling hydrocarbon products of improved octane rating with the aid of a particulate crystalline catalyst having pore opening and maximum cage dimensions of 55 nm to 70 nm, an active dehydrogenating metal being disposed within the interior of the crystals.

EP-A-0 026 674 discloses an improved sequential Thermal Regenerative Cracking (TRC) process, together with an improved solids quench procedure, an improved preheat vaporization system and improved fuel gas generation system.

None of these references, however, contains any suggestion as to the simultaneous selective production of ethylene and aromatics by catalytically cracking a hydrocarbon feedstock.

The present invention, therefore, proposes a process for catalytically cracking a hydrocarbon feedstock to selectively produce ethylene and aromatics, comprising the steps of: (a) introducing the hydrocarbon feedstock to a cracking reactor; (b) delivering simultaneously hot deactivated, or low-activity, cracking catalyst solids to the cracking reactor; (c) cracking catalytically and thermally the hydrocarbon feedstock with heat supplied by the hot catalyst solids to form a cracked product; (d) separating the cracked product from the hot catalyst solids, and, (e) quenching the separated cracked product, characterized in that the total kinetic residence time of the hydrocarbon feedstock from step (a) to step (e) is from 0,05 s to 2,0 s, the temperature of the cracking reaction being from 482 ° C to 815 ° C (900 ° F-1500 ° F), the pressure of the cracking reactor being of from 0,69 bar to 6,9 bar, the weight ratio of the catalyst solids to the hydrocarbon feedstock being from 1:1 to 60:1, and the deactivated, or low-activity, cracking catalyst being a zeolitic catalyst.

The preferred residence time is from 0,1 s to 0,5 s. The typical definition of residence time in a catalytic cracking process is the time during which the feedstock remains in contact with the catalyst: this definition is acceptable if the temperatures are so low that thermal reactions do not occur to any appreciable extent. Thermal and catalytic reactions however, proceed in parallel, and, although the withdrawal of the catalyst stops the catalytic portion of the reaction, the thermal reactions, or pyrolysis, will continue until the temperature is reduced to so low a level that the reaction rate is virtually insignificant (quenching).

In this situation, the kinetic residence time, which is a critical parameter in the process of this invention, is intended herein to connote the time elapsed from the introduction of the hydrocarbon feedstock into the system to the quenching of the effluent, the time necessary for withdrawing the solids from the reaction being therefore included.

This distinguishes the present process from the other processes in which the measurement of the residence time is terminated prior to the point of separation and quench.

To the ends of the present invention, the hydrocarbon feedstock is selected from C_4 to C_7 paraffins, naphthas and light gas oils.

According to another aspect of this invention, the present process futher comprises the steps of: (f) delivering the separated catalyst solids to a stripper to remove residual cracked gas products; (g) combusting the separated catalyst solids to remove carbon deposits and to heat the stripped catalyst solids to form regenerated catalyst solids, and (h) trasporting the regenerated catalyst solids to the cracking reactor.

In a preferred embodiment of the instant process, the temperature of the catalytic cracking reaction is from 538°C to 704 °C (1000°F-1300°F) and the residence time is from 0,1 s to 0,3 s.

The process of the present invention proceeds by delivering the preheated hydrocarbon feedstock of the kind referred to above, together with steam, to the top of a downflow tubular reactor. Simultaneously, hot catalyst solids are introduced to the top of the reactor, and the combined stream of hydrocarbon feedstock, steam and catalyst solids passes through the reactor zone, a separation zone, and a quench zone: in this latter the hydrocarbon undergoes cracking at low severity and short residence times and the effluent is stabilized to prevent product degradation.

As outlined above, the tubular reactor is operated under the conditions of a total kinetic residence time of the hydrocarbon feedstock from 0,05 s to 2,0 s, at a temperature of the cracking reaction from 482°C to 815°C (900°-1500°F), under a pressure of the cracking reactor of from 0,69 bar to 6,9 bar (10 psi-100 psi), the weight ratio of the catalyst solids to the hydrocarbon feedstock being from 1:1 to 60:1, and the deactivated, or low-activity, cracking catalyst being a zeolitic catalyst.

Fluidized solids, short-residence time cracking apparatus, such as described in US-A 4 370 303, and US-A-4 433 984 are well adapted for use in the process of the present invention.

These apparatus have been indicated herein for information, inasmuch as the present invention relates to the procedure only, and is not bound to any particular apparatus form, so that any apparatus or installation can be used, provided that it be suitable for carrying out the operational steps referred to in the foregoing. However, the present process will now be described in detail, with the aid of the accompanying drawings, in order to make the entire processing run quite clear. In the accompanying drawings:

FIG.1 is a simplified diagram of the step sequence of the instant process;

FIG.2 is a cross-sectional, elevational view, of a reactor feeder which can be employed in an apparatus adapted to be used for performing the instant process;

FIG.3 is a cross-sectional, elevational view of a separator which can be employed in the instant process;

FIG.4 is a sectional view through line 4-4 of Fig.3;

FIG.5 is a simplified diagram of the quenching process step in the process of this invention;

FIG.6 is illustrative of the overall arrangement of a complete system which can be employed for performing the instant process;

FIG.7 is a cross-sectional, elevational view of a reactor and gas-solids separator useable for the instant process;

FIG.8 is a sectional plan view through line 8-8 of Fig.7, and

FIG.9 shows a solids regeneration assembly.

Referring now to the drawings and, at the outset, to Fig.1, a short residence time fluidized cracking system, briefly called a QC system hereinafter, is generally indicated at 1, and comprises a tubular reactor 2, a reactor feeder 4, a separator 6, a quenching means 24 and a solids stripper 8: the system 1 also comprises catalyst regenerating means, such as an entrained bed heater 10, wherein the catalyst solids can be regenerated and reheated, a transport line 12, and a fluid bed vessel, 14, wherein the solids are stripped of combustion gases and fed back to the reactor 2.

In operation, hot catalyst solids from the fluid bed vessel 14 enter the reactor feeder 4 and are admixed with steam entering through a line 16. The hydrocarbon feedstock is delivered, through a line 18, to a preheater, 20, and then, through a line 22, to the upper region of the tubular reactor 2. The preheated hydrocarbon feedstock, along with the catalyst solids and steam from the reactor feeder 4, are passed through the tubular reactor 2. Intimate mixing of the hot catalyst solids, steam and preheated hydrocarbon feedstock occurs in the reactor, and cracking is started immediately.

Upon exiting the tubular reactor 2, the cracked hydrocarbon effluent and the steam are immediately separated from the catalyst solids in the separator 6, and the cracked effluent product passes overhead through the quench area 24, where the cracked product is immediately quenched with steam, or a light hydrocarbon, delivered to the quench area 24 through a quench line 26. This operation reduces the temperature of the mixture below the point where substantial thermal reactions occur.

Optionally, quenching of the cracked product exiting the tubular reactor 2 and separated from the catalyst solids in the separator 6 may take place by passing the entire mixture through a catalytic bed, 25, in which the catalyst solids are contained, and which is located immediately downstream of the separator 6.

The quenched product is passed through a cyclone, 28, where small amount of the entrained catalyst solids are removed, and delivered, through a line 30, to the solids stripper, 8, where they are combined with the bulk of the stripped solids delivered from the separator 6 through a line 32. In the solids stripper 8, the catalyst solids are stripped of residual hydrocarbon by steam, nitrogen, or other inert gases, delivered to the solids stripper 8 through a line 34.

The catalyst solids, which have accumulated carbon or coke deposits from the tubular reactor 2, are then passed to the entrained bed heater 110.

Air, delivered to the heater 10 through a line 36, is mixed with the stripped catalyst solids in the heater 10, and the mixture is fed into the transport line 12 for conveying the catalyst solids back to the fluid bed vessel 14. In the presence of air from the line 36, the carbon deposits on the catalyst solids are removed by combustion to provide the heat which is required for the cracking reaction. If additional fuel is required, it may be added into the entrained bed heater 10 from any conventional fuel source.

The hydrocarbon feed, of the kind referred to above, is delivered through the line 18 to the preheater 20, wherein the temperature of the hydrocarbon feedstock is raised to 427°C-482°C (800°F-900°F). Simultaneously, catalyst solids from the fluid bed vessel 14 are delivered to the reactor feeder 4 (best seen in Fig.2), where they are admixed with steam supplied through the line 16, and delivered to the reactor at a temperature of from 538°C to 871°C (1000°F to 1660°F). The catalyst solids to the hydrocarbon feed ratio ranges from 1:1 to 60:1, and the water vapour to the hydrocabon feedstock feed ratio is from nil to 1,0 , the preferred range being from nil to 0,3.

As outlined above, the deactivated, or low-activity cracking catalyst is a zeolitic catalyst.

The cracked effluent product and catalyst solid effluent from the tubular reactor 2 flow directly into the separator 6 (best seen in Fig.3), where a separation into a gas product phase, and a catalyst solid phase is effected.

The gas product is removed via the line 24, while the catalyst solids enter the solids stripper 8 through the line 32. An in-line quench of the gas product is provided in the quench area 24, through the quench line 26. Cold solids, water, steam, light hydrocarbons, and recycle oils are suitable quench materials, or quenching can take place through a catalyst bed, as outlined above with reference to Fig.5 of the drawings.

The preferred kinetic residence time, as defined hereinabove, is from 0,1 s to 0,3 s.

In the solids stripper 8 the catalyst solids are stripped of gas impurities by a stream of steam, nitrogen or inert gas, delivered through the line 34. The vapours are removed from the solids stripper 8 through the line 30. The stripped catalyst solids are removed from the stripper 8 through a line 38. The catalyst solids which have accumulated carbon from the tubular reactor 2 are passed to the entrained bed heater, 10, where air is delivered through a line 36 to provide the necessary atmosphere for regenerating the catalyst solids. The catalyst solids are entrained in the heater 10 and returned to the fluid bed vessel 14 through the transport line 12, where the catalyst solids continue to regenerate. In addition, the regeneration of the catalyst solids raises their temperature to 649°C-927°C (1200°F-1700°F) prior to delivery of the catalyst to the fluid bed vessel 14.

A suitable reactor feeder, 4, is described, for example, in US-A-4 330 187, and has the capability of rapidly admixing the hydrocarbon feedstock and the catalyst solids. As seen in Fig.2, the reactor feeder 4 delivers catalyst solids from a solids receptacle, or fluid bed vessel, 70, through vertically disposed conduits, 72, to the tubular reactor 2, and simultaneously delivers hydrocarbon feedstock to the tubular reactor 2, at an angle into the path of the catalyst solids which are being discharged from the conduits 72.

An annular chamber,74, to which hydrocarbon is fed by a single entry comprising a toroidal feed line 76, terminates in angled openings 78. A mixing baffle, or plug, 80, also assists in effecting rapid and intimate mixing of the hydrocarbon feedstock and the catalyst solids. The edges, 79, of the angled openings 78 are preferably convergently bevelled, as are the edges 79 at the reactor end of the conduits 72.

In this way, the gaseous hydrocarbon stream from the chamber 74 is angularly injected into the mixing zone, and intercepts the catalyst solids phase flowing from the conduits 72. A projection of the gas would form a cone, shown by dotted lines, 77, the vertex of which is beneath the flow path of the solids. By introducing the gaseous hydrocarbon phase angularly, the two phases are mixed rapidly and uniformly, and form a homogeneous reaction phase.

The mixing of a solid phase with a gaseous phase is a function of both the shear surface between the solid phase and the gas phase, and the flow area.

A ratio of the shear surface to the flow area (S/A) of infinity defines a perfect mixing, while poorest mixing occurs when the solids are introduced at the wall of the reaction zone. In the system which carries out the instant process, the gas stream is introduced annularly to the solids, that which ensures a high shear surface. By also adding the gas phase transversally through an annular feed means, mutual compenetration of the phases is obtained, and an even faster mixing results.

By using a plurality of annular gas feed points, and a plurality of solid feed conduits, an even more intimate mixing is more rapidly promoted, since the shear surface to flow area ratio for a constant solids flow area is increased. Mixing is also a known function of the legnth to diameter ratio of the mixing zone. A plug creates an effectively reduced diameter, D, in a constant length, L, thus improving mixing.

The plug, 80, reduces the flow area and forms discrete mixing zones. The combination of annular gas addition around each solids feed point, and a confined discrete mixing zone greatly enhances the conditions for mixing. By so doing, the time required to obtain an essentially homogeneous reaction phase in the reaction zone is quite short and kinetic residence times below 1 s can be obtained, and even much shorter kinetic residence times can be achieved, such as below 100 ms. Because of the environment of the tubular reactor 2 and the reactor feeder 4, the walls are lined with an inner core 81 of a ceramic material.

The separator 6 of the QC system, as shown in Fig.3, can also be relied on for rapid and discrete separation of product and catalyst solids being discharged from the tubular reactor 2. The inlet to the separator 6 is directly above a right-angle corner, 90, at which a mass of catalyst solids, 92, collect within a chamber 93. An optional weir, 94, downstream of the right-angle corner 90, facilitates accumulation of the mass of solids 92, especially when run on a small scale rather than a commercial scale production.

The gas outlet 24 of the separator 6 is oriented 180 degrees from a separator gas-solids inlet 96, and the solids outlet line 32 is directly opposed in orientation to the gas outlet 24 and downstream of both the gas outlet line 24 and the weir 94.

In operation, centrifugal force propels the catalyst solids to the wall opposite inlet 96 of the chamber 93, while the gas portion, which has less momentum, flows through the vapour space of the chamber 93. Initially, catalyst solids impinge on the wall opposite the inlet 96, but subsequently accumulate to form a static bed of solids, 92, which ultimately form in a surface configuration having a curvilinear arc having an angular width of approximately 90 degrees. Solids impinging upon the bed 92 are moved along the curvilinear arc to the solids outlet 95, which is preferably oriented for downflow of solids by gravity. The exact shape of the arc is determined by the geometry of the particular separator and the inlet-stream parametres, such as velocity, mass flow rate, bulk density, and particle size.

Erosion is minimal because the force imparted to the incoming solids is directed against the static bed 92 rather than against the separator 6 itself.

Separator efficiency, defined as the removal of solids from the gas phase leaving through the outlet 95 is, therefore, not affected adversely by high inlet velocities, up to 45,75 m/s (150 ft/s), and the separator 6 is operable over a wide range of dilute phase densities, preferably between 0,016 g/cm^3 to 0,16 g/cm^3 (0,1-10,0 lbs./ft.^{3}).

The separator 6 achieves efficiencies near to 90%, but efficiencies as high as a 97%-removal of catalyst solids can be obtained.

It has been found that, for a given height, H, of the chamber 93, efficiency increases as the 180-degree U-bend distance between the inlet 96 and the outlet 97 is brought progressively closer to the inlet 96. Thus, for a given height, H, the efficiency of a separator, such as 6, increases as the flow path decreases, and, hence, residence time decreases. Assuming an inside diameter, D_i, of the outlet 96, the distance, CL, between the centre lines of the inlet 96 and the outlet 97 is preferably not greater than 4 times D_i, while the most preferred distance between said centre lines is between 1,5 times and 2,5 times D_i. Below 1,5 times D_i, better separation is obtained, but the construction of the separator may prove difficult.

It has also been ascertained that the height H should be at least 1,5.D_i, or 10,16 cm (4 inches), whichever is the greater. If not so, the incoming stream might disturb the bed solids 92, so that the solids might be entrained in the gas product leaving through the outlet 97. Better separation efficiencies are obtained if H is at least the double of Di, but too large a height, H, would merely increase the residence time without substantially increasing the separation efficiency. In practice, the width, W, of the flow path (Fig.4) is, in its turn, preferably between 0,75 D_i and 1,25 D_i, the most preferred range being from 0,9 D_i to 1,10 D_i.

The outlet 97 may be of any inside diameter (symbolized as Dog), but velocities over 23 m/s (75 ft./s) can cause erosion because of residual solids entrained in the gas stream. The inside diameter, Dog, of the outlet 97 should be so sized that a pressure differential may exist, between the stripper 8 (Fig.1) and the separator 6, such that a static height of solids is formed in the outlet line 32. Such static height of solids provides a positive seal preventing gases from entering the stripper 8. The magnitude of the pressure differential referred to above is determined by the force required to move the solids in bulk flow to the outlet

95, and also by the height of the solids in the line 32. As the pressure differential increases, the net flow of gas to the stripper 8 decreases. Solids, which have a gravitational momentum, overcome the pressure differential, whereas gas preferably leaves through the outlet 97.

If a single outlet 97 is used, it is preferred that the inside diameter, Dog, of outlet 97 is the same as the Dog of the inlet 96, to provide outlet velocity less than, or equal to, the inlet velocity.

FIG.4 is a cutaway view of the separator 6.

It is essential that the longitudinal sidewalls 101 and 102 be rectilinear, or slightly arcuate, as shown by the dotted lines 101a and 102a. Thus, the flow path through the separator 6 is essentially rectangular in cross-section, with a height, H, and a width, W, as shown in Fig.4, which defines the geometry of the flow path by adjustment of the lining width of the sidewalls 101 and 102.

Baffles, weirs, inserts and like flow deviation means can be used, and the configuration of the walls 103 and 104 transverse to the flow path can be similarly modified, if necessary.

The separator shell and manways may be lined with erosion resistant linings, such as, for example, Carborundum Precast Carbofrax D (Registered Trade Mark) or Carborundum Precast Alfrax 201 (Registered Trade Mark) whenever necessary or expedient. A thermal insulation lining, 106, may be inserted between the shell and the lining 105, and between the manways and their erosion resistant linings, whenever high temperature service is required for the separator 6.

The details of a separator such as 6 are more fully described in US-A-4 288 235.

Referring now to Figs.6 to 9, a system, 202, is described, which comprises a reactor system, 204, a solids regeneration assembly, 208, and a solids delivery system, 210.

The reactor system 204 (Fig.7) includes a convergent mixing section, 211, an elongate reaction section, 212, a divergent section, 213, downstream of section 212, a separator, 206, and a quench system (Fig.8). The mixing sections 211 are formed with a plug section, 214, shown in cross-section as having an arcuate lower surface, 215. A horizontal plate, 217, is arranged over the plug section 214 and in spaced relationship relative thereto, to form solids inlet passages 219 to the interior of the

mixing section 211. The solids inlet passages 219 are configured, in cross-section, with a right-angle turn, and terminate in rectangular openings, 225, through which the particulate solids enter the mixing section 211, in the form of a curtain of solids, 226. The openings 225 are directly above each hydrocarbon feedstock inlet. Venturi-shaped passages, 203, extend from the solids inlet passages 219 to the hydrocarbon feedstock inlets, 228.

Steam plenums (not shown) are arranged along each longitudinal edge of each horizontal opening 225 to deliver pre-acceleration gas (steam) through nozzles (not shown) into the curtain of solids 226 passing through the horizontal openings 225.

A gas-delivery line (not shown) is provided to deliver gas, usually steam or a light hydrocarbon, under pressure, to the nozzles, these latter being arranged at a downward angle of 45 degrees to the horizontal. The pre-acceleration gas is delivered to the plenums under a pressure of from 0,207 bar to 0,345 bar (3 to 5 psi) above the pressure in the reactor, and discharges through the nozzles at the same relative pressure at a velocity of 45,75 m/s (150 feet/s). The pre-acceleration gas accelerates the flow of solids through the horizontal openings 225, for example, from a nominal 0,915 m/s to from 1,83 m/s (3 to 6 ft/s) to 15,25 m/s (50 ft/s) for the mix of solids and pre-acceleration gas. The hydrocarbon feedstock inlets 228 are located on the reactor wall, and are arranged either perpendicularly to the solids curtain 226, or at a 30-degree angle upwardly into the solids curtain 226. The hydrocarbon feedstock is delivered to a manifold, 223, through a line 224. The feed inlet nozzles 228 are fed with hydrocarbon feedstock from the manifold 223. The feed inlet nozzles 228 are diametrically opposed relative to each other in the same horizontal plane (Fig.7). The mixing zone, 211, of the reactor is rectangular with the configuration making a transition to the tubular reactor at the elongate reaction section 212.

The feedstock entering the mixing zone 211 through nozzles 228 immediately impinge the solid curtains 226 and the desired mixing of feedstock and hot particulate solids occurs.

With the opposing set of nozzles 228, the opposing feed jets and the entrained solids from the curtain 226 will be directed, by the arcuate contour 215 of the plug section 214, and impact with each other at approximately the vertical central axis of the mixing zone 211. When a gas-liquid mixed phase hydrocarbon is fed through the nozzles 228, the nozzles 228 are arranged at an angle perpendicularly to the solids curtain 226. When the hydrocarbon feedstock is a gas, the nozzles 228 are arranged at an upwardly directed 30-degree angle into the solids curtain. The quantity of solids entering, through the horizontal inlets 219, the mixing zone 211 of the reactor system 204, is controlled in large part by the pressure differential between the mixing zone 211 of the reactor system 204, and the chamber 231a above the solids reservoir 218 in a solids control hopper 231, directly above the horizontal inlets 219.

Pressure probes, 233 and 235, are located in the mixing zone 211 of the reactor system 204, and in the control hopper chamber 231a, respectively, to measure the pressure differential referred to above.

Gas (steam) under pressure is delivered through a line 230 to the control hopper chamber 231a to regulate the pressure differential between the mixing zone 211 of the reactor system 204, and the control hopper chamber 231a, to promote or interrupt flow of the solids from the solids control hopper 231 to the mixing zone 211.

As best seen in Fig.7, the separator 206 is comprised of a mixed phase inlet 232, a horizontal chamber section 234, a plurality of cracked gas outlets 236 and particulate solids outlets 238.

The separator 206 is arranged in combination with the elongate cracking zone 212 and divergent section 213 of the reactor system 204. The divergent section 213 terminates in the separator mixed phase inlet 232, which is centrally disposed at the top of the horizontal section 234. As a result of the configuration of the composite reaction system including the separator 206, a solids bed, 242, develops on the floor, 240, of the horizontal section 234 with the cross-sectional profile 243 of the bed 242 forming a curvilinear arc over which the mixed phase gas and solids travel. The expansion of solids and cracked gas in the divergent section 213 enchances heat transfer and limits the velocity of the solids-gas mixture entering the separator 206.

The solids are sent to the lateral ends 246 of the horizontal section 234, and discharge downwardly through the solids outlets 238. The cracked gases follow a 180-degree path and, after separation from the solids, discharge through gas outlets 236, that are located on the top of the horizontal section 234 intermediate the lateral ends 246. The plurality of solids outlets 238 and gas outlets 236 provide simultaneously for both minimum time in the separation zone, and maximum solids-gas separation.

The separation or quench system, 207, also includes a conventional cyclone separator, 250, directly downstream of each gas outlet 236, as best seen in Fig.8. The entry line 254 to each cyclone separator 250 is arranged at an angle of 90 degrees to the gas outlet 236 with the cyclone separator 250 vertically disposed in the system. The cyclone separators 250 serve to collect the remaining entrained particulate solids from the cracked gas discharged from the separator 206. A solids-discharge line 249 (schematically indicated in Fig.8 and descending from the relevant cyclone separator 258) returns the particulate solids to the regeneration assembly 208 (Fig.6) and the cracked gases are sent for further processing through the gas outlet 251.

Each cyclone entry line 254 extending from the cracked gas outlet 236 of the cyclone 250 is provided with a direct quench line 252.

Quench oil, usually the 38°C-204°C (100°F-400°F) cut from a downstream distillation tower, is introduced into the cyclone 250 through the direct quench line 252 to terminate the reactions of the cracked gas.

As best seen in Fig.9, the regeneration assembly 208 is comprised of a stripper, 253, a control hopper 255, an entrained bed heater 258, a lift line 257, and a regenerated solids vessel 260.

The stripper 253 is a tubular vessel into which the particulate solids from the separator 206 are delivered through solid outlet legs (not shown) and from the solids-discharge lines 249 of the cyclones 250.

A ring 262 having nozzle openings 264 is provided at the bottom of the stripper 253. A stripping gas, typically steam, is delivered to the ring 262 for discharge through the nozzles 264. The stripping steam passes upwardly through the bed of particulate solids to remove impurities from their surfaces. The stripping steam and entrained impurities pass upwardly through the particulate solids in the stripper 253, and discharge through a vent line (not shown).

The stripped solids are accumulated in the control hopper 255 to be finally delivered to the entrained bed heater 258. The control hopper 255 is a collection vessel in which the solids enter through a standpipe 266 and from which an outlet line 273 extends to deliver solids to the entrained bed heater 258. The assembly of the control hopper 255 and the standpipe 266 provides for a slumped bed solids transport system.

The pressure differential maintained between the slumped bed surface 268 in the control hopper 255 and the exit 270 of the outlet line 273 determine the solids flow rate between the control hopper 255 and the entrained bed heater 258. A line 272 is provided to selectively introduce steam under pressure into the control hopper 255 to regulate the pressure differential. Pressure probes 267 and 269 are placed in the control hopper 255, and in the entrained bed heater 258, respectively, to monitor the pressure differential and regulate a valve 265 in the steam line 272.

The entrained bed heater 258 is essentially tubular in configuration. An array of distinct fuel nozzles 261, fed by fuel lines 263, are arranged symmetrically on the lower inclined surface 275 of the entrained bed heater 258. Pressurized air enters the entrained bed heater 258 through a nozzle 277 arranged to direct air axially upwardly through the entrained bed heater 258. The air jet provides both the motive force to lift the solids particles upwardly through the entrained bed heater 258 to the regenerated solids vessel 260, and the air which is necessary for combustion. The fuel is ignited by contact with the solids in the presence of air.

The combustion gas/solids mixture moving upwardly through lift line 257 enters the regenerated solids vessel 260 tangentially, preferably perpendicularly to the lift line, to separate the combustion gases from the solids. As shown in Fig.9, the vessel 260 has, in its interior, a right-angle tubular extension 285 of the gas outlet nozzle 286 to provide cyclonic movement, that which improves the separation efficiency of the system.

The regenerated solids vessel 260 is a cylindrical vessel provided with a standpipe 271 (Fig.7) extending from the reactor hopper 231. Again, the structure of the regenerated solids vessel 260 provides for accumulation of a slumped bed 281 (Fig.9) above which pressure can be regulated to enable controlled delivery of the regenerated particulate solids to the reactor hopper 231.

The upper solids collection vessel 260 (Figs.6, 7 and 9) contains a stripping section as the lower portion, with a stripping ring 279, and is a part of the solids delivery system 210 (Fig.6). Above ring 279, the solids slump, and are fed to the standpipe 271 (Fig.7). The standpipe 271 feeds the slumped bed in the control hopper 231 (Fig.7). Solids flow into the reactor hopper 231 through the standpipe 271 (Fig.7) to replace solids that have flowed into the reactor 204 (Fig.6). Unaerated solids (slumped solids) will not continue to flow into the reactor hopper 231 once the entrance 232 to the hopper 231 has been covered. Thus, the position of the entrance 232 defines the solids level in the hopper 231. As solids flow from hopper 231 via the pressure differential between the vapor space in the chamber 231a above the bed 218 and the mixing zone 211 (Fig.7), the entrance 232 is uncovered, allowing additional solids to flow into the hopper 231. As outlined above, a QC system is enabled, by adopting the process according to he present invention, to enhance the production of aromatics, specifically benzene.

According to this invention, therefore, the production of aromatics can be enhanced by using a deactivated, or low-activity cracking catalyst, particularly a deactivated zeolitic catalyst. Zeolitic catalyst deactivation is usually a result of prolonged exposure to high temperatures and steam, that which causes the collapse of the zeolitic matrix. The result is a significant reduction of the catalyst surface area and hence catalyst activity.

Typically, in an FCC (Fluidized Catalytic Cracking) unit which uses zeolitic catalysts, the spent catalytic solids are withdrawn, and fresh catalyst is added to maintain activity. Such spent catalyst solids are suitable for use as deactivated catalysts in the process according to the present invention.

Due to the low activity of such spent catalysts, the cracking reaction temperatures required are similar to those required to achieve pyrolysis conversion, and are from 482°C to 815°C (900°F-1500°F), as specified hereinabove.

Quite unexpectedly, there is a substantial increase in aromatics production (spefically benzene), and a corresponding decrease in C_3 and C_4 olefin production, while with a significant concurrent production of ethylene. The ethylene yields are similar to those from pyrolysis, given the predominance of the free-radical cracking reactions at these temperatures.

However, the deactivated catalyst of the kind referred to above provides enhanced aromatization activity at these higher temperatures, and thus aromatics are formed at the expense of the C_3 and C_4 olefins and paraffins.

The tabulation reported hereinafter illustrates the use of a QC system to enhance aromatics production from the cracking of n-hexane and compares the deactivated catalyst used in the process of this invention (Example 3) with the pyrolysis process at a fixed 70% conversion (Comparative Example 1) and with the high-activity catalyst cracking at a fixed 70% conversion (Comparative Example 2).

QC REACTOR

	Pyrolysis Reactor	High Act. Catalyst	Deact. Catalyst
	----comparative---		(invention)
Example N°	1	2	3
Temperature	730°C	550°C	740
Residence time (Quench included)	0,2 s	0,2 s	0,2 s
Conversion	70%	71%	82%
Wt% Feed			
CH_4	6,3	7,0	9,8
C_2H_4	35,0	8,4	35,2
C_3H_6	19,8	27,1	4,6
C_3H_8	nil	19,6	2,1
AROMATICS	nil	2,1	20,9
C_3H_8/C_3H_6	nil	0,72	0,46

The above tabulation shows that, in the comparative Example 1, which refer to pyrolysis, a hydrocarbon conversion of 70% is obtained in the conventional pyrolysis at a reactor outlet temperature of 730 ° C and a residence time of 0,2 s. Pyrolysis, as can be seen, produces significant amounts of olefins, but only trace amounts of paraffins and aromatics. Similar results are obtained when using a completely inert solid, such as pure alumina, in a QC cracking environment.

The comparative Example 2, which refers to the use of a high activity acidic cracking catalyst, shows that a 71% hydrocarbon conversion can be obtained at a reduced temperature of 550 ° C and a residence time of 0,2 s. Ethylene production will be suppressed, while the yields of C_3 olefins and paraffins enhanced. Furthermore, only small amounts of aromatics are produced.

From the comparative examples referred to above, it can readily be appreciated that the production of aromatics is virtually insignificant therein.

It is thus also apparent that, Example 3 being particularly referred to now, by adopting the process according to this invention and the deactivated or low activity catalyst prescribed therefor, the production of aromatics, concurrently with ethylene, is both surprisingly and significantly exalted.

Claims

1. Process for catalytically cracking a hydrocarbon feedstock to selectively produce ethylene and aromatics, comprising the steps of:

(a) introducing the hydrocarbon feedstock to a cracking reactor;

(b) delivering simultaneously hot deactivated or low-activity catalyst solids to the cracking reactor;

(c) cracking catalytically and thermally the hydrocarbon feedstock with heat supplied by the hot catalyst solids to form a cracked product;

(d) separating the cracked product from the hot catalyst solids, and

(e) quenching the separated cracked product, characterized in that the total kinetic residence time of the hydrocarbon feedstock from step (a) to step (e) is from 0,05 s to 2,0 s, the temperature of the cracking reaction being of from 482 ° C to 815 ° C (900 ° F-1500 ° F), the pressure of the cracking reactor being of from 0,69 bar to 6,9 bar (10 psi-100 psi), the weight ratio of the catalyst solids to the hydrocarbon feedstock being from 1:1 to 60:1, and the deactivated or low-activity cracking catalyst being a zeolitic catalyst.

2. Process according to Claim 1, wherein the residence time is from 0,1 s to 0,5 s.

3. Process according to Claim 1, further comprising the steps of:

(f) delivering the separated catalyst solids to a stripper to remove residual cracked gas products;

(g) combusting the separated catalyst solids to remove carbon deposits and to heat the stripped catalyst solids to form regenerated catalyst solids, and

(h) transporting the regenerated catalyst solids to the cracking reactor.

4. Process according to Claim 1, wherein the temperature of the catalytic cracking reaction is from 538 ° C to 704 ° C (100 ° F-1300 ° F) and the residence time is from 0,1 s to 0,3 s.

5. Process according to Claim 1, wherein the hydrocarbon feedstock is selected from C_4 to C_7 paraffins, naphthas and light gas oils.

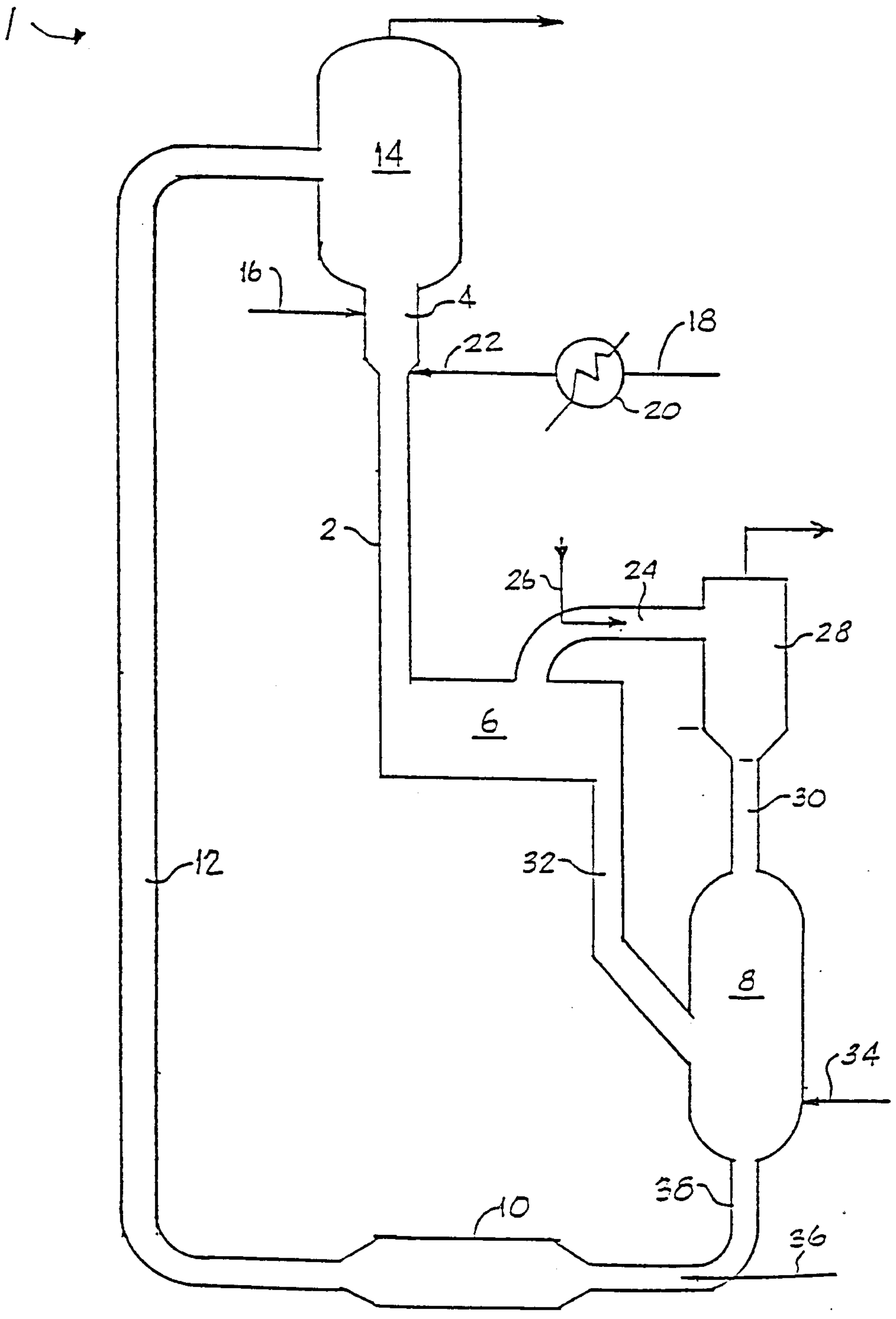

FIG.1

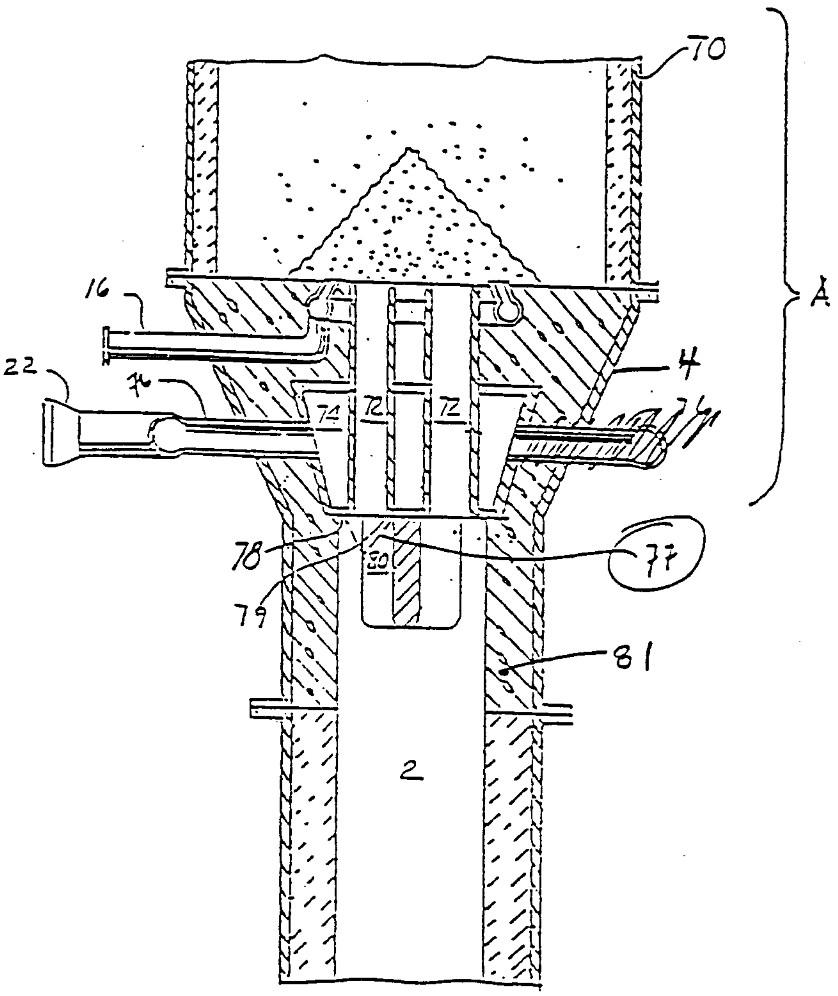

FIG. 2

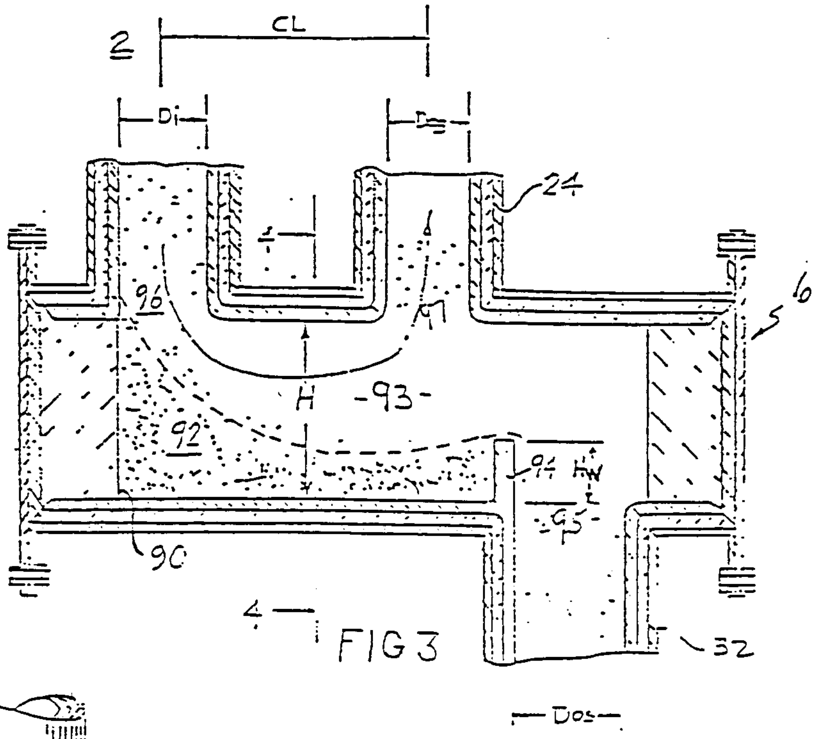
2
CL
Di
Ds
24
6
5
96
97
H
-93-
92
94
HW
95
90
4
32
Dos

FIG 3

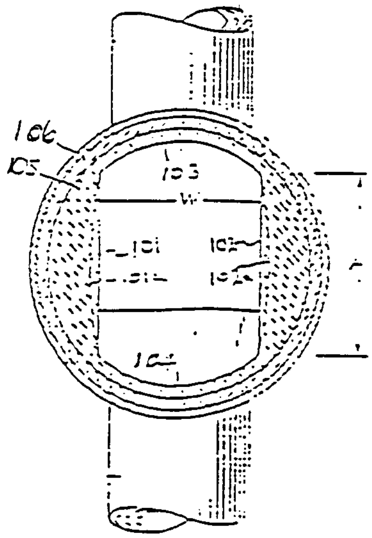
106
105
103
W
101
101
102
102
104
H

FIG 4

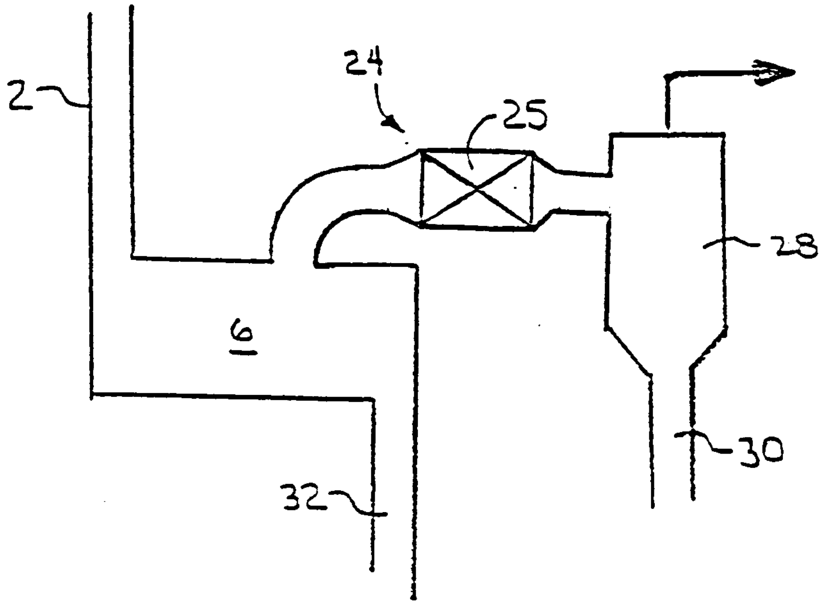

FIG 5

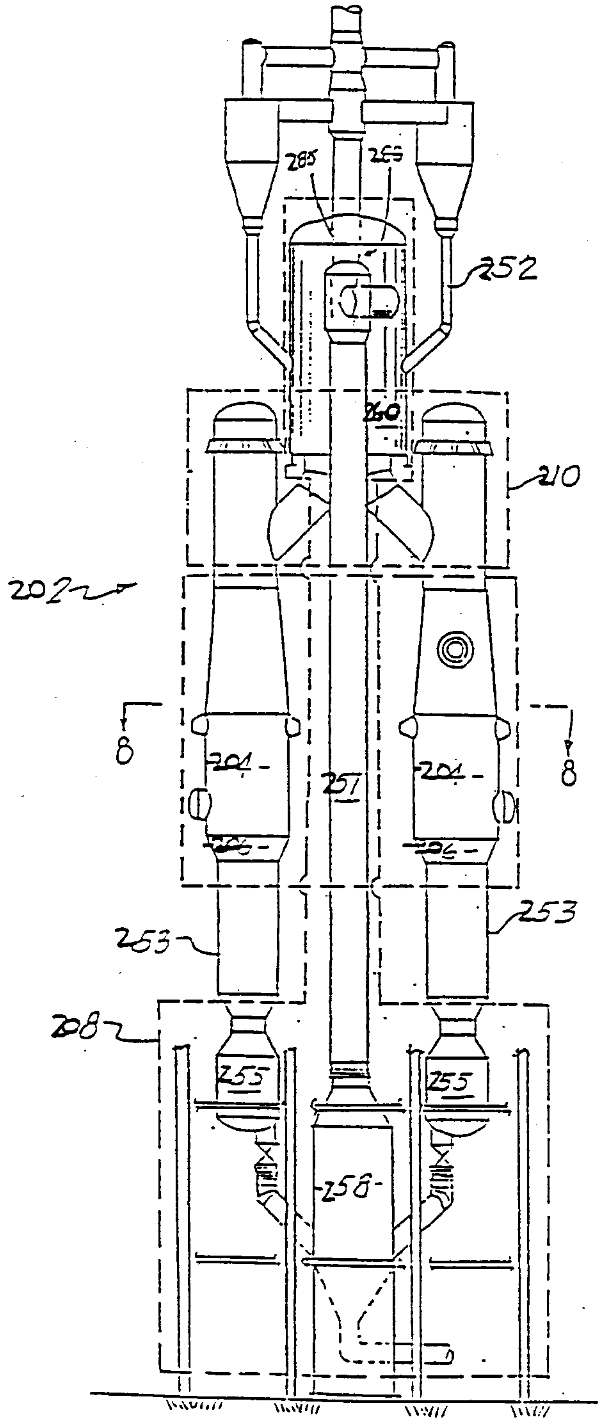
285
255
252
260
210
202
8
204
257
204
8
206
206
253
253
208
255
255
258

FIG. 6

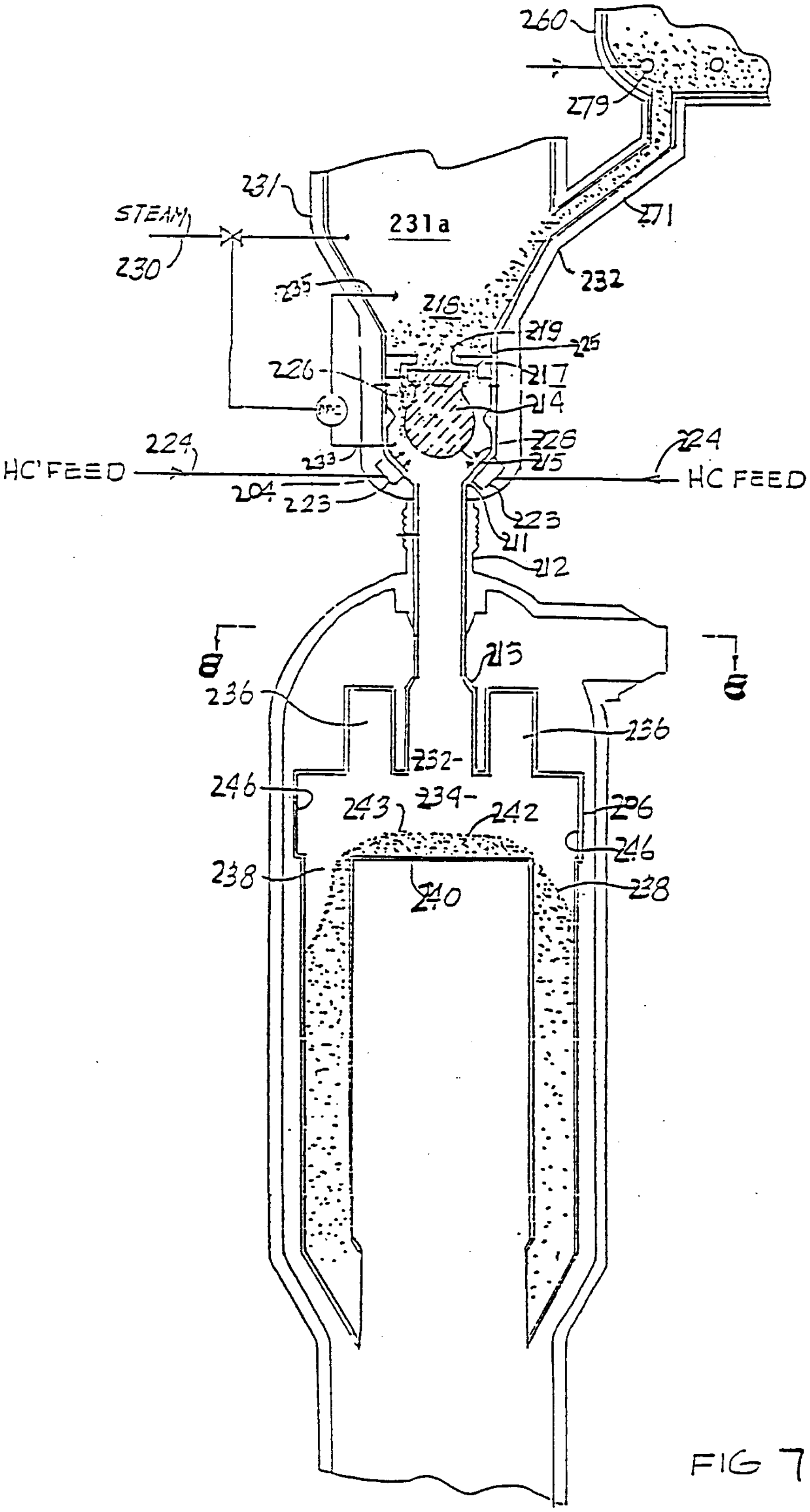
260
279
231
STEAM
230
231a
271
232
235
218
219
225
226
217
214
224
HC'FEED
224
HC FEED
228
233
215
204
223
223
211
212
215
236
236
232
234
246
243
242
226
246
238
240
238

FIG 7

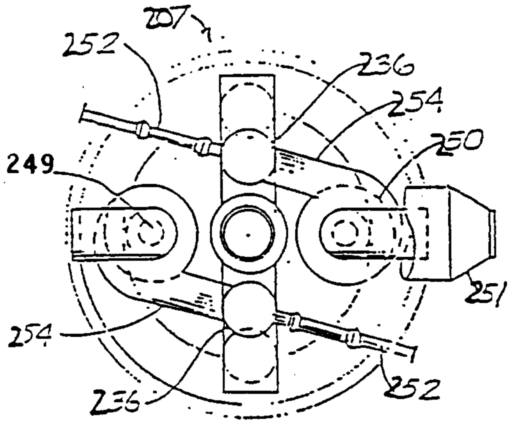
207
252
236
254
250
249
251
254
252
236

FIG.8

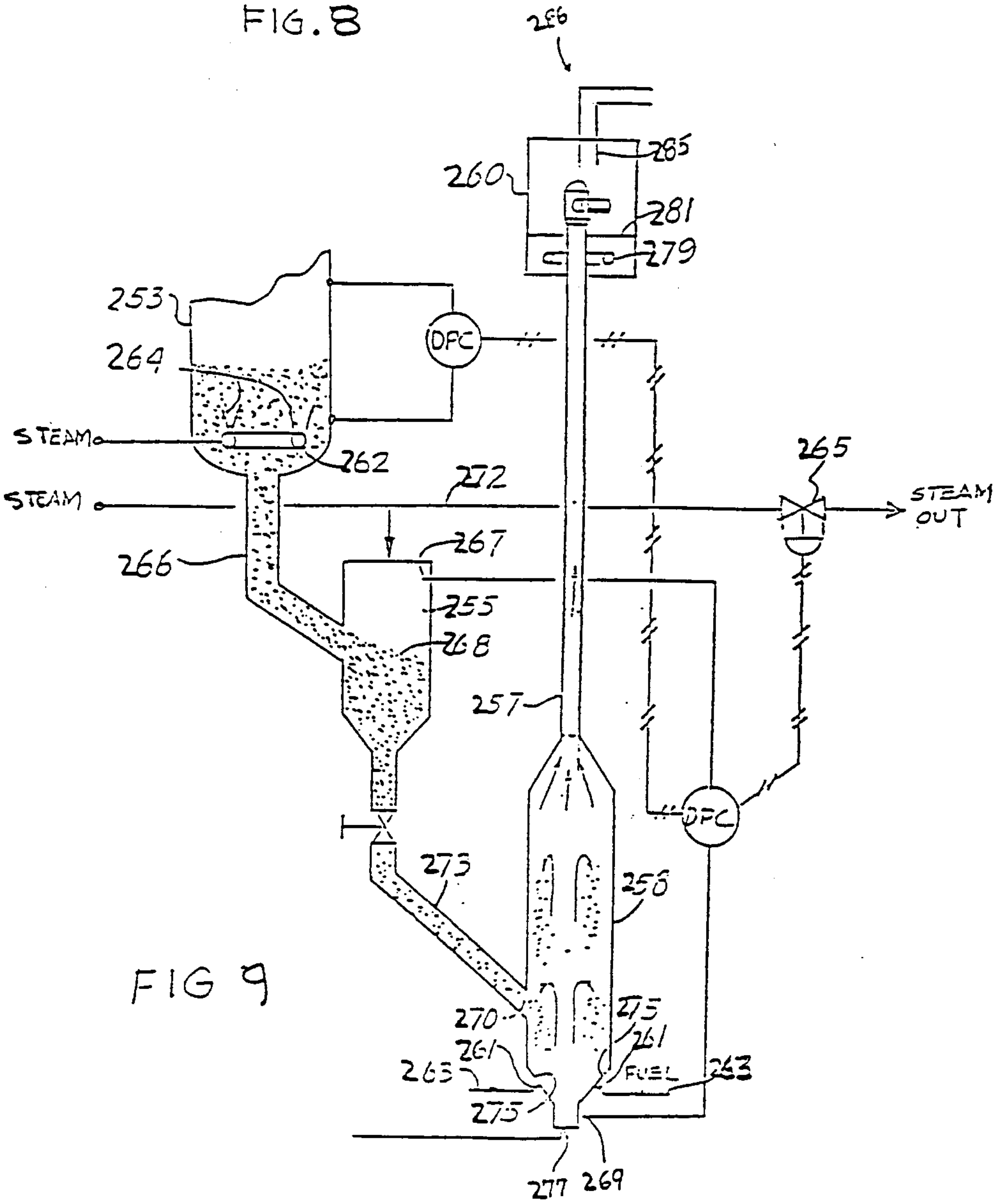
286
285
260
281
279
253
264
DPC
STEAM
262
STEAM
272
265
STEAM OUT
266
267
255
268
257
273
256
DPC
270
275
261
263
261
FUEL
263
275
277
269

FIG 9