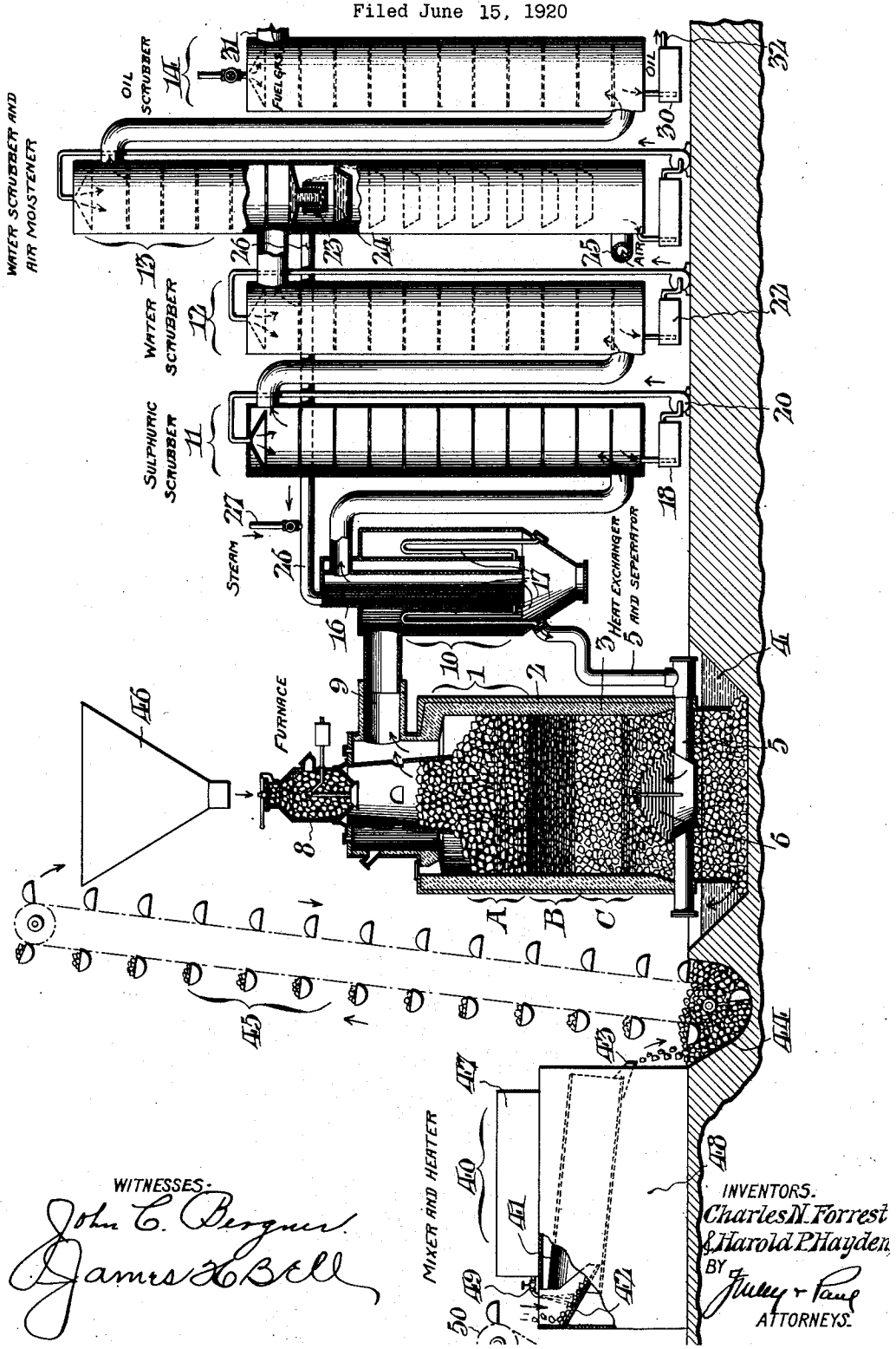
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C. N. FORREST ET AL

TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS.

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To all whom it may concern:

Be it known that we, CHARLES N. FORREST, a citizen of the United States, residing in the city of Rahway, in the county of Union and State of New Jersey, and HAROLD P. HAYDEN, a citizen of the United States, residing in Perth Amboy, in the county of Middlesex and State of New Jersey, have invented certain new and useful Improvements in Treatment of Hydrocarbons, whereof the following is a specification, reference being had to the accompanying drawing.

Our invention relates to the treatment of hydro-carbonaceous or bituminous substances or materials (hereinafter referred to in a general way as "hydrocarbon materials" or "hydrocarbons" simply, for the sake of brevity) to obtain useful products from them: on the one hand, in particular, products heretofore obtained by oil refinery methods, such as gasoline or naphtha, fuel oils, and even heavier oils; and, on the other hand, products heretofore obtained by gas retort or gas producer methods, such as fuel gas, ammonia, cyanides, etc.

The hydro-carbonaceous and bituminous materials or hydrocarbons heretofore commonly treated by such known processes and methods as those just referred to comprise, in the first place, both light and heavy bodied mineral oils and tars (of liquid or semi-fluid character), and, in the second place, such solids as oil shales, coal, and coke. In respect of these and other such materials, however, these processes and methods have serious drawbacks and limitations; and since our invention affords new processes and methods by which such disadvantages can be conveniently and economically overcome,—and by which, in particular. materials not fully or satisfactorily amenable to previous processes and methods (as well as materials so amenable) can be successfully dealt with and made to yield valuable new and old products,—we will briefly explain these old processes and their limitations.

Processes hitherto used in treating light and heavy bodied mineral oils and tars for the production of gasoline, burning oils and lubricating oils, etc., involve the distillation of the mineral oils or tars in horizontal or vertical boiler type stills, or in pipe stills. The usual method followed in such distillations is to raise the temperature of the crude or other oil in the still gradually, and to fractionate the condensate, as it comes off, up to lubricating oil grade. Paraffine oils are sometimes distilled or "run" to dryness, leaving a dry coke in the stills which is thereafter removed as such and applied to various commercial uses. Asphaltic and semi-asphaltic oils, on the other hand, are seldom distilled to dryness, but are run to an asphalt residue which, while yet hot, is sufficiently fluid to be drawn off from the stills by gravity. Sometimes the heavier distillates thus produced are again treated under heat and pressure in order to "crack" them into gasoline. Many such processes are available for the treatment of this class of liquid or semi-fluid carbonaceous materials for all of these purposes; but all of them leave unutilized a final residue,—either of coke or of heavy asphaltic residuum,—and none of them has been applied to the solid natural bitumens to any considerable extent.

Again, both oil shales and coal have been heretofore treated in retorts for the production of gas, coke, and by-products of tar and chemical substances; and coal and coke, also have been treated in gas producer apparatus for the manfuacture of "producer" gas,—both with and without recovery of by-products. Fusible or meltable solid bitumens, however (whether artificial, such as the very heavy asphaltic residues from petroleum distillation, or natural, such as Trinidad and Bermudez asphalts, gilsonite, grahamite, etc.), cannot be—or have not been—worked in gas retorts or in gas producers, for the simple reason that they do melt. As regards gas retorts, melting is of consequence because the molten bitumen would leave a coke in the retort which could not be removed without shutting down and cooling the retort in order to chip away the coke from its sides and bottom; as regards producer plants, because the molten bitumen would form a heavy mass through which the necessary air blast could not pass.

The ability to deal satisfactorily with the viscous residues and artificial asphalts that the oil refiner has discarded, and with the natural solid bitumens in which the oil refiner has never been interested,—a class of materials which we may conveniently distinguish as heavy hydrocarbons,—is, there-

fore, a very important advantage of our invention. The practical value of this advantage will be apparent from the fact that by our invention these heavy hydrocarbons may be so treated as to crack them into lighter and more valuable naphthas or fuel oils and at the same time obtain from them a fair yield of fuel gas and nitrogenous products; —whereas, so far as we are aware, no process for accomplishing this has hitherto been found. And although these materials do not, in general, yield any appreciable amount of oil at temperatures below 700° F., yet in the neighborhood of 750° F., they suddenly crack (frequently with considerable foaming); and if this latter temperature is held, some 60 to 80% by weight of the material may be driven off and recovered as gas and as oil condensate,—leaving a residue of from 20 to 30% of coke that is rich in carbon, lean in ash, and carries the greater part of the nitrogen content of the original crude oil or bitumen. By gasifying this coke, it may be converted into a combustible fuel gas, with recovery of some 70 to 90% of its nitrogen content as ammonia.

For the benefit of those desiring to practice our invention, we will hereinafter describe the best and most highly organized method of doing so at present known to us, together with the plant and apparatus which we prefer to employ for the purpose. Our description and claims will be rendered more readily intelligible, however, by a brief preliminary explanation of certain principles and features of our invention and of the particular methods and modes of operation which we prefer to employ.

One important feature of our invention in its preferred form is the cracking of the hydrocarbons of the material treated, with such vaporization of uncracked hydrocarbons as may occur, and the gasification of its carbon residue, in one operation, and yet with such distinctness of these stages of treatment as permits the material to be heated at suitable cracking temperatures under innocuous, non-combustive conditions for the former, and at appropriate combustion temperatures (higher ones being preferred than are sufficient for cracking) under combustion conditions for the latter. A further important feature is the concurrence of these two stages as regards different portions of the material, so that the material treated and its carbon residue may undergo these respective stages of treatment in one another's presence and with some interdependence additional to the mere fact that the later is performed on a product of the earlier. Several advantages may thus be obtained, including contribution of heat for the vaporizing and cracking from the combustion; improvement of the fuel value of the gasification products by carburization, in the cracking region, of carbon dioxide formed in the combustion region proper; and incidental enrichment of the fuel gas with such products of cracking as it may not be deemed worth while to segregate.

Still another important feature is, of course, avoidance of the formation of "retort" coke,—i. e., relatively thick, massive coatings of coke such as referred to above in the discussion of gas retort practice. This we accomplish by heating the materials treated, for cracking and for gasification, in a state of relative dispersion such as will render massive coke formations impossible, —maintaining this dispersion for the time necessary for both cracking and gasification (which latter consumes and eliminates the carbon residue as such) by suspension. This, of course, also obviates formation of the initial material itself into a mass impermeable to the combustion agent employed for gasification; it is besides, helpful to rapid reaction between gases and solids, and to disengagement and circulation of vaporized cracking products. We prefer to accomplish dispersion and suspension mechanically, so to speak, by charging a solid refractory carrier with the hydro-carbon material to be treated, as by coating or saturating the carrier with the hydro-carbon. By means of an "interstitious" refractory carrier,—which en masse or in the aggregate is porous or affords a multitude of interstices amongst its solid portions, and which when its solid portions are charged will still remain or form a permeable, porous aggregate through which gases and vapors can pass and circulate freely,—a very considerable amount of hydrocarbon can be dispersed and treated in a limited space without any formation of retort coke. The most convenient such aggregate is one consisting of separate pieces of suitably divided refractory material; individually, such pieces may be either porous or otherwise.

Another important feature is the possibility of continuous operation, so that carbonaceous material may be continually introduced at one point in the plant or apparatus and distillation and gasification products continually drawn off elsewhere.

The accompanying drawings shows a diagrammatic view, in elevation, of a plant suitable for the purposes of our invention, certain parts of the apparatus shown being in section or broken away to illustrate the construction and operation more clearly.

To afford a sphere of reaction for our treatment, we employ a vertical cylindrical retort 1, consisting, in general, of a shell 2 of boiler steel lined with firebrick 3 around its circumference and top, with its bottom edge immersed in a pan of water 4, acting as a seal. A blast pipe 5 enters the bottom of the retort 1, and the discharge

opening of this pipe is covered with an iron diffusing grate 6,—which may also cover more or less of the bottom of the retort. The top of the retort 1 is closed, but is provided with a magazine or feed chamber 8 having adjustable valved or covered openings through which the material to be treated may be introduced without substantial admission of air. At or near the top, also, there is an offtake 9 for the withdrawal of vapors, gases, etc. This retort or heating apparatus 1, it will be seen, closely resembles well known commercial types of gas producers; and in practice it will be provided with the usual accessories of such producers, including means for distributing the material to be treated, removing ashes and the like, etc.

At the beginning of operations, a wood and coal fire is started in the retort 1, and this fire is built up gradually until there is accumulated on the grate 6 a bed of ashes some four to six inches thick, with a bed of coals above, resting on the ashes, in process of combustion. As the fuel is consumed in the retort, fresh fuel is added through the magazine 8 on top, and ashes are removed through the water seal 4 at the bottom. With a suitably regulated or limited counterflow or blast of combustion agent from the grate 6 up through the descending fuel, a region of conditions and temperatures appropriate for combustion of residual carbon (ranging up to 2000° F., and over) may be created and maintained in the lower portion of the retort 1, and a region of non-oxidizing, innocuous conditions and temperatures (non-combustive conditions) suitable for vaporizing and cracking hydrocarbons (ranging down to some 700° F., or less) in its upper portion. While the variations of temperature in these regions and the transition between them may be more or less gradual or abrupt, according to varying conditions, it will be convenient and instructive to describe and discuss an assumed case (which appears to be a not unusual one) in which the bed of material in the retort 1 comprises three distinct horizontal zones of temperature A, B, and C, about as follows: A top zone or one third, from 700° to 1000° F.; a middle zone, also one third, from 1000° to 1900° F.; and the lowest zone, 2000° F., and over.

Having started the operation of the retort 1 with coal and proceeded with its operation until a fuel bed having such characteristics as these has been established, we then abandon use of coal and substitute therefor a special mixture (hereinafter described) of the hydro-carbonaceous or bituminous material to be treated with refractory carrier material. For convenience and in correspondence with one of its functions, we shall for the present refer to this special mixture as "fuel", and ignore its special refractory content. With this new fuel, then, operation is continued as before, so that the hydrocarbon thus entering the retort passes in turn through the cracking and combustion regions comprised in the three zones of heat A, B, and C hereinbefore described,—which may conveniently be designated, with reference to temperature, "low", "medium", and "high". Moreover, the operation is self-sustaining, since all the heat required is afforded by the hydrocarbon itself through the combustion of the coke.

As soon as the hydrocarbon enters the low heat zone, it cracks rapidly into a rich non-condensable gas; a thin oil, vaporized but condensable; and coke. The two former substances are swept quickly out of the retort by the leaner gas rising from the lower portions of the fuel bed; the coke descends to and through the moderate heat or middle zone B. While the fuel is passing through this moderate heat zone B, a thorough decomposition of the heavier and higher boiling hydrocarbons not cracked in zone A is accomplished,—the gaseous or vaporous substances formed being carried up with the gases from zone C and drawn out at the top of the retort,—and, at the same time, any carbon dioxide formed in zone C may be carburized and reduced to carbon monoxide by the residual carbon. The dry coke comprising the final carbon residue then passes down into and through the bottom high heat zone C, in which it is completely burned and consumed with the aid of the regulated blast or counterflow of combustion agent introduced through the grate 6 and diffusing upward through the bed of ashes thereon.

Thus the carrier material is freed of carbon and restored to clean, uncharged condition, in other words, regenerated and rendered fit for reuse.

The nitrogen comes off as ammonia at all stages of the operation, but especially during the final combustion of the coke in the high heat zone C.

The combustion agent employed for the blast is air moistened with water and live steam, and it is so regulated in amount that it is completely used up in combustion in the lower portion of the fuel bed; and the water is dissociated and its oxygen similarly used up, so that no free oxygen reaches the upper portion of the fuel bed. In this way the region of cracking temperatures and innocuous, uncombustive conditions hereinbefore mentioned is created and maintained in the upper portion of the retort 1, and the region of combustion conditions and temperatures in its lower portion. The operation goes on continuously in all its stages so long as fuel is continually introduced,

ashes drawn off, and the limited counterflow of combustion agent maintained.

The mingled gases and vapors,—condensable and noncondensable,—from the combined cracking and gasification operation just described are all drawn off together through the offtake 9, and may be conducted through a heat exchanger and separator 10 and through a series of condensers, scrubbers, and absorbers 11, 12, 13, and 14 which are constructed like apparatus now in use for similar purposes, and therefore require no extended description. The heat exchanger and separator 10, it will be seen, affords a large space and a circuitous course for the gases, and produces repeated changes in their direction of flow, so that any solid material that may be entrained with them will be deposited,—as well, perhaps, as a small amount of very high boiling hydrocarbons that might tend to clog the other apparatus if allowed to enter it. In this heat interchanger 10, also, the gases and vapors communicate their heat to the combustion agent, which passes through a central annular drum 16 in the heat interchanger and through a multiplicity of U-tubes 17 on its way to the blast 5. In the scrubber 11, the ammonia content of the gases and vapors is absorbed by a dilute sulphuric acid spray descending through the washing chamber of the apparatus in such a manner as to come into intimate contact therewith. The ammonium sulphate thus formed passes in solution into a tank 18 beneath the washing chamber. The sulphuric solution is repeatedly circulated through the apparatus by a suitable pump 20. In the scrubber 12, the gases and vapors are smilarly subjected to a water spray which serves to condense a large part of their oil content. The oil and water are drawn off from the bottom of the washing chamber into a settling tank 22 beneath it, and the water is thence similarly pumped back to the top of the washing chamber.

It will be seen that the gases and vapors traverse the scrubbers 11 and 12 from bottom to top, while the spraying liquids flow in the opposite direction. This relation of flow is preserved in the next scrubber 13, where the vapors ascending through the upper portion are subjected to a descending spray of water by which a further oil fraction is condensed. Just below the conduit leading from the top of the scrubber 12 to the bottom of the washing chamber in the upper end of the scrubber 13 is a water seal 23, which permits the lower end of the scrubber drum 13 to be employed for moistening the air for the retort blast by permitting the washing water to cascade through a series of pans 24. The air enters the lower end of the scrubber drum through a pipe 25 coming from a suitably regulated blower (not shown), and leave adjacent the seal 23 through the pipe 26 leading to the drum 16 of the heat exchanger. It will be noted that live steam (superheated if desired) may be introduced into the pipe 26 to mingle with the air by mean of a suitably valved pipe 27 connected thereto. The gases and vapor from the scrubber 13 are finally passed through an oil scrubber 14 (similar to the scrubbers 11 and 12, except in the use of oil) where a final portion of their condensable oil content is absorbed by the oil spray and subsequently recovered by means of a settling tank 30 beneath the scrubber. From this scrubber 14, the uncondensable gas (consisting of gasification products from the combustion zone C of the retort, mingled with any products of the other zones not segregated by the various scrubbers) may be led away through a pipe 31 for storage or use as fuel gas.

It will be observed that the pipe leading from each of the scrubbers 11, 12, 13 and 14 to its subjacent tank extends nearly to the bottom thereof, and it will be understood that each of these tanks may be provided with a draw-off for such oil as may rise to the surface of the liquid therein,—as at 32 for the tank 30.

In order to deal with hydrocarbon materials which are meltable or fusible at the temperatures involved in our process, we may incorporate them (as intimated above) with some refractory inorganic material adapted to serve as a carrier before introducing them into the sphere of treatment. Suitable divided refractory materials for our purpose are pieces of pumice stone; broken firebrick, or other infusible fragments of burnt fire clay; carborundum; ash or, indeed, any inert fragmentary material which is infusible at the maximum heat of our retort, and which may be selected and graded to produce a compact but porous aggregate whose largest particles are, say, from 1 to 2 inches in diameter. The exact mode of incorporating together the hydrocarbon and the carrier may vary to some extent, according to the degree of hardness of the hydrocarbon material to be treated and whether it can be pulverized or must be melted in order to charge with the pieces of suitably divided inactive, infusible carrier. Hard natural bitumens such as gilsonite and grahamite may simply be crushed or powdered before combining with the refractory aggregate, while the softer oil asphalts and the like may be melted in advance,—or else merely broken into chunks and distributed over the surface of the aggregate, during the mixing operation, while the latter is hot. However, the principle is the same in any event.

At the left of the drawing is shown suitable apparatus 40 for charging the divided carrier material with the hydrocarbon mate-

rial. This apparatus comprises a revolving metal drum or cylinder 41 in which the carrier and the hydrocarbon may be intimately mixed together. As shown, this drum is slightly inclined, so that as it revolves the material received by it from the chute 42 is caused to travel from end to end of the drum while being mixed, so as to drop into the chute 43, which delivers it to a storage pocket 44, whence it is elevated by a bucket conveyor 45 and deposited in the feed hopper 46 above the retort magazine 8, ready to be charged into the latter by gravity as required. If the hydrocarbon material to be treated requires to be previously melted or rendered freely fluid by the use of heat, this may be done in a tank 47 above the mixing drum 41,—both drum 41 and tank 47 being heated by means of a furnace 48. A suitably valved discharge pipe 49 on the tank 47 delivers the liquid hydrocarbon into the chute 42 upon the refractory carrier material delivered to the latter by a bucket conveyor or elevator 50. The furnace 48 may be heated or fired in any suitable manner, as by waste heat or fuel gas from the retort operations.

The hydrocarbon material and the refractory aggregate may be incorporated together in any suitable proportions, according to the character of each,— say from 10 to 50% hydrocarbon and 90 to 50% aggregate. If the pieces of aggregate be themselves porous, the hydrocarbon may be absorbed into them to some extent, besides being coated upon them and thus dispersed and suspended in a filmy state. In any case, however, the charged aggregate en masse must retain a granular, interstitious, and porous character and condition during its passage through the retort, and the pieces must likewise hold or retain their carbonaceous coatings or charges in their original state as well as after decomposition,—since otherwise the fuel bed would become clogged and the process would be rendered inoperative. When the refractory carrier is properly charged, however, the films of hydrocarbon on the surface of its particles are cracked almost instantly by contact with the hot gases (whose temperature at leaving the retort, is about 1200° F.) as the charged carrier enters the retort, and the resultant carbonaceous residue is no longer fusible. This coating of infusible carbonaceous material seems to prevent further fusion or melting of hydrocarbon so as to cause it to run off the particles of carrier and give rise to retort coke formations. The final carbonaceous material or carbon entering the high heat zone C is, of course, quite infusible, and hence retains its state of dispersion and suspension.

The refractory material leaving the retort through the bottom water seal is preserved, dried, and reused as long as it remains in serviceable condition, thus insuring a minimum of waste. Suitable conveyors and other mechanical means may, of course, be employed for removing this material from the retort and handling it back again to be recoated with bitumen. The process is somewhat facilitated when the fuel entering the retort is preheated,—as from the operations in the apparatus 40 described above.

Having thus described our invention, we claim:

1. The continuous self-sustaining process of destructively distilling and gasifying hydrocarbon materials which comprises continually introducing the material to be treated into the zone of reaction, charged upon pieces of inert refractory material as a carrier; passing the charged carrier material progressively through the sphere of reaction, and withdrawing it; and subjecting the advancing material to a limited counterflow of combustion agent, so as to create in the sphere of reaction a region of cracking of the hydrocarbon material under treatment and a subsequent region of combustion of the coke from such cracking, thereby furnishing heat for the cracking and restoring the carrier material to clean, uncharged condition.

2. The process of destructively distilling and gasifying hydrocarbon materials which consists in charging therewith pieces of divided inert refractory material as a carrier; passing the resultant porous charged aggregate progressively through the sphere of reaction; and subjecting the aggregate, towards its exit therefrom, to a limited counterflow of combustion agent, so as to create in the sphere of reaction a region of combustion and a preceding region of cracking, thus eventually consuming the coke formed from the cracking and restoring the carrier material to clean, uncharged condition.

3. The continuous process of destructively distilling and gasifying heavy hydrocarbons which consists in continually introducing the material to be treated into one zone of the sphere of reaction, charged upon pieces of an interstitious inert refractory aggregate as a carrier, and continually withdrawing the carrier aggregate from another zone; subjecting the advancing aggregate, towards its exit, to a limited counterflow of combustion agent, so as to create in the sphere of reaction a region of combustion and a preceding region of cracking; and drawing the products of combustion through the cracking region and withdrawing them from the sphere of reaction along with the products of cracking.

4. A continuous process of destructively distilling hydrocarbon material charged upon an interstitious inert refractory car-

rier, and using the same carrier material repeatedly; which method comprises heating the charged carrier to cracking temperature under non-combustive conditions and thereafter to combustion temperature under combustion conditions, thus eventually consuming the coke from the cracking; and recharging, reheating, and again regenerating the same carrier material.

In testimony whereof, we have hereunto signed our names at Madison, Ill., this 9th day of June, 1920.

CHARLES N. FORREST.
HAROLD P. HAYDEN.