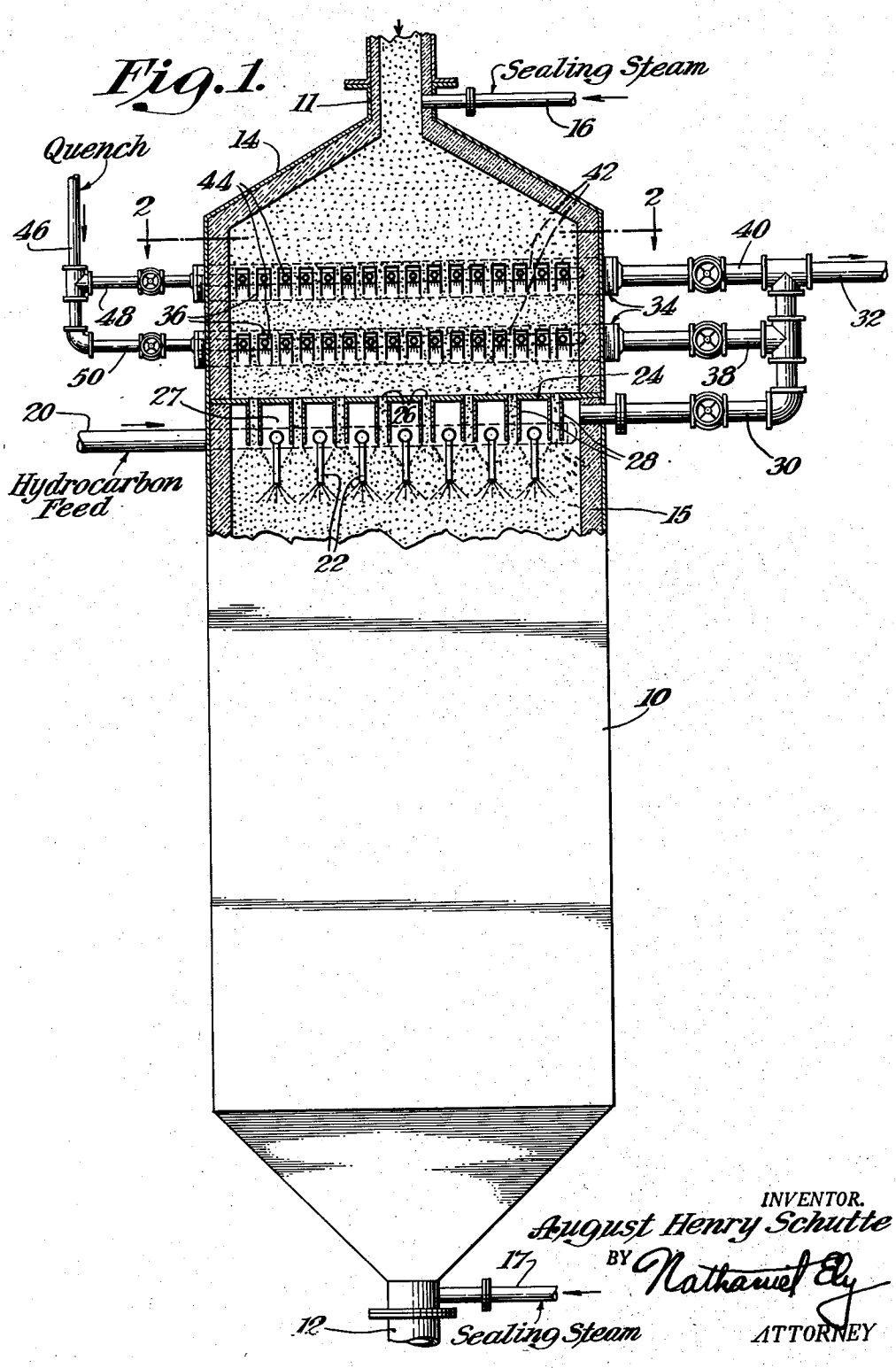
Oct. 24, 1950 A. H. SCHUTTE 2,526,696

PROCESS FOR THE SIMULTANEOUS PRODUCTION OF COKE AND GASEOUS UNSATURATED HYDROCARBONS AND APPARATUS THEREFOR

Filed March 2, 1946 2 Sheets-Sheet 1

Fig. 1.



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Filed March 2, 1946 2 Sheets-Sheet 2

Fig. 2.

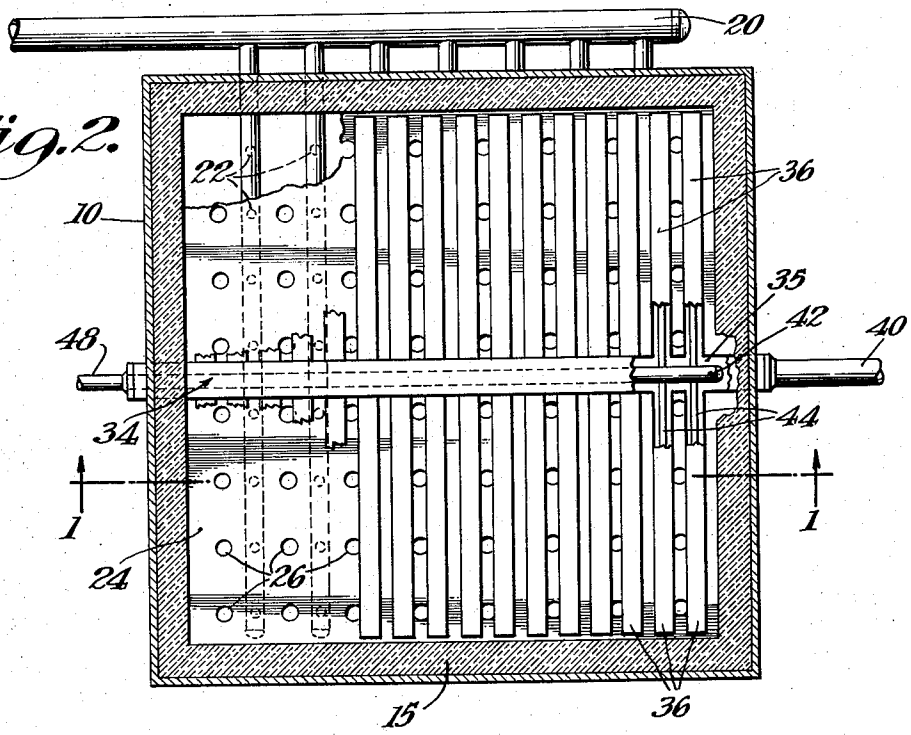


Fig. 3.

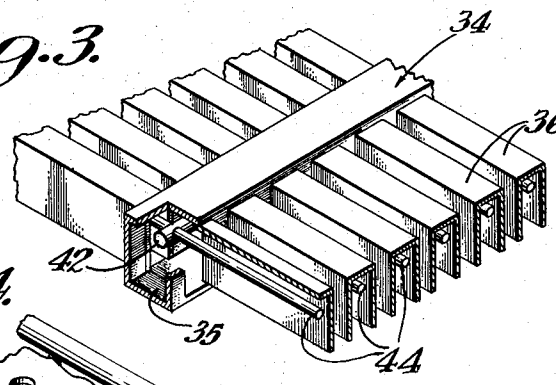
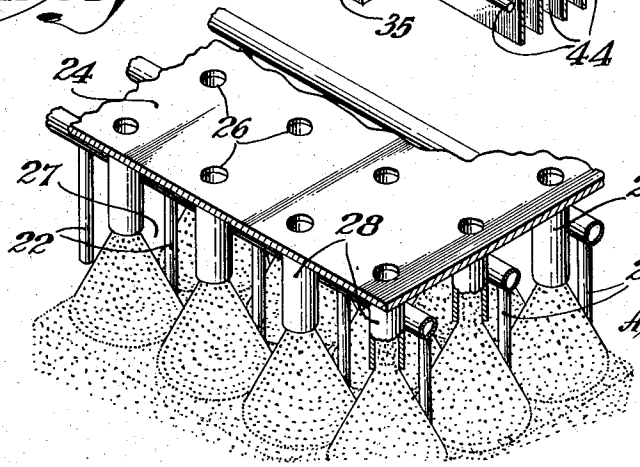


Fig. 4.



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2,526,696

PROCESS FOR THE SIMULTANEOUS PRODUCTION OF COKE AND GASEOUS UNSATURATED HYDROCARBONS AND APPARATUS THEREFOR

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4 Claims. (Cl. 196—55)

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This invention relates to the conversion of hydrocarbons and in particular to the controlled cracking of hydrocarbons by the use of a free gravity-flowing bed of granular material.

In the copending applications of myself and Vernon O. Bowles, Serial No. 510,118, filed November 13, 1943, now abandoned, entitled "Treating Hydrocarbons," and Serial No. 510,119, filed November 13, 1943, now abandoned, entitled "Continuous Coking," reference has been made to the cracking of various hydrocarbon stocks by the introduction of the hydrocarbon charge to a preheated continuously moving bed of porous solids which pass through a confined reaction zone solely by the effect of gravity. It is pointed out in such applications that the contact material may be an inactive or inert material acting only as a heat carrying and coke deposit receiving medium, and under proper control of the ratio between the rate of feed of the charge with respect to the rate of bed movement, gumming, sticking, or cementing together of the bed particles is avoided.

It is also pointed out that the temperature limits possible in such an operation are dependent only on the character and properties of the contact material and the normal temperature limitation of cracking in a tubular heater is avoided. It is well known, of course, that except for relatively light stocks, temperatures in a tubular heater cannot be excessive because of the undesirable coke which deposits in the tubes. It is for this reason that charge stocks boiling above 800 to 900° F. at atmospheric pressure, as well as residual stocks, have usually been sold as fuel oil.

In accordance with the present invention, advantage is taken of the continuously moving upper bed of granular material for a vapor phase cracking operation, and not only is it thus possible to have a continuously fresh uncontaminated surface as the bed moves past the point of feed, but it is also possible, as herein described, to operate at substantially higher than normal temperatures. Normal temperatures, as referred to, are the usual temperatures that can be obtained in either the tubular cracking heater or in catalytic cracking.

With a substantially higher temperature at which the cracking is accomplished in accordance with my invention, a very short time is required and a precise control of the cracking is obtained by controlling the distance through which the cracking vapors pass and by arranging

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a suitable quench so that optimum proportions of the desired end products are obtained.

At the same time that this high temperature, shallow bed, short-time vapor cracking is being carried out, it is also possible in accordance with my invention to include a long-time, less drastic liquid phase cracking in which the vapors produced will also be cracked with the initial vapors passing through the shallow, high-temperature bed. Temperature and time controls can be coordinated to assure most effective operations in both zones.

One of the broad objects of this invention is the provision of a new and improved method and apparatus for economically effecting controlled cracking of hydrocarbons by the use of a free gravity-flowing bed of granular material which has a decreasing temperature in its direction of flow and with a resulting hydrocarbon conversion in the path of the hydrocarbon flow.

It is a further object of this invention to provide a hydrocarbon conversion method and apparatus offering a high degree of flexibility and control whereby the type and composition of the product may be readily and conveniently controlled within rather narrow limits by provision for removal of cracked hydrocarbons after their passage through varying predetermined depths of the free gravity-flowing bed of granular material.

A more specific object of my invention is to produce as a preferred end product a high percentage of gaseous olefins by high temperature cracking on a shallow continuously moving gravity packed bed of granular coke.

A still further object of my invention is to simultaneously perform a vapor phase cracking of high temperature and of short duration in one part of a continuously moving bed of granular material, while simultaneously obtaining the optimum conditions for liquid phase cracking in the lower portion of the same bed with the resulting supplemental cracking of the vapors produced by the liquid phase cracking.

Further objects and advantages of my invention will clearly appear from the following description of a preferred form of embodiment thereof taken in connection with the attached drawing in which:

Fig. 1 is an elevation, partly in section and partly broken away, of a reactor constructed according to this invention for accomplishment of the method of this invention;

Fig. 2 is a transverse section, partly broken away, of the apparatus of Fig. 1 taken substan-

tially on the plane indicated by the line 2—2 of Fig. 1;

Fig. 3 is an isometric view, partly in section and partly broken away, showing details of construction of a vapor collector embodied in the apparatus shown in Fig. 1; and

Fig. 4 is an isometric view, partly in section and partly broken away, showing details of the structure forming the feed, liquid phase cracking vapor release space and associated vapor collector in the structure shown in Fig. 1.

In the customary cracking operation, whether in a tubular heater or in a catalytic fixed bed or flowing bed operation, it is well known that some of the products will be C 3's and lighter, specifically including the gaseous olefins, such as ethylene, which are of considerable use in the petroleum chemical industry. Ordinarily, the production of ethylene is largely incidental and small because of the limited temperature conditions. Conventional cracking methods for producing large yields of gaseous olefins employ very expensive equipment employing special alloys and the run length is seriously limited by coke deposition on the heating surface. These processes charge propane or light distillates such as kerosene and which are relatively expensive. Propane is not available in most sections of this country.

I have found, however, that I can obtain large percentages of the gaseous olefins by the direct feed of a hydrocarbon, which may vary from heavy liquid oils or crude residues down to and including available lighter components. This is accomplished by applying the charge to a preheated gravity packed and free-flowing body of granular material which is preferably non-catalytic and may, for example, be of a high refractory nature, such as "Alundum," "Carborundum," pumice, fire brick, porous ceramic particles, spent catalyst, "Koppers" coke, petroleum coke, or other normally inactive granular material which will withstand temperatures from 1400 to 2000° F. Cokes are ideal materials since they will withstand extremely high temperatures and may be reheated by partial combustion or partial conversion by the air gas or water gas reaction in simple equipment.

By applying the charge to the hot solids, I obtain a controlled vapor phase cracking of the vapors as they pass through the hot bed above the feed on their way out of the apparatus, thereby obtaining greater quantities of gaseous olefins along with high octane number gasoline and aromatics. This method avoids the expense of further processing in other equipment and obviates the difficulties arising from coke formation which is inherent in the revaporization of the heavier components of such charge stocks.

It will be possible to obtain this vapor phase cracking in the top bed of hot contact mass whether or not a liquid phase cracking is simultaneously accomplished. While I prefer to feed a liquid charge and accomplish a full conversion, I can, of course, feed a sufficiently heated hydrocarbon to obtain only vapor phase cracking.

The conditions existing in gravity moving beds of inert material, above the feed inlet or entry point, are ideally suited to vapor phase cracking whether it follows the liquid phase cracking step or is an independent cracking of a vapor feed. Specifically, these conditions are as follows:

(1) There is present a continuous, moving, non-turbulent mass of heated solid particles which presents, in effect, a continuously supplied clean heating surface.

(2) The rate of heat trasnfer and the particle surface area provided for heat transfer to the vapor phase cracking zone are both of a high order of magnitude permitting high-temperature, short-time cracking.

(3) Time factors are subject to precise control during operation.

(4) Flexibility of operation is accomplished by the selected removal of the vapors at different levels or distances of flow.

(5) Maximum temperatures possible are greater than with heating in tubular heaters or on active catalyst beds.

(6) The cracking bed is relatively shallow.

(7) If cracking is desired at low hydrocarbon partial pressures, steam or other gas may be introduced with the charge to produce the required effect. Steam or gas is not required for the purpose of adjusting the cracking time, as in the case of high-temperature, short-time coil cracking.

(8) For deep or severe cracking operations, this method has a unique advantage over coil cracking in that the cracking reaction heat requirements are very small or negligible when cracking on solids and depositing solid coke, whereas in coil cracking, where coke formation cannot be allowed, the reaction heats may be as high as 1000 B. t. u. per pound of charge when running for the optimum production of ethylene.

As an illustrative form of embodiment of the apparatus which I find preferable to carry out my invention, I have shown a reactor **10**, the main portion of which is preferably of uniform cross section and forms an upright column through which is passed, at predetermined rate and solely by gravity, the porous, inert, solid particles.

The reactor, as shown, tapers downwardly and outwardly from the bed inlet **11**, which is connected with any suitable source of solid particles, and then tapers downwardly and inwardly to the bed outlet **12**, through which inert, porous, solid particles are continuously and uniformly removed at a controlled rate by means not shown. The reactor **10** is preferably formed with a metal casing **14** provided with an interior heat insulating lining **15** and, optionally, with a corrosion or erosion resistant lining, not shown. It may be round or rectangular, as desired.

A sealing steam inlet **16** communicates with the interior of the bed inlet **11** at its inner end and a similar sealing steam inlet **17** communicates with the interior of the bed outlet **12** adjacent its inner end. The sealing steam inlet **16** provides means for applying sealing steam to the upper end of the interior of the reactor **10** to form a sealing zone preventing passage of cracked vapors through the solids stream and escape through the bed inlet **11**. The sealing steam inlet **16** provides means for applying sealing steam to the interior of the reactor **10** at its lower end to prevent passage of vaporous products downwardly out of the reactor **10**, with the bed particles issuing from the outlet **12**.

Additional steam inlets may be provided, if necessary, to permit control of the oil partial pressure in the liquid phase and vapor phase cracking zones.

The hydrocarbon feed to the reactor **10** is through pipe **20** and the feed is effectively distributed over substantially the entire horizontal cross section of the reactor **10** as by a suitable

sparger 22 or feed spreading mechanism of the type more particularly shown in my copending application, Serial No. 577,707, filed February 13, 1945, now Patent No. 2,482,137 and entitled "Converting Hydrocarbons." The sparger 22 will substantially uniformly distribute the hydrocarbon feed throughout the cross sectional area of the reactor 10 in such a manner as to afford a substantially uniform distribution. It may have the nozzles as shown to provide a suitable pressure drop when necessary.

As will hereinafter be emphasized, the hydrocarbon feed inlet 20 and sparger 22 are substantially spaced away from the bed inlet 11 so that the continuous flow of granular material will pass through a portion of the reactor before reaching the feed inlet section.

Preferably, a baffle 24 is provided immediately above the hydrocarbon feed zone, such baffle being shown more particularly in Fig. 4 and consisting of a perforated plate, the apertures 26 of which communicate with short conduits 28 to form a controlled flow of the granular material. This results in the formation of cones of repose 29 of the granular material, thus providing a free space 27 not only for the hydrocarbon feed but for vapor release immediately beneath the baffle or wall 24. This space may be effectively connected by means of the lower vapor collection and draw off 30 with the vapor outlet line 32.

Between the bed inlet 11 and the lower collection zone formed under the baffle 24, I also provide a plurality of fluid distribution and vapor collection devices. Generally, these consist of a unit construction, indicated at 34 in Fig. 3, with a transverse, hollow central beam 35 from the sides of which project inverted U-shaped vapor collection beams 36. As will be apparent from an inspection of Fig. 1, all of these collection spaces may be in communication through the U-shaped members 36 and the central beam 35 with vapor collection draw offs 38 and 40, also connected with vapor outlet line 32.

Also as a part of these collector elements, I may provide a series of quench steam distributors consisting of a main distribution pipe 42 with extended feeders 44 extending along under the inverted U-shaped members 36. These may be connected, in turn, with a quench steam line 46 through the branch pipes 48 and 50. The quench may be accomplished external of the reactor 10 if desired.

It is to be understood that the vapors removed from the vapor collector pipe 32 will be carried to a tar separating drum and then to a fractionating system in which the methane and hydrogen can be separated from the ethylene and the light distillate. The ethylene would be absorbed in a well-known manner and the other gaseous olefins, as well as the light distillate and the tarry material, may be reintroduced with the hydrocarbon feed at 20 for further conversion. In such case, the tarry material will penetrate the solids of the granular bed and will be reduced to coke and vapor while the gaseous materials will be further cracked for maximum production of ethylene.

It is to be understood that the reactor unit 10 shown in Fig. 1 is only part of a continuous system in which the bed passes through a regeneration zone, which not only removes at least a portion of the deposited carbon but also reheats the solids to the desired entrance temperature.

In operating the above structure to perform the method heretofore described for the production of preponderant yields of gaseous olefins, bed particles from $\frac{1}{16}$ inch to 1 inch major dimension in lump, pellet, or extruded form, are fed by suitable means, not shown, into the inlet 11 at from 1100 to 1800° F. The bed particles may leave the vapor phase cracking bed at temperatures from 950 to 1400° F., depending on the ratio of solids to hydrocarbon feed employed. The vapors may be introduced at any convenient temperature and will discharge at a close approach to the temperature of the incoming solids.

A solids temperature of 1200° F. permits me to obtain a heat transfer coefficient from solids to vapors, neglecting radiation which is approximately 30 B. t. u.'s/sq. ft. of superficial outside particle surface/degree F./hr., which is equivalent to approximately 4500 B. t. u.'s/hr./cu. ft. of solids/degree F. This extremely high heat transfer rate may be better appreciated when it is considered that with a solids feed rate of 100 tons/hr. an dwith an average temperature difference of only 50° F., it is possible to transfer 11,250,000 B. t. u.'s/hr. of heat, with an extremely shallow bed and a cracking time as low as one-half second.

By adjusting the solids rate and temperature and the depth of bed through which the vapors pass, cracking time may be varied from several seconds to only tenths of a second and thus cracking conditions may be selected to give maximum yields of either normally liquid or normally gaseous hydrocarbons. Operating pressures may vary from atmospheric to 50 lbs. per sq. in., depending upon external requirements.

Vapors released during the residence time are automatically removed at the desired level (temperature-time relation), since the extent of liquid phase cracking cannot exceed that sufficient to permit the heavy oil to vaporize. The solids are readily available for regeneration, i. e. steam generation, fuel, extra heat for the incoming bed, or other purposes. Generally, these solids are regenerated (carbon removed) to the desired extent, and under the predetermined temperature, are again introduced into the feed inlet 11. Agglomeration of the bed is avoided by a controlled rate of feed of the hydrocarbon charge.

I prefer to use coke as the porous, solid bed material for liquid phase cracking, and high quality coke may be produced by the deposition of coke deposits on the bed coke during the cracking reaction. Regeneration of the coke is also readily accomplished for it is necessary to burn only enough of the bed material to replace the heat consumed in the cracking reaction in which the coke deposition occurs. Preferably, such material has a particle porosity of 5 to 50% by volume, measured on the basis of the volume of the discrete bed particles.

As an example of the benefits obtainable from my invention, a feed of a heavy residual oil having a Watson-Nelson characterization factor of 11.6 and an A. P. I. of 14.7 at the equivalent rate per 100 tons of solids per hour of 1,320 barrels per day when fed to a petroleum coke at 1150° F., produced a very high yield of gases having the following analysis in volume per cent:

H_2 27.5; C_1 25.7; C_2— 13.8; C_2 11.0; C_3— 12.4; C_3 2.3; C_4+ 7.3.

Thus, a C_2–C_3 gas stream was produced which contained 35% by volume of ethylene. Higher temperatures will give higher yields of ethylene.

I am also able to produce highly efficient quantities of gasoline from such heavy residual oils

by having a somewhat longer time of cracking and a somewhat lower temperature. Preferred operations of this nature would be carried out at 900 to 1300° F. solids feed inlet temperatures, and with periods of cracking time varying between 1.0 seconds and 10 seconds.

If acetylene is to be produced, the temperature of the solids may be increased to provide a vapor outlet of from 1400 to 1800° F.

While I have shown and described a preferred form of embodiment of my invention, I am aware that modifications may be made thereto and I, therefore, desire a broad interpretation of my invention within the scope and spirit of the description herein and of the claims appended hereinafter.

I claim:

1. The method of continuously producing predominant yields of unsaturated C_2 and C_3 hydrocarbons by the thermal conversion of a residual hydrocarbon feed and also converting a portion of said feed to coke, which comprises, continuously moving downwardly, by gravity alone, a continuous gravity-packed bed of heated solid particles through a confined space having a separate upper, shallow high temperature contact zone, and a deep, lower temperature contact zone; continuously introducing the residual hydrocarbon feed in liquid phase into the upper part of the lower temperature zone; maintaining the temperature of said lower temperature zone such as to mildly crack the liquid portion of the charge, whereby the unvaporized portion of the residual hydrocarbon feed is ultimately converted to dry coke on the bed particles and vapors; passing the vaporous portion of said feed upwardly through increasing temperature levels in the portion of the bed comprising the upper shallow contact zone for a reaction time between several seconds and a fraction of a second; maintaining temperature conditions in said upper bed portion in the temperature range of 1100° F. to 1800° F. so as to yield a high percentage of unsaturated hydrocarbons within said reaction time; quenching the reacted vapors and removing said quenched vapors from the confined space at a selected elevation within the shallow contact zone corresponding to the desired amount of cracking, the amount of contact particles in said upper bed portion being sufficiently small that the temperature drop resulting from cracking in the upper bed portion is great enough to avoid excessive cracking in the lower temperature contact zone, the temperature drop of the particles in said lower temperature contact zone reducing the outlet temperature of the particles to a small proportion of the inlet temperature; controlling the movement of the bed through the confined space by the gravity removal of the particles from the lower part of the confined space as a free-flowing stream; and reheating such particles to a predetermined inlet temperature sufficient for the maintenance of a temperature in the range of 1100° F. to 1800° F. in said upper bed portion.

2. The method of continuously producing unsaturated hydrocarbons as defined in claim 1 in which the heated solid particles are coke and the time and temperature of the reaction in the high temperature contact zone are primarily adapted for the production of ethylene.

3. A reactor for thermal contact conversion of liquid hydrocarbons, comprising a casing defining a substantially vertical reaction chamber having inlet and outlet means at the upper and lower portions thereof respectively to feed by gravity a continuous granular mass through said chamber, a partition extending laterally across the chamber at an upper level therein and having openings distributed thereover for descent of the granular material, a delivery conduit assembly at a level within said chamber adjacent said partition level and including a plurality of transverse feeders having distributed discharge openings arranged to spread a liquid hydrocarbon charge over substantially the entire cross sectional area of the chamber below said partition, a plurality of spaced vapor collection devices at different levels within the chamber above said partition to remove vapors of said feed, means within each of said vapor collection devices of the reactor to feed a quench stream to said vapors, and means to control the proportion of vapors removed at said different levels whereby the distance of travel of vapors through the granular mass may be coordinated with the amount of cracking accomplished.

4. The method of continuously producing unsaturated hydrocarbons as defined in claim 1 in which the heated solid particles are coke and the temperature in the shallow contact zone is maintained in the range of 1400° F. to 1600° F. to enhance the production of acetylene.

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