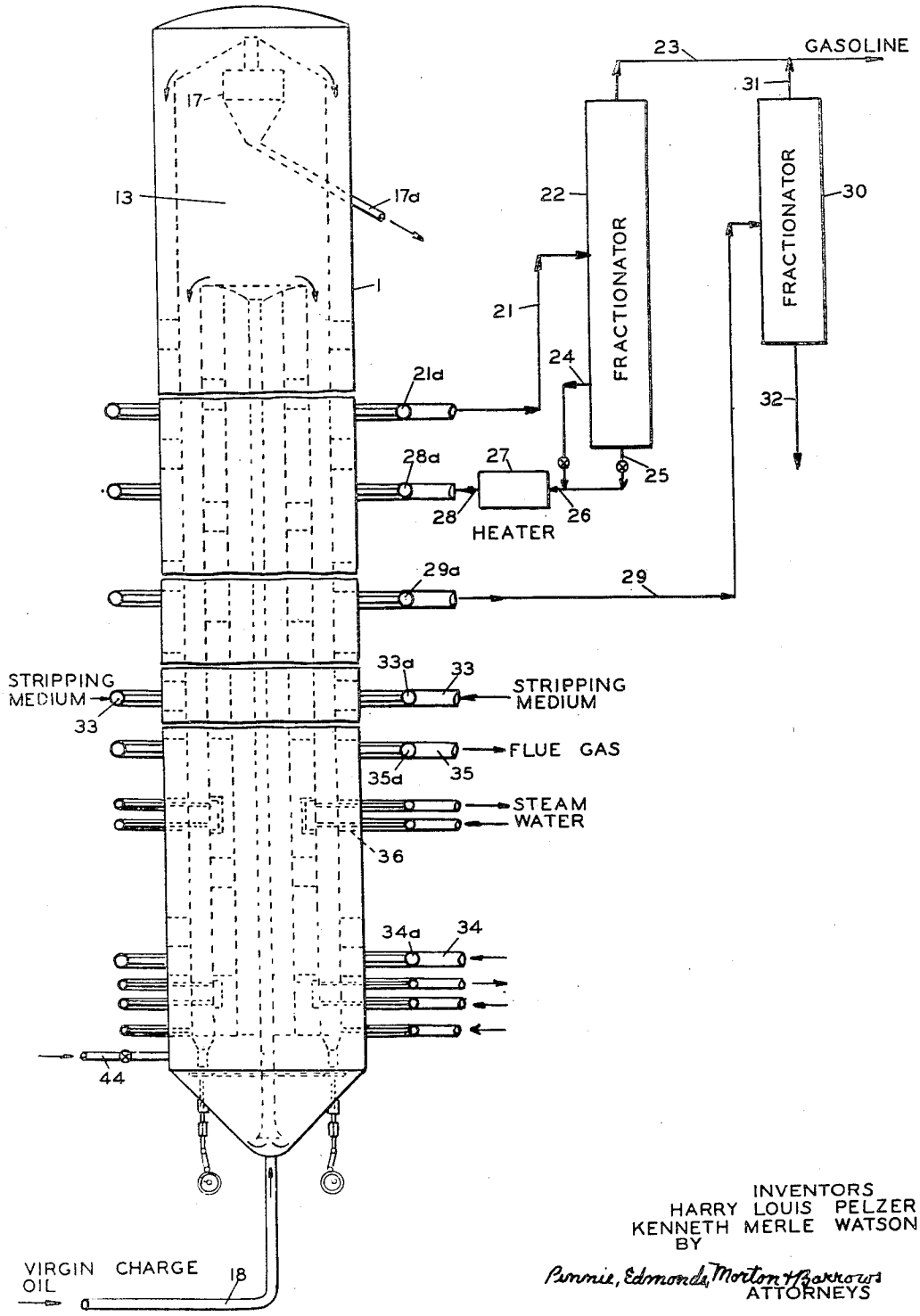
March 15, 1949. H. L. PELZER ET AL 2,464,257

PYROLYTIC CONVERSION OF HYDROCARBONS

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FIG. 1



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FIG. 2

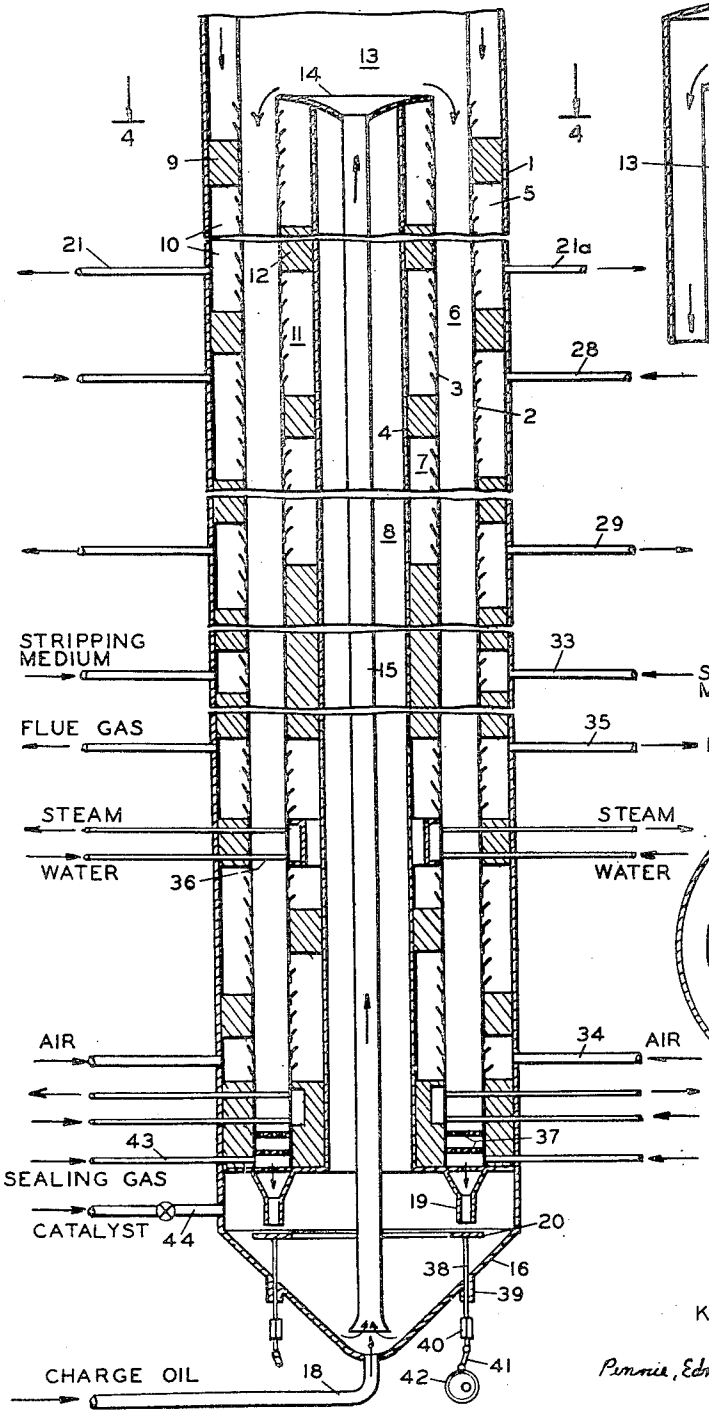


FIG. 3

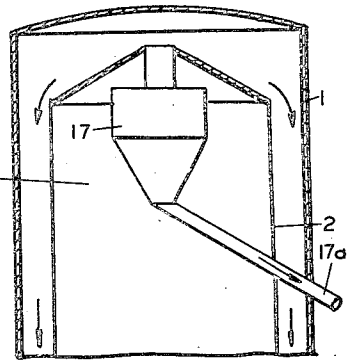
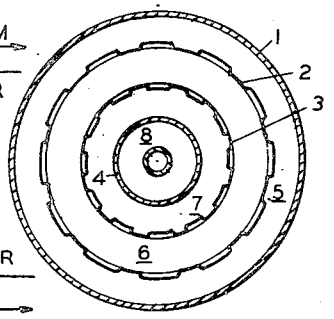


FIG. 4



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2,464,257

PYROLYTIC CONVERSION OF HYDROCARBONS

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Application June 27, 1947, Serial No. 757,652

3 Claims. (Cl. 196—52)

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This invention relates to the pyrolytic conversion of hydrocarbons and, more particularly, to a pyrolytic cracking process involving the use of a solid catalyst.

In the copending application of Kenneth M. Watson, one of the present joint inventors, Ser. No. 757,639, filed June 27, 1947, there is described and claimed an improved catalytic conversion process whereby a downwardly gravitating, vertically elongated bed of hot catalyst is maintained by continually withdrawing catalyst from the lower end of the bed, and returning it to the upper end of the bed. The conversion is effected by repeatedly passing the hydrocarbon vapors transversely through the upper portion of the bed at progressively different elevations and the catalyst is regenerated by repeatedly passing regenerating air transversely through the lower portion of the bed at progressively different elevations. Stripping of the spent catalyst prior to regeneration is effected and the mixing of products of combustion with the hydrocarbon vapors is prevented by passing a gaseous stripping and sealing medium into an intermediate portion of the bed.

The present invention is an improvement in the process there described. It relates particularly to cracking and provides an improved method for further cracking the insufficiently cracked fraction, or so-called recycle stock separated from the effluent vapors from the conversion zone.

In a once-through cracking operation, even undermost advantageous conditions, only a portion of the charging stock is cracked to the desired product. In addition to constituents within the desired boiling range, the effluent from the cracking reaction zone contains a relatively larger amount of higher boiling hydrocarbons and it is customary to separate the lighter from the heavier hydrocarbon constituents by fractional condensation.

In order to increase the yield of the desired product from a given amount of charging stock, it has been proposed to return the heavier hydrocarbons to the reaction zone for further cracking in admixture with the fresh virgin charging stock.

Unfortunately, the heavier fraction separated from the effluent vapors and commonly designated recycle stock, contains constituents having cracking characteristics substantially different from those of the fresh virgin charging stock. In general, the recycle stock is more resistant to further cracking than the virgin charge oil. If

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these highly refractory constituents of the cracked vapors are returned to the cracking zone together with virgin gas oil, for instance, in which conditions optimum for the cracking of the gas oil are maintained, they will be inadequately cracked, and if cracking conditions optimum to their cracking are maintained in the cracking zone, the gas oil will be overcracked.

In accordance with our present invention, these objectionable conditions are avoided by separately cracking the virgin charge oil and the recycle stock in different zones of a vertically elongated body of hot catalyst such as just described.

By our improved process, the virgin charging stock may be cracked by passing it repeatedly through an elongated bed of catalyst, as described in the above noted application, and the vapors passed therefrom to a fractionator. Recycle stock from the fractionator is then repeatedly passed, at progressively different elevations, through a separate zone of the elongated body of catalyst. For instance, virgin gas oil may be cracked in the upper zone of the body of catalyst and recycle stock cracked in an intermediate zone, or the recycle stock may be cracked in the upper zone and the virgin gas oil cracked in an intermediate zone.

The invention also contemplates the cracking of other stocks of different cracking characteristics in separate zones of the elongated bed of catalyst.

Our present process is not restricted with respect to the method of regenerating the catalyst, nor the separation of the regenerating zone from the reaction zone nor the stripping of the catalyst, nor the method of returning the catalyst from the lower end to the upper end of the vertically elongated body of catalyst.

The invention will be more fully described and illustrated with reference to the accompanying drawings.

Figure 1 of the drawing represents, diagrammatically and conventionally and partly in vertical section, an assembly of apparatus involving our invention.

Figure 2 is a more detailed vertical section of the intermediate and lower portion of the apparatus in which the vertically elongated body of catalyst is contained.

Figure 3 is a vertical section of the upper section of the apparatus of Figure 2; and

Figure 4 is a horizontal sectional view along the lines 4—4 of Figure 2.

Referring more particularly to the detailed

showing of Figures 2 and 3, the apparatus is enclosed by a cylindrical casing 1, advantageously of sheet metal and closed at its upper end. Coaxially positioned in casing 1 are cylindrical casings 2, 3, and 4 of progressively smaller diameters which, together with the outer casing, form annular chambers 5, 6, and 7 and an interior cylindrical portion 8. The intermediate annulus 6 is substantially unobstructed for its entire height. The outer annulus 5 is completely obstructed by a plurality of vertically spaced partitions 9 of considerable depth forming a plurality of vertically spaced chambers 10. The inner annulus 7 is similarly divided into a plurality of vertically spaced chambers 11 by similar partitions or spacers 12.

Each of the chambers 10 and 11 communicates with the annulus 6 through louvers, the slats of which project upwardly and outwardly from the annulus 6 into the respective chambers.

The casings 3 and 4 terminate short of the upper end of the cylinder formed by casing 1 so as to form an enlarged cylindrical chamber 13 in the upper part of the apparatus. The annulus 6 is in open communication at its upper end with chamber 13. The upper ends of the uppermost chamber 11 and the upper end of the inner cylinder 8 are closed off from chamber 13 by means of partition 14. An elevator conduit 15 extends upwardly through the inner chamber 8 and leads into chamber 13 through an opening in partition 14. The lower end of elevation conduit 15 opens into the conical hopper 16, forming the lower portion of the apparatus, and is flared somewhat at its lower end. The upper end of annulus 5 is connected with the upper end of chamber 13 through separator 17.

The spacers or partitions 9 and 12 are, with advantage, positioned somewhat as shown in the drawing so as to form chambers 10 and 11 in staggered positions such that the lower end of a given chamber 10 is directly opposite the upper end of the next lower chamber 11 and the lower end of said chamber 11 is directly opposite the upper end of the next lower chamber 10. The spacers 9 and 12 are, for clarity, shown in the drawing as solid sections, but it will be understood that they may be either solid or hollow. Further, for reduction in weight and material used in fabrication, the respective casings 1 and 4 may be discontinuous at the points of the respective spacers.

In operation, the annulus 6 is filled wtih granular catalyst, for instance, by charging the catalyst through an opening, not shown, in the top of the apparatus, adapted to be sealed in operation. Vaporized or partially vaporized hydrocarbon oil to be processed is charged through lines 18 into the lower end of hopper 16 directly beneath the lower flared end of elevator conduit 15 and picks up in suspension catalyst, which has passed downwardly into the hopper 16 from the lower end of the column of catalyst through the annulus 19, at a rate controlled by adjustable valves 20, subsequently described. The catalyst is entrained in the stream of hydrocarbon vapors and jetted upwardly into elevator conduit 15.

The hydrocarbon vapors carrying the catalyst in suspension pass upwardly through elevator conduit 15 into chamber 13 wherein the catalyst drops out of suspension, by reason of decreased velocity of the vapors, and falls onto a bed of catalyst maintained in chamber 13 from which the catalyst flows into the annulus 6, keeping it continuously filled with the catalyst.

The separated hydrocarbon vapors pass from chamber 13 through separator 17, for the separation of catalyst fines, and from thence through annulus 5 into the upper end of the uppermost chamber 10 and, from thence, the vapors pass by way of the louvers through the body of catalyst in annulus 6 and into the upper end of the uppermost chamber 11. Separated catalyst fines pass from the separator 17 through conduit 17a to a point without the system. From the lower portion of said chamber 11, the vapors pass back through the body of catalyst into the chamber 10, and so back and forth through the body of catalyst, at progressively lower levels, until the vapors reach an intermediate chamber 10 from which they are withdrawn through lines 21 and bustle pipe 21a to fractionator 22, as more clearly appears on Figure 1 of the drawing.

Light hydrocarbon vapors, containing the desired product, are withdrawn from the fractionator through line 23 and an insufficiently cracked heavier fraction is passed from the fractionator through valved line 24 or valved line 25, or both, into the line 26, through preheater 27, line 28, and bustle pipe 28a, into an intermediate chamber 10 and passes back and forth through the body of catalyst, at progressively lower elevations until the vapors reach a still lower chamber 10 from which they are withdrawn through line 29 and bustle pipe 29a and passed to the second fractionator 30 from which the vapors containing the desired product are withdrawn through line 31 to line 23 and pass therethrough, together with vapors from fractionator 22 to storage or a point of further treatment. A heavier fraction is withdrawn from fractionator 30 through line 32 to storage, or may be passed through a still lower section of the hot catalyst bed for further cracking, or combined with the recycle stock from fractionator 22.

The apparatus of Figures 1 and 2 of the drawing are shown somewhat fragmentary to indicate intervening sections of similar design so that the virgin charge oil and the recycle stock, respectively, may be repeatedly passed through the catalyst bed any desired number of times by the inclusions of a larger number of sections. Further, it is advantageous to provide a plurality of draw-off lines 21 and 29, respectively, connected with different sections of the apparatus so that the space velocity of the virgin charge oil and of the recycle stock may be varied as required to attain the desired depth of cracking.

The catalyst which has been substantially spent continues downwardly through annulus 6 and is stripped of readily vaporizable hydrocarbons remaining thereon by a stripping gas, or vapor, steam for instance, introduced into a still lower chamber 10 through line 33 and bustle pipe 33a.

Air is passed into the lowermost chamber 10 through line 34 and bustle pipe 34a, flows therefrom by way of the louvers, through the bed of catalyst into the lowermost chamber 11 and back through the catalyst into the next higher chamber 10 and so passes back and forth through the catalyst at progressively higher elevations until it reaches an intermediate chamber 10, below that into which the stripping medium is injected and the flue gases pass therefrom through conduit 35 and bustle pipe 35a to a stack, not shown in the drawing.

The air passing in contact with the hot catalyst results in the burning therefrom of the carbonaceous deposit formed on the catalyst during the cracking operation. Excess heat may be

extracted from the catalyst undergoing regeneration by means of cooling coils 36 extending through the bed of catalyst in annulus 6 and through which a cooling medium is circulated. For instance, water may be circulated through the cooling coils and thereby converted into steam. Any number of cooling coils required may be used to extract from the catalyst an amount of heat necessary to prevent excessive temperatures.

Regenerated catalyst passes from the lower end of the regenerating zone through perforations in a series of distributing plates 37 so positioned as to permit the flow of catalyst therethrough at a retarded rate, depending upon the angle of repose of the catalyst, as understood by the art. From thence, the catalyst flows through annulus 19, past valve 20 and falls into the hopper 16 where it is picked up by the entering charge oil, as previously described.

The rate of flow of the catalyst through annulus 19 is controlled by valve mechanism comprising an annular flat ring member 20, of somewhat greater width than annulus 19. The ring 20 is adjustably supported by a plurality of shafts 38 extending downwardly through the walls of the hopper 16 and sealed by suitable glands, indicated on the drawing at 39. The length of the shafts 38 may be adjusted by means of turn buckles 40 and further the lower end of each shaft is connected by linkage 41 to eccentric 42. The eccentrics are connected by suitable conventional means, not shown, so that they will operate together to impart an oscillatory movement to ring 20, adjustments in leveling the ring member 20 and of its distance from the lower end of annulus 19 being made by the turn buckles 40 interposed in the shafts 38.

In the valve arrangement shown, the ring 20 will completely shut off the flow of catalyst without requiring mechanical seating of the valve. By raising the ring to a point where its edges intercept the angle of repose of the catalyst flowing from annulus 19, flow is completely stopped. This method of flow control is particularly advantageous as it avoids crushing the catalyst. The rate of catalyst flow is determined by the height of the ring; and the oscillatory motion maintains uniform flow at all points around the annulus 19.

An inert sealing gas is introduced into the lower end of annulus 6 through lines 43, so as to maintain therein a pressure sufficient to prevent the downward flow of regenerating air into the hopper 16, or the upward flow of oil vapor into the regenerating zone. The depth of the catalyst bed above and below the point of sealing gas introduction should be sufficient to permit maintenance of such pressure without excessive gas flow in either direction. Fresh catalyst may be added as required through line 44.

The thickness of the annulus 6 may be varied over a considerable range, the optimum thickness depending upon the particular operating conditions. Generally, its thickness is, with advantage, about 1 to 2 feet. The depth of the spacers 9 and 12 is, with advantage, considerably greater than the thickness of the bed of catalyst in annulus 6 so as to minimize any tendency of gases or vapors to pass directly from one chamber to that immediately above and below it, rather than through the catalyst bed to the opposite chamber.

The elevator conduit 15 is, with advantage, of such diameter relative to the volume of hydrocarbon vapors to be charged therethrough as to

effect a high velocity of flow so as to entrain the catalyst particles and carry them upwardly into chamber 13. Generally, the superficial velocities of the rising vapors should be within the range of 10 to 50 feet per second, the optimum velocity depending, in large measure, upon the size and density of the catalyst particles and the relative proportion of catalyst to be carried thereby.

The elutriating means for removing finely divided particles of catalyst and the valve mechanism for controlling the rate of flow of catalyst through the annulus 19 are particularly advantageous. However, it will be understood that other elutriating and flow control means may be employed without departing from the spirit of the present invention.

The invention contemplates the use of various types of catalyst, for instance, natural or synthetic earths, silica gel, and the like, or various inert carriers having active catalyst deposited thereon. The size of the particles of catalyst is, with advantage, of a mesh within the range of 25 to 40, though catalysts of larger and smaller particle size may be employed. Pelleted catalyst as coarse as 4 to 10 mesh may be employed. Usually, powdered catalyst, such as used in the fluid catalyst processes is less desirable because of a tendency of the catalyst particles to be carried out of the catalyst bed along with the gases and vapors, but may be used in conjunction with relatively low gas and vapor velocities through the catalyst bed.

Operating conditions are generally subject to considerable variation, depending upon the particular catalyst employed and the nature and extent of the desired reactions. In cracking gas oil, for instance, using a silica-alumina type catalyst, the temperature in the reaction zone is, with advantage, maintained within the range of about 750 to 950° F., and the pressure within the range of about 10 to 15 pounds per square inch. In the regenerating zone, a temperature within the range of 900 to 1,150° F. is usually satisfactory.

The temperature in the reaction zone is controlled, in large measure at least, by the temperature of the catalyst passing from the lower end of the regenerating zone and the extent of preheat of the charge oil. The temperature of the catalyst undergoing regeneration is controlled by the extraction of heat therefrom, as previously described.

It may frequently be desirable to crack the recycle stock in the uppermost zone of the body of catalyst where it will be passed in contact with the freshly regenerated catalyst at maximum temperature. However, by regulation of space velocities, as previously described, the more refractory stock may be subjected to more severe cracking conditions even in an intermediate zone.

We claim:

1. In a process for the pyrolytic conversion of hydrocarbons wherein the hydrocarbons in vapor phase are continuously passed in intimate contact with a solid catalyst at an elevated temperature and the effluent vapors fractionated to segregate an insufficiently cracked fraction, the improvement which comprises passing the catalyst in a relatively narrow, vertically elongated body downwardly through an enclosed, vertically elongated chamber, effecting the conversion of the virgin charge oil by repeatedly passing it in vapor phase transversely through the body of hot catalyst, at progressively different elevations and effecting the further cracking of the insufficiently cracked fraction by passing it in

vapor phase transversely through the body of hot catalyst at progressively different elevations in a different zone of the chamber.

2. In a process for the pyrolytic cracking of hydrocarbons in which the catalyst in a relatively narrow, vertically elongated body is passed downwardly through an enclosed vertically elongated chamber and conversion of the hydrocarbons is effected by repeatedly passing the hydrocarbon vapor transversely through the body of hot catalyst at progressively different elevations and the effluent vapors are fractionated to segregate an insufficiently cracked fraction, the step of further cracking the said fraction by repeatedly passing the fraction in vapor phase transversely through the body of hot catalyst, at progressively different elevations, in a separate zone of the chamber.

3. In the process for the pyrolytic cracking of hydrocarbons wherein a relatively narrow, vertically elongated body of catalyst at an elevated temperature is continuously passed downwardly through an enclosed vertically elongated chamber, the hydrocarbons to be cracked are continuously and repeatedly passed in vapor phase transversely through the body of catalyst in a conversion zone in an upper portion of the chamber at progressively different elevations, the

catalyst is regenerated by continuously and repeatedly passing air at progressively different elevations transversely through the body of catalyst in a regenerating zone in a lower portion of the chamber, catalyst is continuously withdrawn from the lower end of the chamber and returned to the upper end thereof, and the effluent hydrocarbon vapors from the conversion zone are fractionated to segregate an insufficiently cracked fraction, the step of further cracking the last said fraction by repeatedly passing it in vapor phase transversely through the body of catalyst at progressively different elevations in a different conversion zone of the chamber also at an elevation higher than the said zone of regeneration.

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