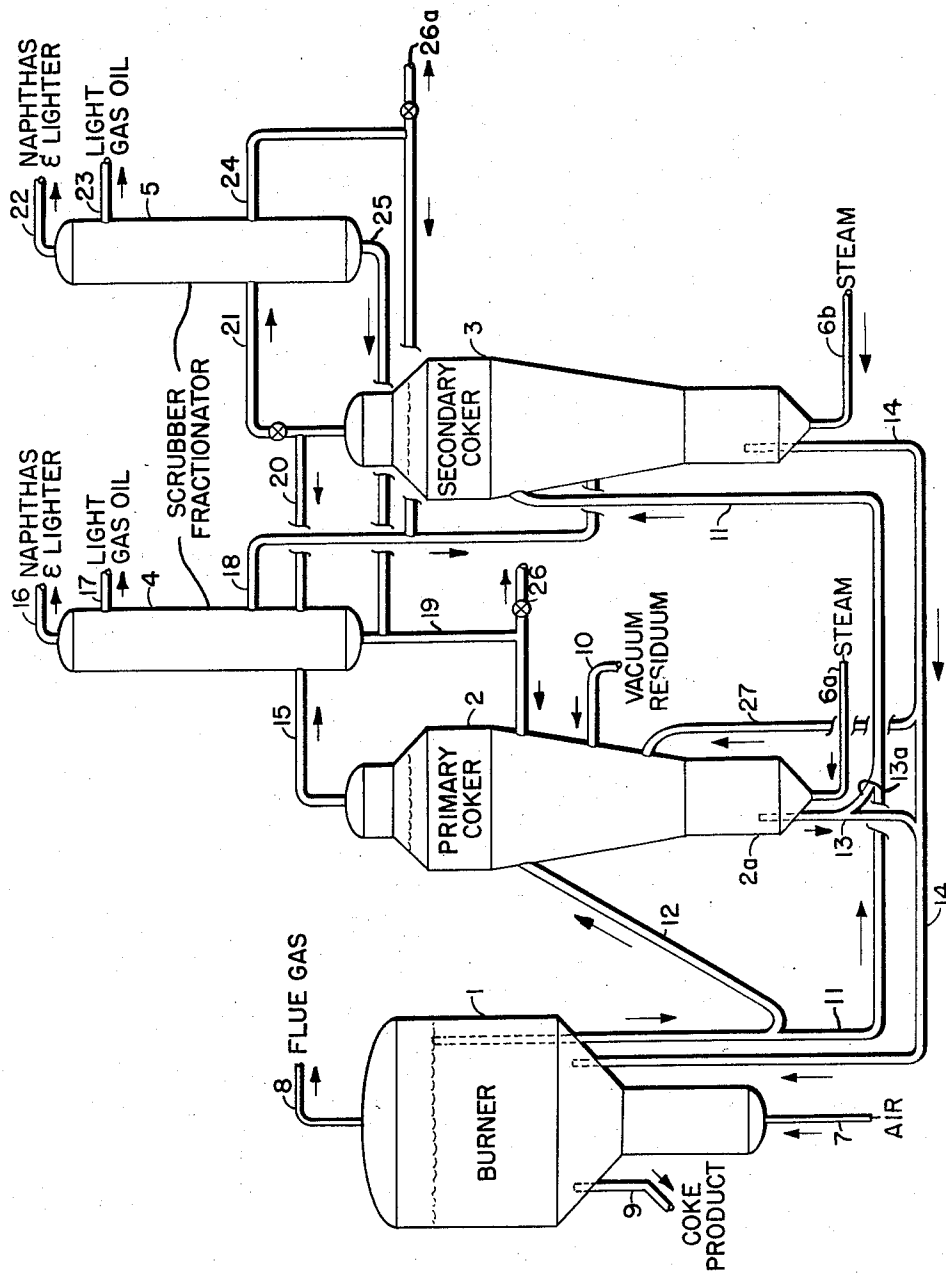


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FLUID COKING PROCESS

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3 Claims. (Cl. 196—49)

This invention relates to the upgrading of hydrocarbon oils including petroleum oils, shale oils and coal oils. More particularly, it pertains to a two-zone or a two-stage process for coking petroleum oils such as whole crudes, distillate or residual fractions therefrom, or mixtures thereof. This invention has particular applicability to heavy petroleum oil upgrading processes when it is necessary by reason of the character of the oil, market conditions, etc. to produce products having a low end boiling point.

Recently it has been proposed to coke hydrocarbon oils such as petroleum residua by injecting them into a coking vessel containing a fluidized bed of high temperature finely divided solids, e. g., coke produced by the process, sand, spent catalyst and the like. In the coking vessel, the oil undergoes pyrolysis in the fluidized bed, evolving lighter hydrocarbons and depositing carbonaceous residue on the solid particles. The necessary heat for the pyrolysis is supplied by circulating a stream of the fluidized solids through an external heater, generally a combustion zone, and back to the coking vessel. This fluid coking process is more fully depicted in co-pending application, entitled "Fluid Coking of Heavy Hydrocarbons and Apparatus Therefor," Serial No. 375,088, filed August 19, 1953, by Pfeiffer et al.

In conventional fluid coking processes, the overhead products boil up to around 1100° F. and normally show high ash and Conradson carbon content. The products boiling above about 1000° F. may be recycled to the coker to improve the 1000° F. gas oil, but the resulting gas oil is still around 2% Conradson carbon and of borderline quality in ash and nitrogen content. To secure a good catalytic cracking gas oil, it is sometimes necessary to reduce the end point of the gas oil to about 700° F. to avoid catalyst contaminants and to recycle the heavy gas oil to the coking zone, but to do so causes the recycle rate to become prohibitively high.

Also, in some instances it is desirable or necessary to make products boiling entirely below about 700° F., particularly when the coker feed stock is highly aromatic or high in nitrogen content such that even the light gas oil from the coker is of exceptionally low value as feed for catalytic cracking.

In many cases when a low end point product is desired, the feed to a fluid coking vessel will of necessity be a long residuum because of prior processing limitations, market demands, etc. and will contain an appreciable amount of heavy, say 700° to 1000° F. virgin gas oil. Consequently, the total amount of heavy gas oil recycle which must be converted to light gas oils will be quite large. A fluid coker normally is operated at about 950° F. when middle distillates are desired as the principal products. If the heavy gas oil is recycled to the fluid coker, it will be converted at this temperature predominantly in the vapor phase and will be severely degraded to gas because of the relatively high vapor cracking intensity and because of the high recycle rate.

It is an object of the present invention to make pos-

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sible the production of maximum quantities of naphtha and middle distillates from a petroleum oil, particularly from a high boiling residual oil, by coking the oil by fluidized solids technique at relatively mild severities while avoiding the necessity of using high recycle rates of the higher boiling constituents in the coker overhead products.

This invention involves coking of an oil in a conventional fluid bed coking vessel at conventional temperatures, e. g., 800° to 1600° F. at severities to obtain 700° F.+ conversions in the range of 20 to 70%. 700° F.+ conversion is defined as: 100 volume percent feed minus products boiling above 700° F. The effluent from the coker is separated to obtain lower boiling products, e. g., naphtha, light gas oil; a heavy gas oil boiling in the range of about 700° to 1000° F.; and bottoms. The heavy gas oil is then subjected to relatively mild thermal cracking conditions at relatively low temperatures, e. g., 600° to 850° F., to obtain further quantities of lower boiling products. The above-referred-to bottoms are recycled to the coker substantially to extinction.

Preferably the second thermal cracking zone utilizes the fluidized solids technique and uses the same particulate solids as is used in the first coking zone. As alternatives, however, the process of this invention may be carried out using a delayed coking arrangement or hydrogen donor diluent cracking unit as the second thermal cracking zone. The conditions are adjusted in the second cracking zone to attain, as compared to the first zone, relatively mild vapor cracking severities.

Because of the relatively mild temperature used in the second zone, the conversion of the heavy gas oil takes place predominantly in the liquid phase and the vapor phase cracking intensity is greatly reduced or eliminated; as a result, the yield and quality of the products are increased.

Thus it can be seen that the heavy gas oil from the first coking zone that boils just beyond the end boiling point of the desired product hydrocarbons is not unduly cracked or too severely degraded. Consequently the quality and yield of the final products are greatly increased.

Another object of this invention is to devise a two-stage hydrocarbon oil coking process whereby a maximum yield of hydrocarbons boiling below an end boiling point in the range of 600° to 950° F., preferably 700° F., is attained.

Other objects and advantages will appear as this description proceeds and the attached drawing, forming a part of the specification, is discussed in detail. The attached drawing depicts diagrammatically a preferred embodiment of this invention applied to the upgrading of a heavy vacuum residuum. A fluidized solid system is used with particulate petroleum coke produced by the process as the heat-carrying contact solid.

The major items of equipment shown in the drawing are a fluid bed combustion vessel 1, a primary coker 2 containing a bed of fluidized particulate coke, a secondary coking vessel 3, also containing a fluidized bed of particulate coke and separator means or scrubber-fractionators 4 and 5 used to process the effluent vapors. The fluidized beds are maintained in the coking and combustion vessels in a manner well known in the art. Steam, light hydrocarbon gases, etc. are admitted to the base of the coking vessels by lines 6a and 6b in amounts sufficient to attain superficial fluidizing gas velocities in the range of 0.2 to 5 feet per second. Air or other free oxygen-containing gas is admitted by line 7 to the burner or combustion vessel 1 to fluidize the coke contained therein and to support a partial combustion of the coke whereby the coke is maintained at a temperature in the burner in the range of 1000° to 1800° F. preferably 1050° to 1200° F.

In this example, a portion of the coke produced by the process is burned to generate heat. Broadly, however, any suitable means of supplying heat may be used. A transfer line burner or gravitating bed burner will, in most applications, be equally satisfactory. Another alternative can be the use of an inert, substantially heavier and/or denser, heat-carrying medium, e. g., "shot," and this heavier medium can be used to transfer heat to the coke in a separate zone or may be circulated through the coking system. Further, when the value of other liquid, solid or gaseous fuels is less than the value of the coke produced by the process then they may be used as a source of heat, either by direct or indirect heat exchange means.

As illustrated, the air supplied to the burner passes upwardly through the particulate coke fluidizing it and the flue gases generated during the combustion are removed overhead by line 8. The net coke produced by the process is removed by line 9 from the burner as product.

Because the fluidized solids technique is used, it is preferable to maintain a select size distribution of the contact solids to obtain optimum performance. It is preferred to use coke having a particle size in the range of 40 to 500 microns with a median particle size in the range of 200 to 300 microns. The coke particle size may, however, vary from 0 to 1000 microns or more.

The oil to be upgraded, such as a vacuum residuum, is injected into the primary coker at a plurality of points, one of which is shown by line 10. The coke is maintained in the primary coker at a temperature in the range of 900° to 1600° F., preferably from 950° to 1200° F. The injected oil upon contacting the coke undergoes pyrolysis depositing carbonaceous residue on the coke and evolving considerable quantities of relatively lighter hydrocarbon vapors. Heat for the pyrolysis is supplied to the coker by particulate coke transferred from the burner via line 12. The amount of coke circulated to the primary coker will normally be in the range of 5 to 20 lbs. per pound of fresh oil injected into the coker. Coke is circulated from the base of the coker by line 13, after having been stripped in stripping zone 2a by the fluidizing steam, to the burner for reheating.

The effluent from the primary coker, after having entrained solids removed, is transferred by line 15 to the scrubber-fractionator 4. The extent of the separation made at this point may be varied. As shown, naphthas and lighter vapors are removed overhead by line 16 as product. A light gas oil boiling in the range of about 430° to 700° F. is removed by line 17 as product. This end point can, of course, be varied, say from 600° to 950° F., to meet the demands of particular processes. The materials withdrawn as products can be subjected to further processing or finishing techniques such as hydroforming, clay treating, hydrodesulfurization, blending, catalytic cracking, etc.

A heavy gas oil, boiling above the end point of the light gas oil, is transferred to the secondary thermal cracking zone by line 18 and because it is a distillate will be a relatively clean stock. The bottoms from the scrubber-fractionator 4, which may have initial boiling point in the range of 900° to 1150° F., preferably 1015° F., is recycled to the primary coker by line 19 to be treated therein to extinction. It is to be appreciated that by removing the bottoms, which have a high Conradson carbon content, from the heavy gas oil to be treated in the secondary cracking zone certain advantages are obtained. If these bottoms are charged along with the heavy gas oil to the secondary coker, particle agglomeration and bogging of the bed will occur.

The secondary thermal cracking or coking zone is operated in a manner similar to that of the primary coking zone. Heat-carrying particulate coke is supplied to the secondary zone by line 11 and coke is removed

and transferred to the burner 1 from the secondary coker by line 14. The amount of coke circulated to the secondary coker will be substantially less than that circulated to the primary coker as the operating temperature of the secondary coker is substantially less. Normally 1 to 10 lbs. of coke per pound of heavy gas oil injected into the secondary coker is circulated. The heavy gas oil will normally be injected into the coker in amounts in the range of 0.1 to 3 lbs. per pound of fluidized coke contained therein.

The secondary coking zone operates at a temperature in the range of 600° to 850° F., preferably in the range of 700° to 800° F. and consequently predominantly all of the heavy gas oil will remain as a liquid on particulate coke until it is cracked. The secondary coker can be operated under mild pressures, say from 0 to 50 p. s. i. a., so as to maintain the gas oil as a liquid and to enhance liquid phase cracking conditions. Because of the milder conditions prevailing, the heavy gas oil will have a substantially longer residence time in the secondary zone as compared to the oil injected into the primary coker. Conditions are maintained in the secondary coker to attain 50 to 100% 700° F.+ conversion.

After entrained solids are removed, the cracked vapors issuing from the secondary coker are transferred (in the simplest arrangement of this invention) by line 20 to scrubber-fractionator 4 to be separated therein. Alternatively these vapors may be transferred by line 21 to a second scrubber-fractionator 5 to avoid commingling of the products from the respective cokers. If so, naphthas and lighter gases can be removed from fractionator 5 by line 22 and middle distillates by line 23. The heavy gas oil is recycled by line 24 to the secondary coker and the high boiling bottoms are recycled by line 25 to the primary coker.

It is desirable, when processing certain types of oils, to bleed a portion of the recycled bottoms to prevent buildup of excessive amounts of contaminants or refractory constituents in the recycled stream. This can be done by line 26, or 26a if it is desired to bleed off some 700° to 1015° F. material.

Alternative modes of operation of the present invention will be apparent to those skilled in the art. For example, coke from the primary coker may be transferred to the secondary coker by lines 13a and 11 to supply heat thereto. This will obviate the necessity of stripping the coke removed from the primary coker to avoid loss of valuable hydrocarbons during the combustion process. Conversely, coke may be removed from the secondary coker and transferred to the primary coker by lines 14 and 27, and this will remove the need for stripping coke removed from the secondary coker. This latter mode of operation is particularly advantageous when the secondary coker is operated under pressure as the most refractory unconverted liquid oil still adhering to the particulate coke in the secondary coker would be transferred along with the coke to the higher severity primary coker wherein it would be completely converted.

The following example will typify the advantage secured by the process of this invention when processing the feed stock indicated. The primary fluid bed coker is operated at a temperature of 950° F. with a 700° F.+ conversion of 45% and the secondary fluid bed coker is operated at a temperature of 700° F. with a 700° F.+ conversion of 100%.

Feed stock-----	Bashaquero residuum.
Inspections-----	700° F.+ boiling range, 9.5° API gravity, 10 wt. per- cent Conradson carbon.

The results are shown in Example 1 when the 700° F. to 1015° F. products from the primary coker were processed in the secondary coker. Example 2 illustrates the products attained from the same feed stock using a con-

ventional one-stage fluid coking vessel operated at 950° F. with recycle of 700° F.+ products.

Ultimate Yields	Example 1	Example 2
Coke, Wt. Percent.....	21	21
C ₁ -Gas, Wt. Percent.....	12.5	21
C ₂ -430° F. Naphtha, Vol. Percent.....	41	48.5
430°-700° F. Gas Oil, Vol. Percent.....	40	25
Vol. Percent Total Liquid.....	81.0	73.5

From the above table it can be noted that there is a 10.2% increase in the volume of liquid products by use of the process of this invention.

It will be apparent to those skilled in the art that the teachings of this invention may be practiced in a single vessel fluidized solids system. A coking vessel may be suitably partitioned so as to contain two essentially independent fluidized solids zones, one operating at high temperatures with relatively short vapor contact times and the other at low temperatures with relatively long liquid holding times. The zones can be arranged in such a two-zone vessel so that the solids flow from the high temperature zone to the low temperature zone or vice versa, or solids can be independently supplied to and removed from each of the zones. The vapors issuing from the zone can be commingled with the vapors from the other zone or the effluent from one zone can be used to supplement the fluidizing gas used in the other zone.

A recently devised process termed hydrogen donor diluent cracking (HDDC) can also be used to convert the heavy gas oil fraction with excellent results. In this HDDC process, an oil is upgraded by admixing it with a prepared hydrogen donor diluent material, aromatic in nature, and cracking the mixture either thermally or catalytically. The donor diluent is an oil, such as a thermal tar obtained from catalytic cycle oil, boiling in the range of preferably 650° to 900° F., having the ability to take up hydrogen in a hydrogenation zone and readily release it to the material being upgraded in a thermal cracking zone. The donor material is prepared by partial hydrogenation using conventional methods and using preferably a sulfur insensitive catalyst black molybdenum sulfide. This HDDC process is carried out in conventional thermal cracking equipment with or without a soaking drum. This technique of HDDC is more fully depicted in co-pending application entitled, "Upgrading of Heavy Hydrocarbon Oils" by Langer et al., Serial No. 365,335, filed on July 1, 1953, now abandoned. If the HDDC process be used, the temperature of operation will be in the range of 600° to 900° F., preferably 750° to 850° F., with donor diluent to gas oil ratios in the range of 0.25 to 2, with residence times of 0.05 to 1.0 hour and with pressures in the range of 100 to 500 p. s. i. g. Under these conditions, a 700° F.+ conversion in the range of 60 to 90% will be attained.

Having described the invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims:

What is claimed is:

1. A process for upgrading heavy petroleum oils to obtain maximum quantities of light and middle distillates with a minimum of degradation products, comprising introducing a high boiling petroleum oil into a coking zone

containing a fluidized bed of particulate coke maintained at a coking temperature in the range of 950° to 1200° F., whereby said high boiling petroleum oil is pyrolytically upgraded depositing carbonaceous residue on said particulate coke and evolving relatively lighter hydrocarbon vapors, withdrawing and separating from said relatively lighter hydrocarbon vapors, products having an end boiling point in the range of 600° to 950° F., an intermediate heavy distillate fraction boiling above said end boiling point and residue boiling above a temperature in the range of 950° to 1150° F., recycling said residue to said coking zone for further treatment therein, injecting said heavy distillate fraction into a milder thermal cracking zone containing another fluidized bed of particulate coke maintained at a thermal cracking temperature in the range of 600° to 850° F., whereby said heavy distillate fraction is converted predominantly in liquid phase to relatively lower boiling hydrocarbons, recovering said relatively low boiling hydrocarbons, and circulating portions of the fluidized coke in said coking and thermal cracking zones to an external heating zone and back to maintain said coking and thermal cracking temperatures.

2. In a petroleum upgrading process wherein a heavy hydrocarbon oil is injected into a coking zone containing a fluidized bed of particulate solids maintained at a coking temperature, in the range of 900° to 1600° F. wherein a portion of said solids is continuously circulated to an external heating zone and back to maintain said coking temperature, wherein coke produced in the process is removed as product, wherein vapors are removed from said coking zone and said vapors are separated in a separation zone to obtain products boiling below a specified end point in the range of 600° to 950° F., the improved method for obtaining maximum amounts of middle distillates from said heavy hydrocarbon oil which comprises introducing intermediate distillable hydrocarbons from said vapors boiling above said end point and at a temperature less than 1150° F. into a milder thermal cracking zone while recycling at least a portion of the residue from said vapors to said coking zone, thermally cracking in said thermal cracking zone comprising a liquidized bed of particulate solids said intermediate distillable hydrocarbons under liquid phase conditions including a thermal cracking temperature in the range of 600° to 850° F., circulating a portion of the solids in said thermal cracking zone to said external heating zone and back to maintain said thermal cracking temperature, and separating from the effluent from said thermal cracking zone further amounts of product hydrocarbons boiling below said end point.

3. The method of claim 2 wherein the heavy gas oil fraction of said effluent boiling above said end point is recycled to said thermal cracking zone and wherein the residue of said effluent is recycled to said coking zone.

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