

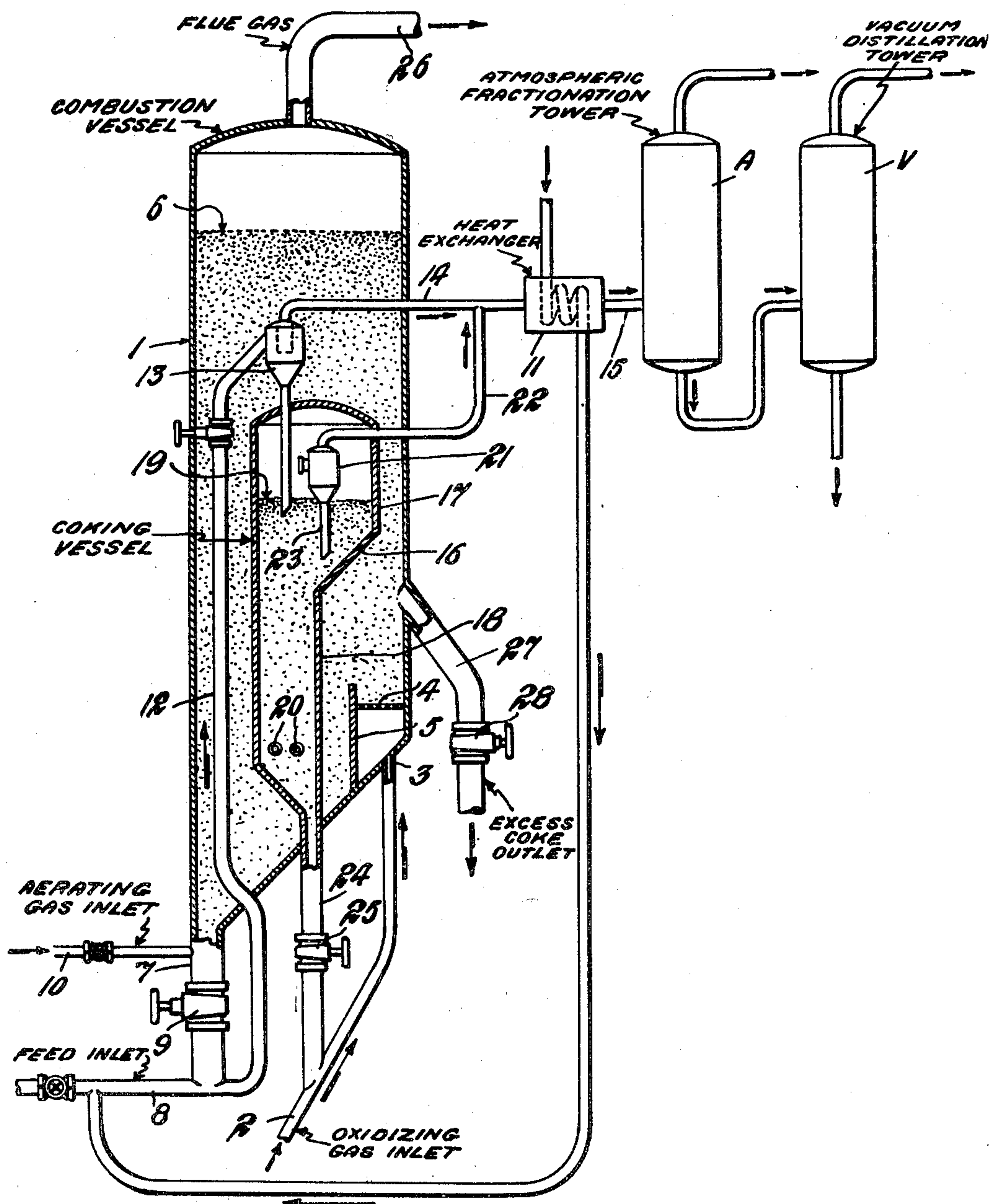
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PROCESS FOR CRACKING AND COKING HEAVY HYDROCARBONS

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PROCESS FOR CRACKING AND COKING
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This invention relates to an improved process for the production of valuable distillates by the coking of heavy hydrocarbon fractions obtained from crude petroleum or from synthetic oils. More particularly, it relates to a process for preparing high-grade gasoline and gas oils suitable as catalytic cracking feed stocks from residue, petroleum residues or pressure tars, part or all of the finely divided coke produced in the operation being used as the heat transfer medium. It relates especially to a method comprising a first rapid cracking step wherein the vapor contact time is very short and a second step wherein the more refractory fractions of the residuum are allowed a considerably greater residence time in the reaction zone to transform them into coke and relatively low-boiling constituents.

Economic considerations and increased demands for distillate fuels are constantly stimulating the efforts of the oil industry in its search for methods allowing the best possible conversion of crude petroleum into high-grade products. One of the major problems to be solved in this connection is to improve the conversion of heavy residues into high yields of valuable distillates, such conversion consisting essentially of separating the heavy and/or refractory coke-forming fractions present in the residues in such a manner as to obtain optimum yields of gasoline and of gas oils suitable for catalytic cracking and coking the heavy fraction in such a manner that the resulting coke interferes as little as possible with the continuous operation of the process.

Prior to applicant's invention, the conventional methods of processing residues were operations known in the art by the names of de-asphalting, viscosity breaking and delayed coking respectively. These processes, however, were usually characterized by the fact that they had to be interrupted at intervals to remove the formed coke.

It has also been proposed to coke heavy residual oils in a continuous manner by spraying the oil unto a continuously moving mass of highly heated solids. For example, according to one mode of operation, a relatively cool residuum is sprayed over and passed downwardly through a hot rabbled bed of lump coke. The top temperature of the bed may, for example, be of the order of 1000° F. The oil on contacting the hot coke is subjected to partial vaporization and the unvaporized constituents of the residual oil are maintained on the coke lumps for a

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period materially greater than the vaporized portion.

While this operation has certain advantages, it is subject to other inherent limitations. For example, the mechanism for rabbling the hot coke is subject to frequent failures due to the high temperature conditions maintained in the coking zone. Also the operation requires the use of an extremely heavy residual oil which contains a minimum amount of vaporizable constituents in order to minimize the amount of heat required for the coking operation. It has also been found that when coking heavy residual oils containing substantial amounts of sulfur, the sulfur is retained in the coke which makes the resulting coke inferior, particularly for such specialty products as metallurgical coke and coke used for making carbon electrodes.

It is the object of this invention to provide an improved method for converting heavy or residual hydrocarbon oils, which are characterized by the widely different refractoriness or resistance to cracking of their several constituents, into high yields of gasoline and feed stock suitable for catalytic cracking. Another object is to devise a process for coking residuum oils in such a manner as to reduce or control the extent to which the resulting vapors re-crack or polymerize. A further object is to provide a continuous fluidized process for coking residuum oils in such a manner that the coke produced thereby is partially used for supplying the necessary heat of reaction. Another object is to design an apparatus adapted for coking heavy petroleum fractions employing a two-stage fluidized technique so as to obtain the greatest possible yield of useful distillate and to produce a coke of relatively low sulfur content. Still other objects will become apparent from the subsequent description.

The present invention is concerned with a process in which the heavy residual oils to be converted into lighter components are initially mixed with a stream of hot finely divided coke particles. The temperature of the particles and the amount of particles introduced into the residual oil are sufficient to effect at least a partial vaporization of the oil to thereby form a suspension of oil vapors, finely divided coke particles and unvaporized oil residue. The resulting suspension is then passed through a conduit wherein the oil may be subjected to further heating and wherein mild cracking of the less refractory components of the feed may be carried out. The resulting products following the heat treatment are

passed into a separating zone wherein the vapors formed during the vaporization and cracking treatment are separated from the coke particles and the unvaporized portion of the residual feed. The mixture of coke and unvaporized residue is then introduced into a coking chamber. According to one of the specific phases of this invention, the coking chamber is immersed in a body of carbon particles undergoing combustion by passing an oxidizing gas upwardly through the combustion zone at such a rate as to maintain a relatively dense fluid turbulent layer of coke particles in the bottom of the combustion zone. A stream of non-oxidizing gas is also introduced into the bottom portion of the coking zone and passes upwardly therethrough at such a rate as to maintain the coke particles therein in a similar dense phase fluidized condition. The relatively dense fluidized layer of coke particles in the combustion zone and in the cooking chamber serves to transfer heat from the combustion zone to the coking zone and tends to maintain the coking zone at a substantially uniform temperature throughout. Furthermore, the gas passing upwardly through the coking chamber accelerates the removal of vapors formed from the residual oil during the coking treatment. As a result, such vapors are retained in the coking chamber for a relatively short period of time, thus materially reducing the amount of cracking of such materials in the coking zones. The vapors removed from the coking zone are rapidly cooled and thereafter subjected to suitable fractionation to recover the desired distillate products therefrom.

In order that the invention may be better understood, reference is made to the attached drawing which forms a part of the specification and which is a schematic illustration of an apparatus suitable for carrying out the invention.

Referring to the drawing, a stream of air, oxygen or other suitable oxidizing gas intermixed with finely divided coke particles is introduced into a combustion vessel 1 through line 2 which enters the combustion vessel at point 3 below a perforated grid 4. The perforated grid 4 may extend over a substantial portion of the combustion vessel 1 or over a rather restricted portion, as shown in the drawing. In the latter case, an upwardly extending vertical partition 5 is provided having its lower end connected to the bottom of the vessel and its upper end connected to the perforated grid 4 to form a distributing zone below the perforated grid 4. The mixture of oxidizing gas and coke particles passes upwardly through grid 4 into the main body of the combustion vessel 1 wherein the velocity of the oxidizing gas is reduced to cause the carbon particles to segregate into a relatively dense layer in the bottom portion of the combustion vessel which is maintained in a relatively dense turbulent state by the gases rising therethrough. The superficial velocity of the gas will depend upon the size of the carbon particles in the combustion vessel. The size of the carbon particles may vary over an extended range, such as from 5 microns up to $\frac{1}{4}$ " or more. When using extremely fine carbon particles, such as those ranging from 5 to 150 microns in diameter, the superficial velocity of the rising gas will be of the order of from .5 to 3 feet per second. The term "superficial velocity" as here employed means the velocity that the gases would assume in the absence of any solid material in the combustion space.

Under properly controlled conditions a rela-

tively dense layer of particles undergoing combustion is maintained in the lower portion of the combustion vessel having a relatively well-defined upper level as shown by numeral 6.

The amount of air introduced into the combustion vessel 1 is sufficient to burn a portion of the carbon introduced and to supply sufficient heat thereby for carrying out the process. The temperature within the combustion vessel 1 may be maintained within the range of from 1000° F. to 1400° F. and advantageously between the temperatures of from 1100° F. to 1200° F.

A stream of heated carbon particles is continuously removed from the combustion vessel 1 through standpipe 7, which communicates with the residuum feed line 8. The standpipe is provided with a control valve 9 adapted to regulate the flow of coke into line 8 for admixture with the residuum. Also, it may be desirable to introduce an aerating gas through line 10 near the bottom of the standpipe 7, to prevent packing of the particles and to facilitate their flow. The gas used for aerating the coke in the standpipe may advantageously be an oxygen-containing gas such as air and/or flue gas so as to supply additional heat to the system by combustion in subsequent steps, but others may prefer to use a non-oxidizing stripping gas, such as steam, nitrogen or carbon dioxide so as to prevent undesirably high quantities of oxygen from entering feed line 8. The heavy residual oil to be coked which may be a topped or reduced crude oil may first be preheated in a heat exchanger such as heat exchanger 11 to insure proper flow, and then is carried by line 8 and mixed with a sufficient amount of hot coke particles from standpipe 7 to cause a substantial vaporization of the feed so as to form a suspension of coke particles and hydrocarbon vapors, the density of this dispersion being advantageously kept below 10 lbs./cu. ft. preferably within the range of about 0.1 to 2 lb./cu. ft. This mixture or dilute dispersion, is then passed through the high-temperature transfer line 12, immersed in the relatively dense layer of fluidized coke in combustion chamber 1. However, instead of causing vaporization of the feed by means of the heat content of the coke particles admixed to the feed, the vaporization may be caused at least in part by the heat exchange between conduit 12 and the combustion vessel 1. In this manner the resulting hydrocarbon vapors are maintained at a temperature of about 850 to 1200° F. or higher, preferably at about 900 to 1100° F. The contact time of the suspension in the transfer line 12 should be between $\frac{1}{2}$ second to 50 seconds, advantageously from 1 to 10 seconds, with the result that very little true coking takes place in this step. The mixture from line 12 containing cracked products from the less refractory feed fractions is then carried into separating means 13 which for purposes of illustration is assumed to be a cyclone separator. The vapor stream which may contain small amounts of coke particles is withdrawn from the separator means through line 14, to the heat exchanger 11 wherein the incoming feed may be conveniently used as the cooling medium. However, instead of the heat exchanger 11, it is also possible to cool the vapors by injecting cold fresh feed into line 14, the feed stock being withdrawn from the bottom of one of the fractionation towers and then introduced into line 8 for admixture with the hot coke. Finally, the products are transferred through line 15 to suitable recovery equipment which may be advantageously an atmospheric

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fractionation tower A followed by a vacuum distillation tower V. Thence the final distillate products are withdrawn. A substantial proportion of these products is very well suited as a catalytic cracking feed stock while another proportion consists of high octane gasoline. The bottom fraction obtained in the fractionation towers will normally contain a small amount of coke and may be used for fuel purposes or a portion of it may be recycled to the process for further treatment.

The hot coke particles are admixed to the feed in a sufficient proportion to avoid the formation of a separate liquid phase in conduit 12. In other words, the coke particles become coated by the more refractory high-boiling materials present in the feed during their passage through hot transfer line 12. The coke particles containing the unvaporized oil absorbed thereon separated in cyclone 13 are passed into coking vessel 16, which consists of an upper section 17 and a lower section 18. In this reactor the particles are maintained at a suitable reaction temperature above 850° F., preferably between 900° F. and 1200° F., as a dense fluidized mass having an upper level 19. The fluidized mass of coke particles continuously passes downwardly from section 17 into the lower stripping section 18. A gaseous stripping medium such as steam, nitrogen or carbon dioxide is introduced near the bottom of the stripping section 18 through nozzles 20. This stripping medium passes upwardly through the stripper and reactor at such a rate that the coke particles are maintained as a dense turbulent fluidized mass. The stripping medium also serves to sweep the hydrocarbon vapors formed in the reactor through separating means 21 and line 22 to line 14 where they merge with the vapors therein. In some cases it is of advantage to subject the vapors from the coking vessel to separate fractionation independently of the vapors formed during initial vaporization and cracking.

The unvaporized residue is caused to remain within the coking vessel 16 for a period sufficient to be converted into vapors and coke. To this end, the vessel should be of such size that the residence time of the coke particles and residue within the vessel may range from 1 to 10 minutes. For most residual stocks a period of from 1 to 3 minutes is sufficient to effect the desired conversion.

The coke particles separated in cyclone 21 are returned to the fluidized reactor bed through dip line 23 which preferably extends below particle level 19. After passing through the coking vessel 16, the coke particles, which consist essentially of the original coking particles mixed into the feed stock plus additional coke formed during the coking operation, are withdrawn from bottom of stripper section 18 through standpipe 24 provided with a control valve 25 adapted to regulate the rate of withdrawal of the coke particles therefrom. The particles withdrawn from standpipe 24 are picked up by a stream of oxygen-containing gas passing through line 3 and are thus carried back into combustion vessel 1 for further combustion to supply the necessary process heat as described previously. The flue gas resulting from the burning of the coke in vessel 1 is removed overhead through line 26, part of the flue gas being useful for recycling through line 3.

Since the coke produced from this process is usually more than enough to make up for the coke burned up for process heat, leg 27 containing a

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control valve 28 is provided through which the excess coke may be withdrawn from the system. This must be cooled before being withdrawn or it will burn on contact with air.

The unit illustrated in the drawing has the high temperature conduit 12 and coking vessel 16 within the combustion vessel 1. This arrangement is advantageous in that considerable heat loss is thus saved, especially when operating at extremely high temperatures. However, it is also practicable to operate a process according to the present invention using equipment where the conduit 12 and vessel 16 are located outside of the said combustion vessel and where all the necessary heat of reaction including heat losses to the atmosphere, is supplied exclusively by the coke particles which are mixed with the oil to be treated. Also, while the high temperature conduit 12 is shown discharging into cyclone 13 above the coking vessel 16, the conduit 12 may discharge directly into reactor vessel 16 above level 19 so that vapors from conduit 12 would pass through separator 21 together with the vapors formed in the reactor 16. Also, it will be readily understood that whereas the unit shown in the drawing discharges excess coke from the combustion chamber 1, this excess coke may be withdrawn from a different part of the system, for instance, from coking vessel 16.

In cases where it is desired to briquette the excess coke formed in the process, it is of advantage to withdraw the excess coke either from the upper portion of the coking vessel 16 or directly from the dip leg leading from the separator 13. This latter material will have a substantial quantity of tarry matter which may serve as a binder in forming the briquettes.

The particles of the circulated coke can be of a wide size range, for instance, 5 to 160 microns or even as large as 1/4" since the larger particles tend to break up into smaller ones by attrition or otherwise. The coke produced in the process is very desirable for many purposes in view of its very low ash content and may be prepared for marketing by briquetting or balling up the finely divided discharged particles in a rotary kiln using heavy pitch in a manner which is well known per se. With certain feed stocks it will also be found that the resulting coke will have a sufficiently low sulphur content to make the coke valuable in the production of carbon electrodes or metallurgical coke. This will be particularly true where extremely high temperatures substantially in excess of 1000° F. are used, which temperatures are unfavorable to the formation of stable carbon-sulphur components.

From the above description it is apparent that I have found a novel and efficient process for producing optimum yields of valuable distillate oils including catalytic cracking feed stocks and gasoline, and also a readily marketable high-grade coke from a cheap starting material. The specific description, however, is intended for purposes of illustration only and my invention is not to be limited to any specific embodiment presented herein.

I claim as my invention:

1. A process for the production of valuable products from heavy residual hydrocarbon oils which comprises contacting said heavy residual hydrocarbon oils with hot finely divided coke in an initial conversion zone at a temperature above 900° F. for a relatively short period to cause mild cracking and vaporization of the less refractory portions of the oils but for an insufficient time to

effect extensive coking of said oils, segregating and recovering the vapors from said initial conversion zone, passing the coke particles and unvaporized portion of said oils into a coking zone at a temperature of at least 850° F. and allowing said coke particles and unvaporized portion of the oil to remain in contact in said coking zone for a substantially longer period of time than the period of residence in the reaction zone and sufficient to convert said unvaporized portion of the oil into vapors and coke and withdrawing a stream of hydrocarbon vapors and relatively high grade coke from said coking zone.

2. A process for the production of valuable products from heavy residual hydrocarbon oils which comprises contacting said heavy residual hydrocarbon oils with hot finely divided coke in an initial conversion zone at a temperature above 900° F. and for a period of time between $\frac{1}{2}$ second to 50 seconds to cause mild cracking and vaporization of less refractory portions of the feed stock, segregating and recovering the vapors from the initial conversion zone, passing the coke particles and unvaporized portion of said oil into a coking zone at a temperature of at least 850° F. and allowing the oil to remain in contact with the coke for a period of time of from 1 to 10 minutes to convert said unvaporized portion of the oils into vapors and coke and withdrawing a stream of the vapors and a relatively high grade of coke from said coking zone.

3. A process for the production of valuable products from heavy residual hydrocarbon oils which comprises contacting said heavy residual hydrocarbon oils with hot finely divided coke in an initial conversion zone at a temperature above 900° F. and for a period of time of between 1 to 10 second to cause mild cracking and vaporization of less refractory portions of the feed stock, segregating and recovering the vapors from the initial conversion zone, passing the coke particles and unvaporized portion of said oil into a coking zone at a temperature of at least 850° F. and allowing the oil to remain in contact with the coke for a period of time of from 1 to 3 minutes to convert said unvaporized portion of the oils into vapors and coke and withdrawing a stream of the vapors and a relatively high grade of coke from said coking zone.

4. A process for the production of valuable products from heavy residual hydrocarbon oils which comprises contacting said residual hydrocarbon oils with finely divided coke for a relatively short period of time in an initial conversion zone at a temperature sufficient to effect a partial vaporization of the oil but for an insufficient time to effect extensive coking of said oil, segregating and recovering the vapors from said initial conversion zone, passing the coke particles and unvaporized portion of said oil into a coking zone at substantially the same temperature and allowing said coke particles and unvaporized portion of the oil to remain in contact in said coking zone for a substantially longer period of time than the period of residence in the reaction zone and sufficient to convert said unvaporized portion of the oil into vapors and coke and withdrawing a stream of hydrocarbon vapors and relatively high grade coke from said coking zone.

5. A process for converting heavy residual oils into coke and lower boiling products, comprising mixing the heavy oils with a sufficient quantity of hot finely divided coke particles to vaporize a substantial proportion of said oil, subjecting the resulting mixture to a relatively brief

period of treatment in a high temperature conversion zone to vaporize and convert a portion of the oil into lower boiling hydrocarbon compounds but insufficient to effect extensive coking, separating the mixture issuing from the said zone into a hydrocarbon vapor stream and a stream comprising coke particle and unvaporized oil, introducing the last named stream into a hot coking zone, passing a fluidizing gas upwardly through the coking zone at a rate controlled to maintain the coke particles as a dense, turbulent bed in the lower portion of said coking zone, maintaining the said bed at a temperature between 850 and 1200° F. for a substantially longer period of time until the said components become coked on the coke particles, and the particles become dry, withdrawing an overhead stream containing cracked vapors from the coking zone, quenching said cracked vapor stream and recovering valuable distillates therefrom, transferring the dry coke particles including the coke formed in the process from the coking zone to a combustion zone, passing an oxidizing gas upwardly through the combustion zone to maintain the coke particles as a dense fluidized burning mass in the lower portion of said combustion zone, removing a stream of hot coke particles from the combustion zone for admixture with additional heavy oil feed, withdrawing excess coke from the process subsequently to the coking of the said heavy components, and removing combustion gases as an overhead stream from the combustion zone.

6. A process for the production of gas oil and gasoline from a petroleum residue boiling substantially above the gas oil range which comprises charging finely divided coke particles into a combustion zone, passing an oxygen-containing gas upwardly through the combustion zone at a rate controlled to maintain the coke particles as a burning, dense, turbulent bed in the lower portion of said combustion zone, withdrawing a stream of combustion gases from the upper portion of the combustion zone, removing a stream of hot coke particles from the dense bed of the combustion zone and mixing them with a petroleum residue in a proportion sufficient to vaporize a substantial portion of the said fraction, passing the resulting mixture of coke and hydrocarbons through a confined high-temperature zone contained within the combustion zone at a rate to provide only a relatively brief period of residence and to avoid extensive coking, separating a vapor stream from the mixture issuing from the high-temperature zone, passing the said stream to a recovery zone and separating distillate product therefrom; also, separating from the mixture issuing from the high-temperature zone, a stream comprising coke particles and unvaporized residue and passing the last named stream downwardly through a coking zone which is maintained in indirect heat exchange relation with the combustion zone, passing a stripping gas upwardly through the coking zone in counter-current with the stream of coke particles whereby the particles are maintained as a hot, dense, turbulent moving bed within the said coking zone, maintaining the unvaporized residual oil in the hot coking zone for a substantially longer period of time than the period of residence in the confined high-temperature zone and for a time sufficient to convert said oil into vapors and coke, withdrawing an overhead vapor stream from the coking zone, passing the stream to a recovery zone and

separating distillate products therefrom; withdrawing stripped coke particles from the bottom of the coking zone and mixing them with additional oxygen-containing gas for further combustion in the combustion zone; and separately withdrawing a stream of excess coke from the combustion zone.

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