Jan. 24, 1950

M. H. TUTTLE
METHOD OF AND APPARATUS FOR
CRACKING TARRY MATERIALS

2,495,613

Filed May 21, 1946

3 Sheets-Sheet 1

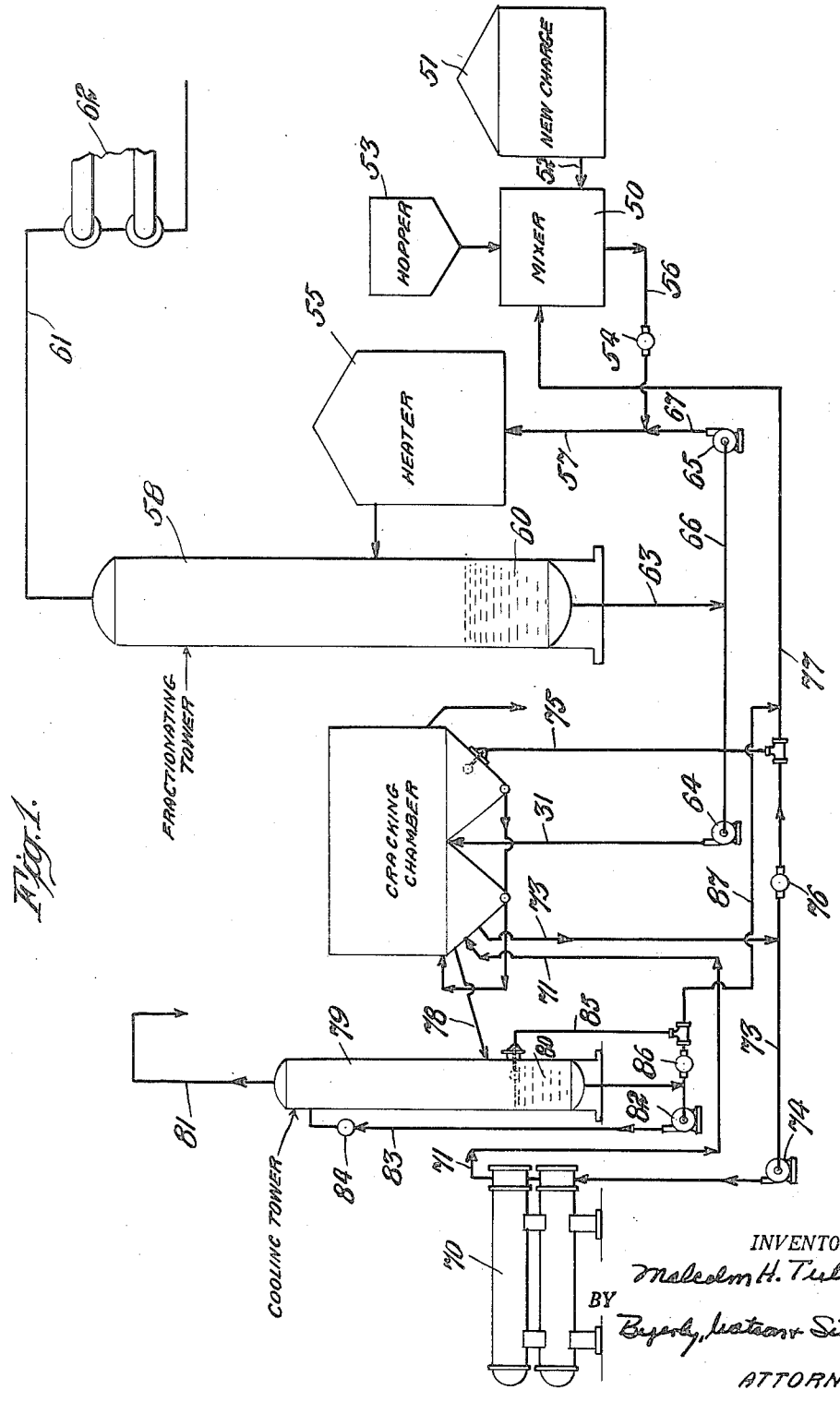


Fig. 1.

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3 Sheets-Sheet 2

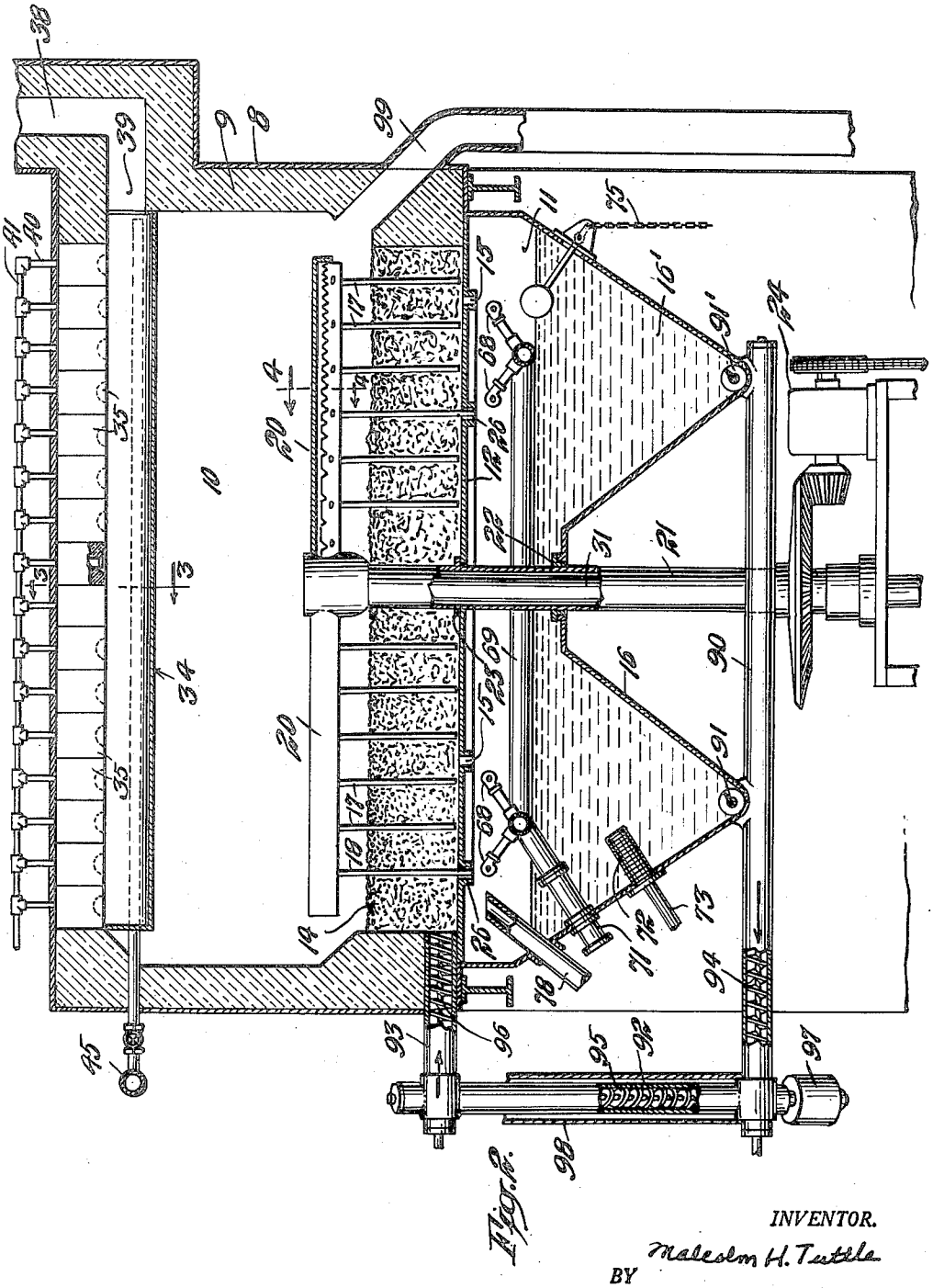


Fig. 2.

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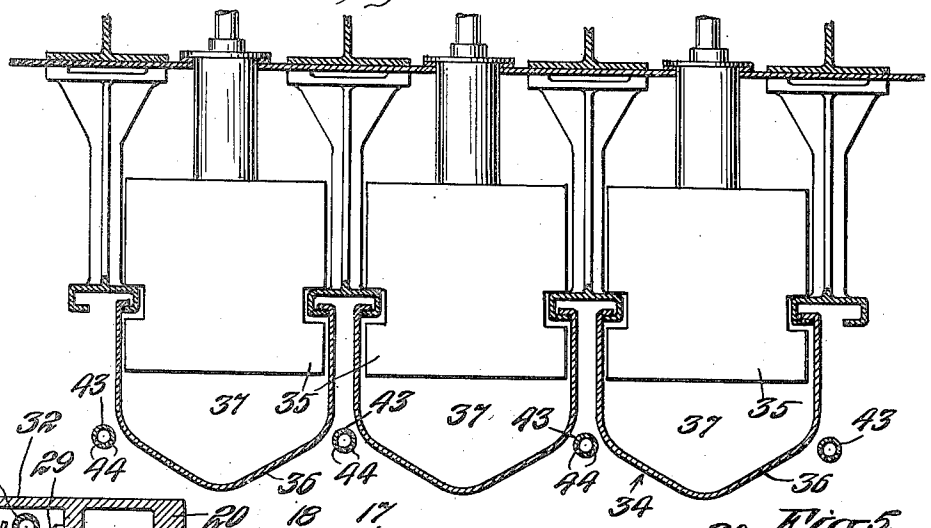
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3 Sheets-Sheet 3

Fig. 3.



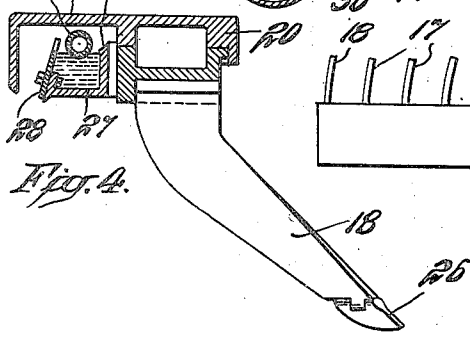


Fig. 4.

Fig. 5.

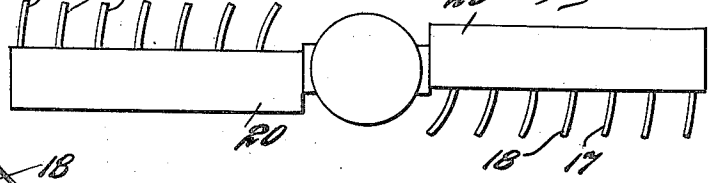
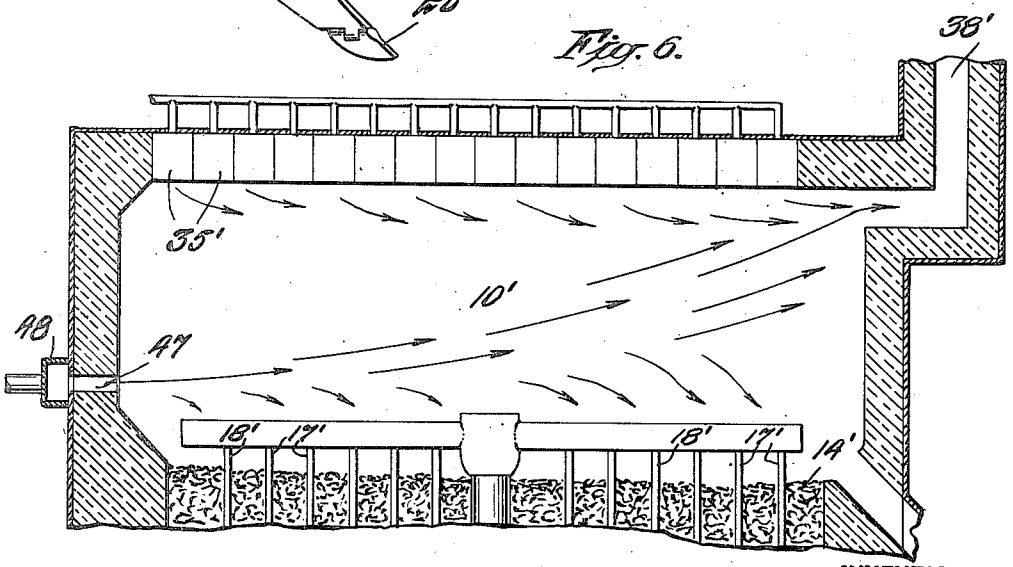


Fig. 6.



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UNITED STATES PATENT OFFICE

2,495,613

METHOD OF AND APPARATUS FOR CRACKING TARRY MATERIALS

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Application May 21, 1946, Serial No. 671,219

18 Claims. (Cl. 196—55)

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This invention relates to petroleum refining and aims to provide an improved method of and apparatus for cracking tarry materials.

In petroleum refining it has long been common practice to crack liquid hydrocarbons in stills having metal walls through which heat is supplied. Another process which has been used to some extent involves spraying petroleum hydrocarbons upon a bed of coke which is heated to incandescence. In each of those processes the formation of free carbon during the cracking operation has proved to be a distinct disadvantage which has seriously limited the extent to which those processes may be practiced.

The use of a still having heated metal walls has been found satisfactory for the cracking of clean stocks under relatively mild conditions but when the stock contains high boiling tars and the cracking is continued to the extent necessary to produce the desired high yield, there is deposited on the walls of the still a tenacious crust of carbon which builds up rapidly in thickness until it becomes necessary to interrupt the cracking operation and remove the crust from the walls of the still. This is a troublesome and expensive operation. When the cracking is not continued to the end point, there remains a by-product of low value commonly known as pressure tar.

In the past process which employed a bed of incandescent coke, free carbon is liberated in the bed and the pieces of coke become cemented to each other until they form a continuous mass which makes it necessary to discontinue operations in order to remove the bed and start afresh. The coke obtained from such a bed is fragile and difficult to handle and is of a spongy structure. Such coke has been burned in furnaces but it is a very unsatisfactory fuel. A further disadvantage which has accompanied the spraying of hydrocarbons on an incandescent bed of coke arises from the fact that the volatile fractions tend to vaporize as soon as they are heated to their boiling points and as a consequence frequently fail to reach the high temperature of the coke bed which is necessary for efficient operation.

I have discovered that the cracking of tarry materials may be carried on as a continuous operation notwithstanding the liberation of a substantial quantity of free carbon, and that the free carbon liberated during the cracking operation may be recovered in the form of a very superior solid fuel. It is a special feature of my invention that it makes possible the complete conversion of materials of low value and very limited utility

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into products of much greater value and usefulness.

The materials which can be converted by my invention, and which are referred to herein as "tarry materials," include pressure tar and even gilsonite. The materials which can be obtained from the conversion as end products include a distillate, solid fuel, and fixed gases. The solid fuel consists essentially of amorphous carbon fused into dense non-porous, generally rounded lumps. Any hydrocarbons withdrawn from the cracking chamber which are not of the composition of the desired end products can be recycled through the cracking chamber where they are cracked to form the desired end products.

Tarry materials are cracked in accordance with my invention by feeding them in liquid form to the top of a bed consisting of pieces of refractory material which are prevented from becoming cemented together. The bed is heated from above to maintain a temperature gradient from its top to its bottom which ranges from a point above cracking temperature to a point below the temperature at which thermal reactions occur. Hydrocarbons which are fed to the top of that bed are decomposed at the top and upper portion of the bed to form fixed gases, hydrocarbon vapors and carbon. The fixed gases and hydrocarbon vapors are then withdrawn from the bottom of the bed.

The apparatus in which this is accomplished consists of a chamber having a cracking compartment and a quenching compartment. Those compartments are separated by a partition which is adapted to support a bed of loose pieces of refractory material and which contains slits for the passage of hydrocarbons from one compartment to the other. The cracking compartment has a source of heat, means for feeding hydrocarbons to the top of the bed, and means for preventing the pieces of refractory material in the bed from becoming cemented together. The quenching compartment has means for providing a curtain of cooling liquid along the slits in the partition.

In order that my invention may be clearly understood, I will describe in detail a mode of practicing it by means of the apparatus illustrated in the accompanying drawings in which:

Fig. 1 is a diagrammatic elevation of the apparatus;

Fig. 2 is a vertical section of the cracking chamber;

Fig. 3 is an enlarged detail along the lines 3—3 of Fig. 2;

Fig. 4 is an enlarged detail along the lines 4—4 of Fig. 2;

Fig. 5 is a diagrammatic plan view of the plows; and

Fig. 6 is a fragmentary vertical section of an alternative form of cracking chamber.

The cracking chamber illustrated in Fig. 2 has an outer casing 8 of sheet steel whose upper side walls are lined with a refractory material such as fire brick 9 and contain a cracking compartment 10. The cracking compartment 10 is separated from a quenching compartment 11 by a partition 12 adapted to support a bed 14 of loose pieces of granular material. Circular slits 15 are provided in the partition 12 to permit hydrocarbons to flow from one compartment to the other. The casing at the bottom of the quenching compartment 11 is shaped to form a pair of connected troughs 16, 16' which extend along the length of the cracking chamber.

The pieces of refractory material which constitute the bed 14 are prevented from becoming cemented together by means of plow blades 17, 18 attached to radial arms 20. A hollow rotary shaft 21, journalled in the casing 8 at 22 and in the partition 12 at 23, supports the arms 20 and is rotated in a counterclockwise direction by motor 24. The plow blades 18 have fingers 26 which travel in the slits 15 when the shaft 21 is rotated to prevent those slits from becoming clogged with carbon. The plow blades 17, 18, as they travel through the bed 14, exert a sorting action on that bed raising the larger particles to the top and permitting the smaller particles to sink to the bottom. This is accomplished by forming each blade so that, although the entire blade travels around a circular path of uniform radius, as illustrated in Fig. 5, it is slanted from base to tip in the direction of rotation at an angle of about 45° from the perpendicular (Fig. 4.)

Liquid hydrocarbons are fed to the top of the bed 14 from the radial arms 20 as those arms rotate. The trailing edge of arm 20 contains a channel 27 having a notched plate 28 secured thereto to form trough 29. Pipe 30 connects that trough with the conduit 31 which extends through the interior of shaft 21 to supply liquid hydrocarbons to the troughs. The spaces between the notches in plate 28 decrease as their distance from the shaft 21 increases so that substantially the same quantity of hydrocarbons is fed to each part of the top of bed 14. A shield 32 extends over the top of trough 29 to protect it from heat directed to the bed.

Radiant heat is supplied to the top of bed 14 by radiators 34 of the type forming the subject matter of my co-pending application Serial No. 654,932, filed March 16, 1946. Each radiator 34 consists of a row of radiant gas burners 35 and a trough-shaped shield 36 whose side edges are loosely supported along the sides of the burners 35. The shield 36 forms a combustion space 37 for the burners 35 and separates that combustion space from the cracking chamber 10. A small portion of the products of combustion is permitted to leak around the edges of shields 36 into the cracking chamber 10. The balance of the products of combustion are led from combustion space 37 to stack 38 through conduit 39. The burners are connected with a source (not shown) of a combustible mixture of gas and air through conduits 40 and manifold 41. Pipes 43 containing pairs of orifices 44 extend from a steam manifold 45 across the cracking compartment 10 between each pair of radiators 34.

The cracking chamber illustrated in Fig. 6 is of the same construction as that illustrated in Fig. 2 except that the shields 36 and pipes 43 are omitted, and steam is admitted to the cracking compartment 10' through longitudinal slit 47 which communicates with a steam manifold 48. The bed 14' is rabbled by plow blades 17', 18' and is heated to incandescence by radiant gas burners 35'. The major portion of the steam admitted to cracking compartment 10' from slit 47 travels across that compartment between the burners 35' and the bed 14' and is withdrawn through the exhaust stack 38' carrying with it the major portion of the products of combustion from the burners 35'.

The operation of the apparatus is as follows: The cracking compartment 10 is provided with a bed 14 consisting of loose pieces of refractory material (preferably pieces of the solid fuel formed by the cracking process which I am about to describe). The top of the bed 14 is heated by radiant heat to a temperature of about 1000° F. and is maintained at about that temperature in a non-oxidizing atmosphere during the cracking operation. The shaft 21 is rotated in a counterclockwise direction by motor 24 and liquid hydrocarbons are fed to successive portions at the top of the bed from the troughs 29.

The tarry material to be cracked is first mixed with liquid hydrocarbons in the mixer 50. When the charging stock consists of a material such as pressure tar or the residue of a crude oil from which the readily volatile constituents have been topped off, it is fed to the mixer 50 from the tank 51 through conduit 52. When the charging stock consists of gilsonite, the gilsonite is finely powdered and placed in the hopper 53 from which it is fed to the mixer 50.

The mixture of tarry material and liquid hydrocarbons is delivered by pump 54 from the mixer 50 to the heater 55 through conduit 56 and conduit 57 and thence to the fractionating tower 58 where volatile fractions of the liquid hydrocarbons and of the stock are distilled off, leaving a liquid fraction 60. It is of importance that this distillation be carried out at a temperature which is less than the cracking temperature and which may be in the neighborhood of 750° F. and at a reduced pressure which will remove substantially all materials which would vaporize on the cracking bed before reaching cracking temperature. The volatile fractions flow from the fractionating tower through conduit 61 and condenser 62 to a conventional recovery system (not shown) where they are separated and collected as end products. The desired quantity of liquid fractions 60, to be cracked, is conducted from the fractionating tower by means of conduit 63 and pump 64 to the conduit 31 which supplies the troughs 29. Heating of the mixture of tarry material and liquid hydrocarbons may be assisted by combining this mixture with hot liquid fractions 60 in conduit 57. The hot liquid fractions 60 are delivered to conduit 57 by means of pump 65 and conduits 66, 67, and, after combining with the mixture, flow through the heater 55 and back to the fractionating tower 58.

The liquid fractions are fed to the troughs 29 so that they flow from those troughs to the top of bed 14 in a thin sheet of liquid which wets the pieces of refractory material in the uppermost portion of that bed with a thin film of

liquid. The temperature of the wet pieces of refractory material is momentarily reduced to a point below the cracking temperature of the stock, and, as additional radiant heat is supplied to them, the liquid hydrocarbons are cracked and converted to hydrocarbon vapors, fixed gas and amorphous carbon. The hydrocarbon vapors and fixed gases flow downwardly through the bed and are withdrawn from the bottom of the bed through slits 15. The carbon remains as a thin layer fused to that piece of refractory material which was wet by the liquid film from which such carbon was released.

The speed of rotation of the arms 20 and the rate at which the liquid is fed to the top of bed 14 are such that each portion of the bed to which hydrocarbons have been fed from the trough in an arm 20 is heated to dryness before it is reached by the plow blades fixed to the other arm 20. The layers of carbon formed during a revolution of shaft 21 are so thin that the lifting action of the plows prevents adhesion between the pieces of refractory material at their points of contact thus maintaining the bed in a loose state. I have found that this can be accomplished in a bed having a diameter of six feet and a depth of two feet by feeding hydrocarbons to the top of the bed at the rate of 0.5 pound per square foot per revolution and by rotating the shaft 21 at the rate of one revolution per minute.

Feeding the hydrocarbons to the top of the bed in the form of a thin sheet of liquid prevents the spattering which results from spraying liquid on the top of the bed. However, some fine particles of carbon escape to the atmosphere above the top of bed 14 and if these were permitted to accumulate, they would form a sooty fog between the bed and the radiators 34 which would interfere with the efficient transfer of heat from those radiators to the top of the bed. The formation of such a fog is prevented by introducing steam into the cracking compartment through pipes 43 or slit 47 and causing it to flow downwardly through the bed.

The fixed gases and hydrocarbon vapors formed during cracking are withdrawn from the bed 14 to the quenching chamber 11 through slits 15 and are quenched by a spray of cooler liquid hydrocarbons: Pairs of nozzles 68 are attached to a circular manifold 69 and are adapted to direct droplets of the liquid into and along the edges of the slits 15. In Fig. 2 of the drawings only two pairs of nozzles 68 are shown. It will be appreciated, however, that these pairs of nozzles are spaced together closely enough to form a continuous liquid curtain along the slits 15 through which the hydrocarbon vapors and fixed gases must pass. Liquid is supplied to the manifold 69 from cooler 70 through conduit 71.

The quench spray is an important feature of my invention. It condenses most of the hydrocarbon vapors which are withdrawn from the bed 14, and cools partition 12 and the bottom of bed 14 to a temperature below that at which thermal reactions occur thus sharply arresting polymerization of the hydrocarbons formed during the cracking operation. It also prevents the formation below slits 15 of a crust of carbon which would otherwise build up to such an extent that it would seal those slits. Liquid from the quench spray and fractions which are condensed by that spray are collected in the troughs 16, 16'.

At the commencement of operations the troughs 16, 16' and the cooler 70 are charged with a liquid such as gas oil. As liquid for the quench spray is withdrawn from the cooler 70, it is replenished by liquid withdrawn from the troughs 16, 16' through a strainer 72 and supplied by conduit 73 and pump 74 to the cooler 70 where its temperature is reduced to about 185° F. The quantity of liquid in the troughs 16, 16' is regulated by liquid level control valve 75 so that liquid hydrocarbons are withdrawn from the troughs 16, 16' and are delivered, at the rate at which they are produced, by pump 76 and conduit 77 to the mixer 50 where they mix with new charge for circulation through the heater 55 and fractionating tower 58.

Uncondensed fractions and fixed gases are withdrawn from the quenching chamber 11 through conduit 78 to a cooling tower 79 where the condensable fractions 80 are collected. Hydrocarbon gases flow from the cooling tower through conduit 81 and are preferably conducted to a point (not shown) where they are mixed with air to provide fuel for the burners 35. The liquid fractions 80 are circulated by pump 82 and conduit 83 through a cooler 84 and the cooling tower 79 for thorough separation of fixed gases from the condensable fractions. The quantity of the liquid fractions 80 in the cooling tower is regulated by liquid level control valve 85 which permits such fractions to be transferred through pump 86 and conduit 87 to the conduit 77 and to the mixer 50 at the rate at which they are produced.

By transferring liquid fractions formed in the cracking chamber to the mixer 50 where they are mixed with charging stock and then circulating the mixture through heater 55 and the fractionating tower 58, all volatile fractions of the liquid formed in the cracking chamber are distilled off while the highest boiling fractions are caused to recirculate through the cracking chamber where they are cracked. Consequently, the cracking operation is continued to completion as a continuous operation. Instead of the undesirably heavy hydrocarbons which have been recovered in substantial quantities as by-products in the practice of previous cracking operations, all of the materials recovered through my process are of the composition of the desired end products.

In addition to the hydrocarbon vapors and gases which flow through the slits 15, some pieces of carbon fall through those slits. That carbon settles to the bottom of the troughs 16, 16' and is delivered from them to the bottom of bed 14 by a series of screw conveyors. Carbon is transferred from the bottoms of the troughs 16, 16' to a tube 90 by means of conveyors 91, 91' respectively. The tube 90 is connected by means of tube 92 with a tube 93 which enters the cracking chamber 10 at the bottom of bed 14. Carbon delivered to the tube 90 is conducted by conveyor 94 to the tube 92 and is then delivered to the tube 93 by conveyor 95. The carbon so delivered to the tube 93 is returned to the bed 14 by means of conveyor 96. A motor 97 drives the conveyor 95. Like motors (not shown) drive the other conveyors of the series.

The abrading action of the carbon on the screw conveyors is most severe on the conveyor 95 which carries carbon upwardly from tube 90 to tube 93. Consequently, it is at times necessary to repair or replace conveyor 95 and the tube 92. To permit this to be done with a minimum of confusion

and delay, the tube 92 is mounted in a boot 98 which extends from the tube 90 to a point above the level of the liquid in troughs 16, 16' and it is merely necessary to lift the tube 92 and the conveyor 95 out of that boot to make such repairs as may be necessary.

The smaller pieces of carbon in the bed 14, including those pieces which are returned to the bottom of that bed from the troughs 16, 16', provide seeds which by accretion form the larger pieces of solid fuel recovered as an end product. A passageway 99 leads from the top of bed 14 to the exterior of the cracking chamber. As the bed grows in depth, the larger pieces which are pulled to the top of that bed by the sorting action of the plows 17, 18 fall through passageway 99 to a point (not shown) where they may be quenched and collected.

A tarry material such as 80-penetration Venezuela tar has been cracked through the process which I have described to yield 65% of distillate, 20% of solid fuel and 15% of fixed gases. The distillate is comprised of liquid hydrocarbons which are practically free from fractions that form a substantial amount of carbon and it provides an excellent fuel oil for either residential or industrial use.

I prefer in the practice of my invention to crack hydrocarbons in the liquid phase. However, my invention may be utilized in connection with vapor phase cracking. The conditions under which my process is carried out are subject to close control and it will be appreciated that by raising the pressure and lowering the temperature in the fractionating tower 58, stocks may be prepared for delivery to the cracking chamber which contain fractions that are cracked in the vapor phase.

The terms and expressions which have been employed are terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof but it is recognized that various modifications are possible within the scope of the invention claimed.

What I claim is:

1. The method of cracking hydrocarbons, which comprises maintaining a bed of loose pieces of refractory material in a non-oxidizing atmosphere, supplying radiant heat to the bed from above and cooling the bed from below to maintain a temperature gradient in the bed which ranges from a point above the cracking temperature of the hydrocarbons to a point below the temperature at which thermal reactions take place, feeding hydrocarbons in liquid form to the top of the bed, causing hydrocarbons to flow down through the bed, and withdrawing hydrocarbon vapors from the bed at its bottom.

2. The method of cracking hydrocarbons, which comprises maintaining a bed of loose pieces of refractory material in a non-oxidizing atmosphere, heating the upper portion of the bed to cracking temperature by means of radiant gas burners located above the bed, introducing a layer of steam into the space between the gas burners and the top of the bed, feeding hydrocarbons in liquid form to the top of the bed, and withdrawing hydrocarbon vapors from the bed at its bottom.

3. The method of cracking hydrocarbons, which comprises maintaining a bed of loose pieces of fused, amorphous carbon on a floor having open passageways therethrough, heating the upper portion of the bed to cracking temperature, feeding hydrocarbons in liquid form to successive portions of the top of the bed so that said portions are wet and then heated to dryness, plowing the dried portions of the bed so that the largest pieces of fused, amorphous carbon are brought to and discharged from the top of the bed, withdrawing hydrocarbon vapors from the bed through said passageways, and pushing pieces of carbon from said passageways so that the passageways are kept open.

4. The method of cracking hydrocarbons, which comprises maintaining a bed of loose pieces of fused, amorphous carbon on a floor having open passageways therethrough, heating the upper portion of the bed to cracking temperature, feeding hydrocarbons in liquid form to successive portions of the top of the bed so that said portions are wet and then heated to dryness, plowing the dried portions of the bed so that the largest pieces of fused, amorphous carbon are brought to and discharged from the top of the bed, withdrawing hydrocarbon vapors and small pieces of carbon from the bed through said passageways, and returning to the bed carbon withdrawn through said passageways.

5. The method of cracking hydrocarbons, which comprises maintaining a bed of loose pieces of refractory material on a floor having open passageways therethrough, heating the upper portion of the bed to cracking temperature, feeding hydrocarbons in liquid form to the top of the bed, withdrawing hydrocarbon vapors from the bed through said passageways and simultaneously spraying cooler liquid hydrocarbons through and along the edges of said passageways from below.

6. The method of cracking hydrocarbons, which comprises maintaining a bed of loose pieces of refractory material, heating the upper portion of the bed to cracking temperature, cooling the bottom of the bed, feeding hydrocarbons in liquid form to the top of the bed, withdrawing hydrocarbon vapors from the bed at its bottom, condensing the hydrocarbon vapors by subjecting them to a quench spray of cooler liquid hydrocarbons, collecting the condensate and quench spray, and utilizing a portion of the liquid hydrocarbons so collected to cool the bottom of the bed and to quench hydrocarbon vapors subsequently withdrawn from said bed.

7. The method of cracking hydrocarbons, which comprises maintaining a bed of loose pieces of refractory material, heating the upper portion of the bed to cracking temperature, feeding hydrocarbons in liquid form to the top of the bed, cooling the lower portion of the bed to a point below the temperature at which thermal reactions take place, withdrawing hydrocarbon vapors from the bed at its bottom through a quench spray of cooler liquid hydrocarbons to condense the hydrocarbon vapors, collecting the quench spray and condensate in a receptacle located below said bed, and removing liquid from said receptacle at the rate at which the condensate is produced.

8. Apparatus for treating hydrocarbons, comprising a chamber having a cracking compartment, a quenching compartment, and a partition between said compartments adapted to support a bed of loose pieces of refractory material in the cracking compartment and containing slits for the passage of hydrocarbons from one of said compartments to the other; the cracking compartment having means for supplying heat to the top of the bed, means for supplying hydrocarbons to the top of the bed, and means for preventing the pieces of material in the bed from becoming

cemented together; and the quenching compartment having means adapted to provide a liquid curtain along said slits.

9. Apparatus for treating hydrocarbons, comprising a chamber having a cracking compartment, a quenching compartment, and a partition between said compartments adapted to support a bed of loose pieces of refractory material in the cracking compartment and containing slits for the passage of hydrocarbons from one of said compartments to the other; the cracking compartment having means for supplying heat to the top of the bed, means for supplying hydrocarbons to the top of the bed, and means for preventing the pieces of material in the bed from becoming cemented together; and the quenching compartment having means for spraying liquid through and against the edges of said slits.

10. Apparatus for treating hydrocarbons, comprising a chamber having a cracking compartment, a quenching compartment, and a partition between said compartments adapted to support a bed of loose pieces of refractory material in the cracking compartment and containing slits for the passage of hydrocarbons from one of said compartments to the other; the cracking compartment having means for supplying heat to the top of the bed, means for supplying hydrocarbons to the top of the bed, and means for preventing the pieces of material in the bed from becoming cemented together; and the quenching compartment having a series of nozzles directed toward each of said slits, and means for supplying liquid to said nozzles.

11. Apparatus for treating hydrocarbons, comprising a chamber having a cracking compartment, a quenching compartment, and a partition between said compartments adapted to support a bed of loose pieces of refractory material in the cracking compartment and containing slits for the passage of hydrocarbon vapors from the cracking compartment to the quenching compartment; the cracking compartment having means for supplying heat to the top of the bed, means for supplying hydrocarbons to the top of the bed, and means for preventing the pieces of material in the bed from becoming cemented together; and the quenching compartment having means for supplying a spray of liquid along the slits to condense hydrocarbon vapors flowing through said slits, and means for withdrawing condensed hydrocarbon vapors from the quenching compartment at the rate said condensate is produced.

12. Apparatus for treating hydrocarbons, comprising a chamber having a cracking compartment, a quenching compartment, and a partition between said compartments adapted to support a bed of loose pieces of refractory material in the cracking compartment and containing slits for the passage of hydrocarbons from one of said compartments to the other; the cracking compartment having means for supplying heat to the top of the bed, means for supplying hydrocarbons to the top of the bed, means for preventing the pieces of material in the bed from becoming cemented together, and means for pushing pieces of refractory material from the slits; and the quenching compartment having means adapted to return pieces of material pushed through the slits to the bottom of the bed.

13. Apparatus for treating hydrocarbons comprising a chamber having a cracking compartment, a quenching compartment, and a partition between said compartments adapted to support a

bed of loose pieces of refractory material in the cracking compartment and containing circular slits for the passage of hydrocarbons from one of said compartments to the other; the cracking compartment having means for supplying heat to the top of the bed, means for supplying hydrocarbons to the top of the bed, means for preventing the pieces of material in the bed from becoming cemented together, and means adapted to travel along said slits to prevent the slits from becoming clogged; and the quenching compartment having means for spraying liquid through and against the edges of said slits.

14. Apparatus for cracking hydrocarbons, comprising a chamber having a floor adapted to support a bed of loose pieces of refractory material and containing slits for the passage of hydrocarbon vapors, gas burners located above the top of the bed and adapted to supply radiant heat to the top of the bed, means for supplying liquid hydrocarbons to the top of the bed, means for preventing the pieces of material in the bed from becoming cemented together, means for introducing a layer of steam into the space between the gas burners and the top of the bed, and means for withdrawing hydrocarbon vapors from the bottom of the bed through said slits.

15. Apparatus for cracking hydrocarbons, comprising a chamber having a floor adapted to support a bed of loose pieces of refractory material and containing slits for the passage of hydrocarbon vapors, a series of radiant heaters extending across the chamber above the top of the bed and adapted to supply heat to the top of the bed, means extending across the chamber between adjacent heaters for introducing steam into the space between the heaters and the top of the bed, means for feeding liquid hydrocarbons to the top of the bed, means for preventing the pieces of material in the bed from becoming cemented together, and means for withdrawing hydrocarbon vapors from the bottom of the bed through said slits.

16. Apparatus for cracking hydrocarbons, comprising a chamber having a floor adapted to support a bed of loose pieces of refractory material and containing slits for the passage of hydrocarbon vapors, gas burners located above the bed and adapted to supply radiant heat to the top of the bed, means for introducing a layer of steam into the space between the gas burners and the top of the bed, means for withdrawing products of combustion from said gas burners and steam from the chamber above the bed, means for feeding liquid hydrocarbons to the top of the bed, means for preventing the pieces of material in the bed from becoming cemented together, and means for withdrawing hydrocarbon vapors from the bottom of the bed through said slits.

17. The method of cracking hydrocarbons, which comprises maintaining a bed of loose pieces of refractory material, heating one portion of the bed to cracking temperature, cooling another portion of the bed to a temperature below the temperature at which thermal reactions take place, feeding hydrocarbons in liquid form to the hotter portion of the bed, causing hydrocarbons to flow through the bed from the hotter portion to the cooler portion, and withdrawing hydrocarbon vapors from the cooler portion of the bed.

18. Apparatus for treating hydrocarbons, comprising a chamber having a floor adapted to support a bed of loose pieces of solid refractory material and containing slits for the passage of hy-

drocarbon vapors, means for supplying heat to the top of the bed, means for cooling the bottom of the bed, means for preventing the pieces of solid refractory material in the bed from becoming cemented together, means for feeding liquid hydrocarbons to the top of the bed, means for feeding pieces of solid material to the bottom of the bed, means for discharging pieces of solid material from the top of the bed, and means for withdrawing hydrocarbon vapors from the bottom of the bed through said slits.

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