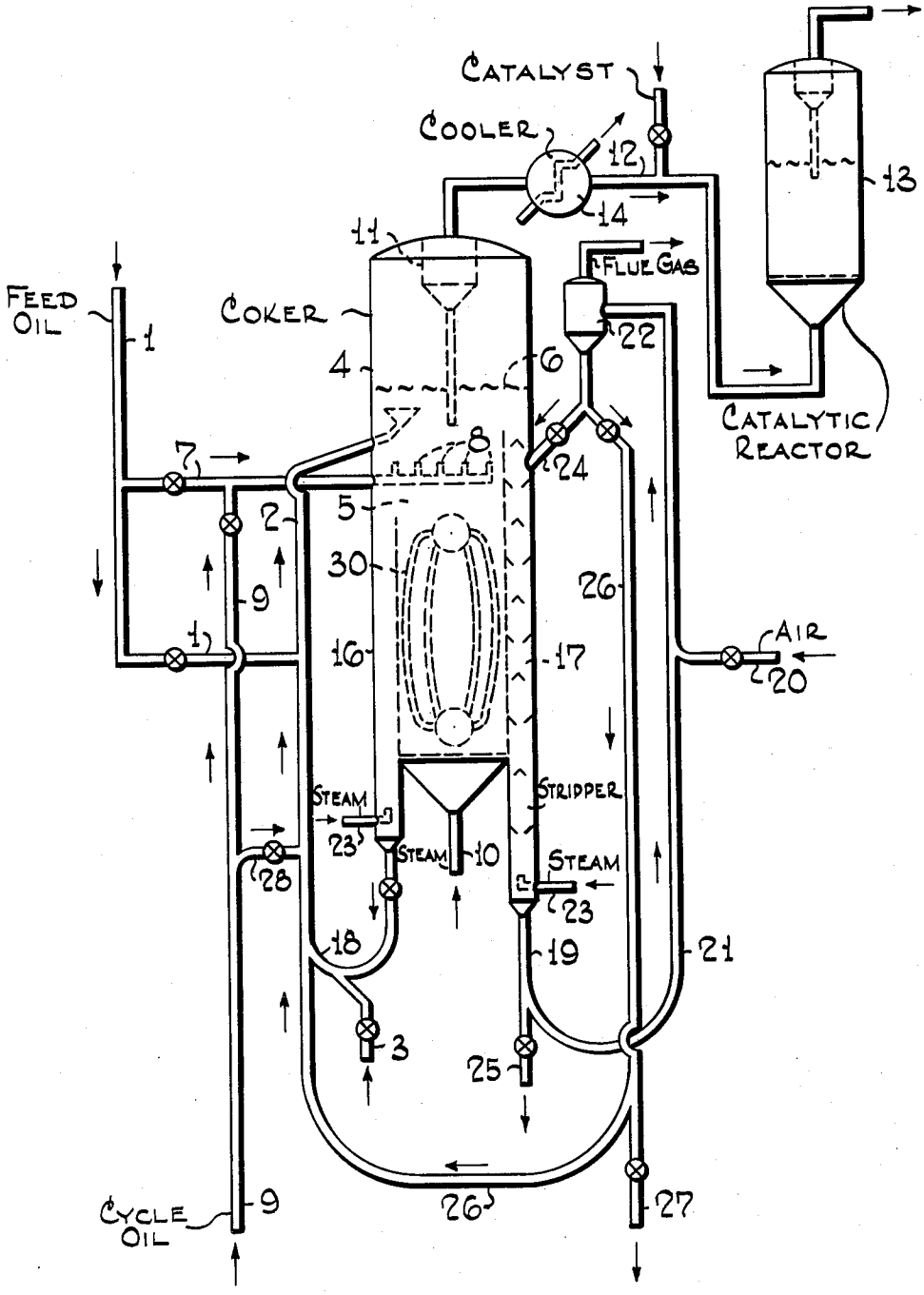
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CONVERSION OF HEAVY HYDROCARBONS

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James W. Brown Inventor

By Peter H. Smolka Attorney

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CONVERSION OF HEAVY HYDROCARBONS

James W. Brown, Elizabeth, N. J., assignor to Esso Research and Engineering Company, a corporation of Delaware

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3 Claims. (Cl. 196—49)

This invention relates to a process for the production of valuable distillates by partial evaporation and coking of heavy or residual hydrocarbons and by subsequent catalytic cracking of the vaporized products. More specifically the invention relates to a combination process wherein a vapor fraction suitable as a catalytic cracking feed stock is obtained by briefly contacting a residual oil with a hot medium under conditions conducive to minimizing any thermal cracking, wherein the resulting vapors are promptly passed to a catalytic cracking zone before they become substantially degraded by undesirable polymerization reactions or by thermal cracking, and additional amounts of distillate are obtained from the unvaporized portion of the feed oil as well as from any recycle stock by "drying" or coking in a dense fluidized bed of finely divided solids.

Continually increasing demand for distillates such as high quality gasoline and gas oil has stimulated efforts toward adapting relatively undesirable heavy residue such as topped or reduced crude or various analogous pitches for eventual use in catalytic cracking processes. Because of the excessive carbon forming tendencies and contamination of catalyst by ash in these materials, their direct use in catalytic processes has proved impractical. Accordingly, efforts to utilize these materials have largely consisted of segregating therefrom thermal gasoline and relatively light gas oil fractions by various applications of vacuum flashing or coking or both, only the gas oils being considered as satisfactory feeds for catalytic conversion. However, conventional vacuum flashing has been only moderately successful to date since at the usual vacuum still bottoms temperatures of about 700° F. the yield of low value bottoms product is quite high, whereas at higher distillation temperatures the problem of maintaining a satisfactory vacuum becomes most difficult. Moreover, such high temperature distillate products have been found to be of substantially poorer quality because of fairly extensive thermal cracking which unavoidably occurs during conventional high temperature distillation.

The various techniques previously proposed for the conversion of residual oils by coking also have left much to be desired. For instance, coking at about 950° F. has been found to produce a fairly desirable feed stock for catalytic cracking, but the rate of reaction is very slow so that it is necessary to provide large, costly reactor vessels and, where the usual fluid solids technique is employed, a large solids hold up for fluidization is also required and occasional fluidization difficulties may be encountered. On the other hand, when higher coking temperatures such as 1100° F. are employed so as to obtain an increased rate of reaction, difficulties are encountered in devising a practical method for removing the resulting vapors from the coking zone before they become degraded by various after-reactions. Specifically, it has been determined that an excellent feed stock for catalytic cracking can be obtained by coking residual oils at 1100° F. in a fluid bed, if the vaporized feed is

removed from the fluid bed and quenched, and preferably introduced in less than one second into the catalytic cracking zone. However, it is apparent that this is not feasible in conventional operation with deep fluidized beds which by their very nature hold a considerable amount of the vapors for 3 to 15 or more seconds in a dilute phase above the bed before the vapors are disengaged and withdrawn. This dilute phase is incorporated in the usual fluid bed reactor to decrease entrainment of powdered solids in the gaseous reaction products.

It has also been proposed previously to minimize undesirable thermal cracking in the conversion of residual oils by employing a two step process wherein the feed is first subjected to high temperature for a brief period, followed by separation of vapors and further coking of the unvaporized portion of the feed, all vapors being finally fractionated to yield the desired distillate fractions such as thermal gasoline and gas oil for use as a catalytic cracking feed stock. However, even this process has had certain shortcomings since the resulting products, and especially the catalytic cracking feed stocks, have been found to degrade appreciably not only during distillation but even on standing at room temperature.

An improvement of the foregoing techniques has been obtained in a process wherein the heavy feed stock is partially vaporized by heating for a period of less than about 1 second, followed by separation of the vapors and the prompt passage of substantially all the vapors, under conditions minimizing thermal cracking thereof, to a catalytic cracking zone, while the unvaporized portion of the feed is thermally coked in a dense fluid bed as described in a copending application of H. Z. Martin et al., Ser. No. 244,968, filed September 4, 1951. But even in that case success was somewhat limited because in large commercial units the recognized object of passing the evaporated feed portion to the catalytic zone under conditions minimizing thermal cracking has proved difficult of attainment. This has been so largely because vapor residence time in a commercial cyclone usually ranges from 0.5 to 1.0 or more seconds, so that a substantial amount of thermal cracking seemed unavoidably to occur during the time when the hot evaporated feed was being separated from the unvaporized portion in the conventional cycle or the like, and before it was practical to quench the vapors or inject cracking catalyst into them or take any other positive step designed to minimize thermal cracking. Furthermore, the unvaporized feed remaining on the separated solids must be carried from the cyclone to the fluid "drier" vessel, the minimum time involved being at least 5 seconds at the temperature of the transfer line vaporizer. Consequently, valuable distillate fractions produced by thermal cracking of the unvaporized feed eventually tend to be partially destroyed or degraded by overcracking or by excessive vapor holding time before they can be removed and recovered.

Rapid quenching by injecting water or the like into the entire mixture of inert solids and vaporized and unvaporized feed portions for the purpose of stopping the reaction and preventing undesirable thermal conversion of the liberated vapors prior to their separation from the unvaporized portion has been found impractical since this would entail an excessive heat load in view of the high ratio of solids-to-pitch normally required in the vaporizing zone. Also, because of the heat load involved in this relatively high solids-to-oil ratio required in most of the other systems, it has been difficult to operate the fluid coking zone at a lower temperature than that of the transfer line vaporizer, though the desirability of such lower coking temperatures was recognized.

It is the object of this invention to avoid the various foregoing difficulties. To accomplish this, the present invention takes advantage of the high reaction rates ob-

tainable in a high-temperature, short-residence transfer line vaporizer and of the longer allowable disengaging times in a subsequent low-temperature fluid coking bed. This particular combination thus utilizes the best features of each step in a single process.

In particular it has been found that by operating a transfer line vaporizer at a temperature of at least 1050° F., or preferably between 1075 and 1150° F., and a fluid bed coker at temperature below 1000° F., preferably between 925 to 975° F., it is possible to minimize thermal cracking of the vapors liberated in the transfer line by introducing the entire contents of the transfer line into the relatively colder fluid bed where the liberated vapors get quenched below 1000° F., thereby greatly reducing the chance for undesirable thermal cracking thereof prior to eventual introduction into a catalytic cracking zone. Thus a substantial portion of the feed is converted to vapor before the fluid bed is reached so that a smaller holdup of feed and fluidizing solids is required for completion of the reaction as compared to a case where the fresh feed is introduced directly into the fluid bed at a temperature below 1000° F. It also appears that a surprisingly small part of the vapors from the transfer line is condensed upon introduction into the relatively cold coker bed, partly because of the vaporizing effect of the vapors rising through the fluid bed. Furthermore, if the transfer line contents are introduced into the coker relatively near to the upper level of the dense fluid bed, e. g. not more than about 1 to 3 feet below the bed level, the vapors may become supercooled below their normal condensation point without actually precipitating, and the cooled vapors can accordingly be withdrawn from the coker for further processing. Thus the desirable result is obtained that a maximum portion of the original feed is vaporized and available for the conversion into high quality products by catalytic cracking, with only a minimum of incidental thermal cracking which generally produces inferior products.

The required temperature difference between transfer line vaporizer and the coker can be conveniently obtained by introducing only a part of the feed into the vaporizer and introducing another part directly into the coker. Alternatively, all feed can be introduced into the transfer line and the fluid bed can be kept at the required lower temperature by other means, as by immersing a water boiler therein, or by indirect heat exchange with incoming feed or with other cold streams, or by direct injecting of cool cycle stock or by water injection. Substantially all hydrocarbon vapors, including the heaviest ends liberated in the process are withdrawn from the coker whereupon some cracking catalyst may be injected into them to prevent undesirable thermal cracking to occur during their passage to the catalytic cracking unit, or the withdrawn vapors may be cooled further to minimize thermal cracking and also to condense out any steam prior to the catalytic cracking unit.

To facilitate better understanding, one exemplary embodiment of the invention is hereafter described in detail with reference to the accompanying drawing, though it will be understood that the scope of the claimed invention is not specifically limited thereto, but includes various modifications thereof which may be thought of by persons skilled in the art.

Referring now particularly to the system illustrated in the drawing, pitch feed such as an 8% vacuum bottoms fraction of a West Texas crude, preferably preheated to about 700 or 800° F. in any convenient manner, is introduced through feed line 1 into transfer line vaporizer 2 where it is mixed with finely divided petroleum coke having a temperature of about 1260° F. or with other hot inert solids in a solids/oil weight ratio of about 2/1 to 10/1, preferably 6/1.

The feed is thus heated to about 1100° F. and partially vaporized on passage through vaporizer 2, but since the residence time in the vaporizer is kept short, preferably less than 1 second, no appreciable cracking of the resulting vapors takes place despite the relatively high temperature. From vaporizer 2 the mixture containing coke and unvaporized pitch suspended in hydrocarbon vapors, plus any steam or other inert gas which may be introduced through line 3 for controlling contact time and density of the suspension in line 2, is passed directly into relatively cooler coking vessel 4 where the mixture is rapidly quenched to about 950° F. This quenching is readily obtained in the coking vessel 4 by virtue of the large heat capacity of the dense, turbulent, fluid bed 5 having an upper level 6 and maintained therein at the required temperature of about 950° F.

The unvaporized portion of feed introduced into fluidized coke bed 5 in admixture with the coke solids from hot line 2 is kept in the fluidized coke bed for an average residence time of about 5 minutes, whereby it is thermally converted into a catalytic feed stock which is of much better quality than if the long-residence bed 5 were kept at a relatively high temperature such as that in line 2.

A convenient way of cooling the fluidized bed 5 to the required temperature is to introduce a portion such as 10 to 50 weight percent of the total pitch feed through branch feed line 7 and spray nozzles 8 into vessel 4, the proportion of feed introduced in this manner depending on the feed temperature and the desired quench temperature. Alternatively, the required cooling may be obtained by means of water boiler 30 which is shown immersed in the fluid bed or by introducing clarified bottoms obtained by fractionation of catalytically cracked product or some other relatively cool hydrocarbon stream which may be brought in through line 9 and spray nozzles 8. Still another way of cooling the fluidized bed may involve injecting low-temperature steam or even liquid water through steam line 10, whereby steam required for proper fluidization of the coke bed can be produced directly in the coking vessel 4.

After cooling in fluidized bed 5, the feed vapors produced in line 2 and additional vapors produced in bed 5 by vaporization of feed directly injected from nozzles 8, as well as vapors resulting from the coking or thermal cracking of the unvaporized feed portion are removed from vessel 4 through a dust separating device such as cyclone 11 and passed through line 12 to further processing, particularly to a catalytic cracking unit 13, which is preferably of the so-called "fluid" type. Preferably, the vapors in line 12 are further quenched by cooler 14 to about 700° F. immediately after leaving cyclone 11 so as further to minimize undesirable thermal cracking of the vapors during their passage to the catalytic reactor.

Solids containing a deposit of incompletely converted feed or low-temperature coke are continuously removed from fluidized bed 5 through internal stripping wells 16 and 17 into which a stripping gas such as steam is introduced through lines 23, or through equivalent external strippers. Stripper 16 may be quite a simple device since its main function is to keep hydrocarbon vapors from being returned with the circulating solids from the fluid bed 5 to the high temperature transfer line 2 where they might degrade. The stripped low-temperature solids from stripper 16 are then returned via line 18 to the relatively hot transfer line 2 in order to complete the coking of any unconverted feed deposited on the solids.

The other stripper, 17, is preferably a more elaborate unit adapted to be operated at higher temperatures than the adjoining fluid bed 5, e. g. at 1050 to 1150° F. In this manner losses of unconverted feed in the burner section hereafter described are minimized, since any hydrocarbon residue deposited on the solids circulating through stripper 17 is substantially completely coked and stripped out before the solids are carried into the burner section. The stripped coked solids are removed from stripper 17 through standpipe 19 into transfer line burner 21 where at least a part of the coke produced in the process is burned by means of an oxygen-containing gas such as

air admitted through line 20. Consequently, the unconsumed solids are raised to a temperature of about 1350 or 1500° F. or higher, and are then used to supply the heat required for continued operation of the process.

For instance, after separation from the resulting flue gases in dust separator 22, the heated solids may be returned to stripper 17 through line 24 as previously mentioned. Dry net coke product may be withdrawn from the process either below the stripper through leg 25 or, especially where a coke product of low volatile content is desired, hot coke may be withdrawn after passage through heater 21, e. g. through lines 26 and 27.

The major part of the hot solids separated in cyclone 22 is returned via line 26 to hot transfer line 2. There it serves to supply the required heat of vaporization to the circulating solids from stripper 16 as well as the various liquid feed streams such as refractory cycle oil introduced through line 28 and residual feed introduced through line 1. In this connection it may be noted that by introducing the refractory cycle stocks through lines 18 and 28 and by introducing the less refractory residual oil separately through line 1, the residence time of the several streams in the hot transfer line 2 can be adjusted in accordance with their individual requirements. Thus the residual oil may be only partially vaporized in the hot transfer line 2 with only a minimum of incidental thermal cracking, while the more refractory cycle stock may be cracked more severely due to its longer residence time in the high temperature zone.

It will be understood that the foregoing specific description has been given for purposes of illustration rather than limitation. Stated more generally, the invention is broadly applicable to heavy hydrocarbons unsuited for direct feeding to catalytic cracking units because of excessive carbon formation and/or other catalyst contaminating characteristics. Accordingly, the feed stock may be a whole crude, or a reduced crude petroleum residue obtained by atmospheric or vacuum distillation and may represent the bottom 2 to 25 volume percent of the virgin crude distilled, or it may be a tar from visbreaking operations or similar tars or pitches. Prior to feeding into the vaporizing zone of the process, such heavy feed stock usually may be preheated to temperatures ranging between 200 and 900° F., preferably 600 to 800° F., and their viscosity may be further reduced by dilution with minor amounts of naphtha or other relatively light hydrocarbons.

The linear gas velocities at the outlet of the vaporizing transfer line 2 and in the burner transfer line 21 may be between about 10 and 100 feet per second, and the apparent density of the mixtures or suspensions at the outlet of such transfer lines may range between about 0.2 to 2 pounds per cubic foot, though at the inlet of line 2 the density may be as high as 40 pounds per cubic foot, before extensive vaporization of the feed has taken place. The residence time of the residuum feed in transfer line 2 may range from 0.1 to 3 seconds, times of less than one second being preferred at temperatures 1100 to 1150° F. or higher, whereas residence times of up to 2 or 3 seconds may be useful at temperatures such as 1050° F. or lower.

In the coking vessel the conditions are those characteristic of the maintenance of a dense, turbulent, fluidized bed, that is, the linear gas velocity may range between about 0.5 to 5, preferably 2 to 3 feet per second, and the apparent density of the dense fluidized bed 5 may range between about 10 and 50 pounds per cubic foot, with a more dilute phase thereabove. The average residence time of the liquid feed in the coking vessel may range from about 1 to 150 minutes depending on temperature and the refractory nature of the feed stock.

The inert contact solids used in the coking vessels, and in the vaporizing lines where indicated, preferably are finely divided particles of petroleum coke whose diameter may range up to about 500 microns, preferably between 100 and 300 microns. Instead of coke, however, finely divided inorganic inerts such as sand, spent clays, pumice and the like may be used similarly, except that in such cases it will be preferable to burn all the coke produced in the process and use any resulting excess heat for steam generation or the like, whereas in the case of petroleum coke a high-quality net coke product may be readily recovered in substantially pure form. The ratio of unvaporized feed to solids in the coking vessels is maintained sufficiently low to allow proper fluidization, desirable ratios being preferably not in excess of about 1 wt./wt./hr. at about 900° F. coking temperatures, or 3 wt./wt./hr. at 1000° F. coking temperatures.

Where a catalytic cracking zone of the fluid type is used for converting the distillate stock produced in the vaporizing and coking portions of the described system, the velocity and density conditions prevailing in the catalytic zone are also substantially within the same range as those described above with respect to the coking vessels, as is well known per se. Moreover, despite the fact that the feed introduced into the catalytic cracking zone contains a very substantial proportion of constituents boiling well above the usual gas oil range, the temperature conditions are essentially the same as those used in conventional gas oil cracking, i. e., between about 800 and 1000° F. The catalyst used in the catalytic cracking zones may be any conventional cracking catalyst such as activated clay, activated alumina, synthetic composites of silica with a minor proportion of alumina, magnesia or boria, and so on. Where some fresh feed is introduced directly into the fluid coking zone 4 as previously described, the weight ratio of such feed to fresh feed introduced into the transfer line 2 is preferably not more than 1:1 or 1:2 or as small as the quenching requirements permit. Of course, enough heat may be removed from the fluid coker 4 by means of boiler 30 so that no fresh feed needs to be fed to the coker.

Moreover, the physical arrangement specifically described herein may be changed or modified by those skilled in the art without departing from the claimed invention. For instance, while a catalytic cracking unit employing the so-called "fluid solid" technique has been described, other types of conventional catalytic cracking units such as fixed bed or moving bed units may be employed similarly. Likewise, the transfer line heater described above for burning some of the process coke so as to generate the heat required for operation of the process may be replaced by other more or less analogous heaters such as a unit wherein the coke is burned while the solids are in the form of a dense, fluidized bed; or hot flue gas may be used for bringing the process solids to the desired temperature, or heat may be supplied by direct or indirect heat exchange with regenerated catalyst as described in copending patent applications Ser. No. 227,169, filed May 19, 1951, and Ser. No. 230,746, filed June 9, 1951, now Patent No. 2,655,464.

Finally, whenever volatization of liquid hydrocarbon feed has been referred to herein simply as "vaporization" and the resulting hydrocarbon vapors have been referred to as "vaporized feed" or the like, it will be understood that at the temperatures employed such vaporization is necessarily accompanied by some mild cracking or coking, and that consequently the resulting vaporized feed contains not only evaporated feed constituents but some cracked products as well.

Having given a full description of the invention and of the manner of using it, the invention is particularly pointed out and distinctly claimed in the appended claims.

I claim:

1. A process for converting a heavy hydrocarbon feed stock into lighter products which comprises mixing finely divided coke heated to about 1200 to 1300° F. with the feed stock preheated to about 600 to 800° F. to form a dilute suspension having a relatively high temperature between about 1075° and 1150° F., passing the hot suspension through a narrowly confined, elongated vaporizing zone so as partially to vaporize the feed during a

residence time not in excess of 1 second at the aforesaid relatively high temperature, thereafter passing the hot suspension of feed vapors, unvaporized feed and coke directly into a dense bed of finely subdivided coke at a point near the upper level thereof and within about 3 feet below the upper level of said bed maintained in the lower part of a coking zone, passing an inert gas upwardly through said bed at a velocity controlled to maintain said bed in dense fluidized condition, also introducing a relatively cool hydrocarbon stream into said bed so as to maintain the coking zone at a relatively low temperature between about 925° and 975° F. whereby the dilute suspension from the vaporizing zone is rapidly quenched without substantial condensation to minimize thermal cracking thereof, withdrawing disengaged vapors from an upper portion of the coking zone, passing the withdrawn vapors through a catalytic cracking zone under catalytic conversion conditions, and recovering desired products from the catalytic cracking zone; withdrawing oil-carrying coke from the dense fluidized bed after an average residence time therein of about 5 minutes, reheating a portion of the withdrawn oil-carrying coke to about 1050–1100° F. in a drying zone by mixing it with hot dry solids heated to at least 1250 to 1500° F. and thus drying the withdrawn coke, removing a stream of dry coke mixture from the drying zone and partially burning the removed coke in a heating zone to obtain hot dry solids having a temperature between about 1250 and 1500° F. for mixing with the aforesaid wet coke to be dried, and recycling a stream of hot dry solids from the heating zone for mixing with fresh feed in the vaporizing zone.

2. A process according to claim 1 wherein the oil-carrying coke is stripped with an inert gas in the drying zone at about 1050 to 1100° F. prior to withdrawal to the heating zone and wherein the hydrocarbon vapors liberated in the drying zone are combined with the other vapors in the coking zone prior to withdrawal to the catalytic cracking zone.

3. A process for converting a heavy hydrocarbon feed stock into lighter products which comprises mixing finely divided inert solids heated to a temperature in the range of 1150° F. to 1500° F. with the feed stock in a ratio sufficient to form a dilute suspension having a relatively high temperature between about 1075° F. and 1150° F., passing the hot suspension through a narrowly confined, elongated vaporizing zone so as to partially vaporize the feed during a residence time not in excess of 5 seconds at the aforesaid relatively high temperature, thereafter passing the hot suspension of feed vapors, unvaporized feed and inert solids directly into a dense bed of finely divided fluidized coke at a point near the upper level thereof and within about three feet below the upper level of said coke bed maintained in the lower part of a coking zone at a temperature between about 925 F. to 975° F. and thereby quenching the suspension to the relatively lower temperature substantially without any condensation of the vapors so as to minimize thermal cracking thereof, further coking the unvaporized feed in the coking zone, withdrawing from the coking zone the hydrocarbon vapors produced in the vaporizing and coking zones, withdrawing coked solids downwardly from the dense bed of the coking zone, heating the withdrawn solids to a temperature of at least 1150° F. and recycling the heated solids for mixing with fresh hydrocarbon feed stock.

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