

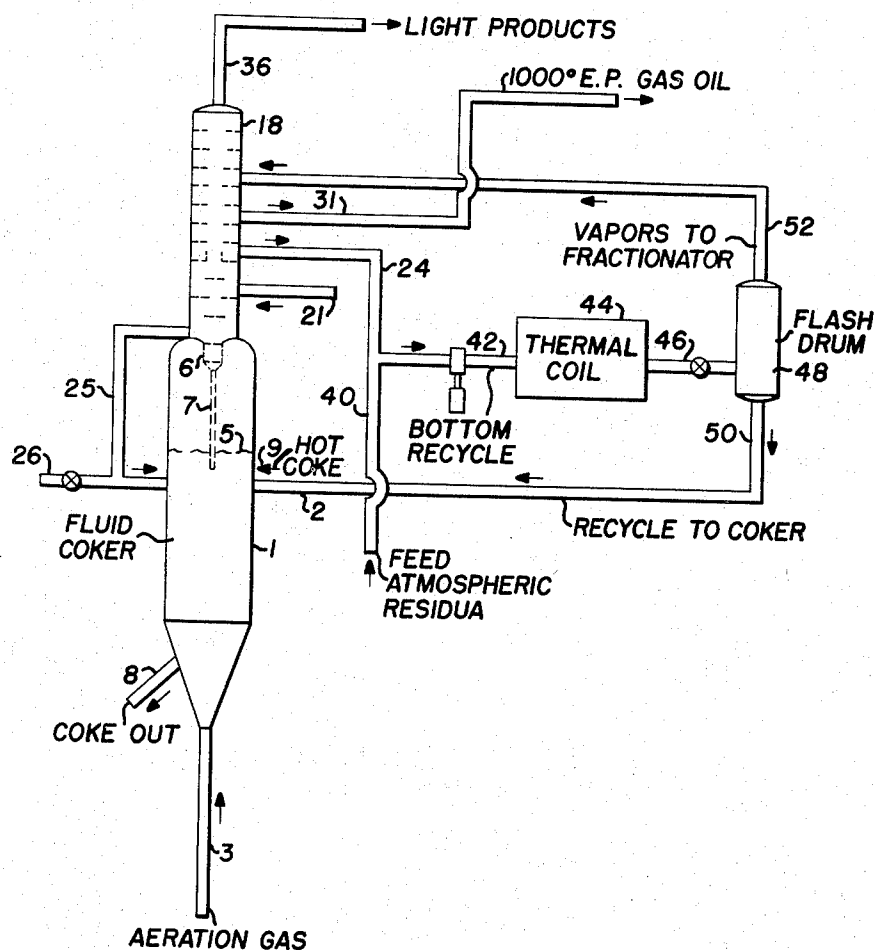
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C. E. HEMMINGER

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HIGH PRESSURE THERMAL CRACKING AND FLUID COKING

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Charles E. Hemminger Inventor

By *L. Cheson* Attorney

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HIGH PRESSURE THERMAL CRACKING AND FLUID COKING

Charles E. Hemminger, Westfield, N. J., assignor to Esso Research and Engineering Company, a corporation of Delaware

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This invention relates to improvements in pyrolytic upgrading heavy hydrocarbon oils by a unique combination of thermal cracking under pressure of the feed together with fluid coking of a resulting residue.

There has recently been developed an improved process known as the fluid coking process for the production of "fluid coke" and the thermal conversion of heavy hydrocarbon oils to lighter fractions, e. g. see allowed cases, U. S. 2,725,349, Serial No. 433,913, filed June 2, 1954 and U. S. 2,721,169, Serial No. 431,412, filed May 21, 1954. For completeness, the process is described in further detail below although it should be understood that the fluid coking process itself is not the essence of this invention.

The fluid coking unit consists basically of a reaction vessel or coker and a heater or burner vessel. In a typical operation the heavy oil to be processed is injected into the reaction vessel containing a dense turbulent fluidized bed of hot inert solid particles, preferably coke particles, but sand and spent catalyst can be employed. A transfer line or staged reactors can be employed. Uniform temperature exists in the coking bed. Uniform mixing in the bed results in virtually isothermal conditions and effects instantaneous distribution of the feed stock. In the reaction zone the feed stock is partially vaporized and partially cracked. Effluent vapors are removed from the coking vessel and sent to a fractionator for the recovery of gas and light distillates therefrom. Any heavy bottoms is usually returned to the coking vessel. The coke produced in the process remains in the bed coated on the solid particles. Stripping steam is injected into the stripper to remove oil from the coke particles prior to the passage of the coke to the burner.

The heat for carrying out the endothermic coking reaction is generated in the burner vessel, usually but not necessarily separate. A stream of coke is thus transferred from the reactor to the burner vessel, such as a transfer line or fluid bed burner, employing a standpipe and riser system; air being supplied to the riser for conveying the solids to the burner. Sufficient coke or added carbonaceous matter is burned in the burning vessel to bring the solids therein up to a temperature sufficient to maintain the system in heat balance. The burner solids are maintained at a higher temperature than the solids in the reactor. About 5% of coke based on the feed, is burned for this purpose. This may amount to approximately 15% to 30% of the coke made in the process. The net coke production, which represents the coke make less the coke coke burned, is withdrawn.

Heavy hydrocarbon oil feeds suitable for the coking process include heavy crudes, atmospheric and crude vacuum bottoms, pitch, asphalt, other heavy hydrocarbon petroleum residua or mixtures thereof. Typically such feeds can have an initial boiling point of about 700° F. or higher, an A. P. I. gravity of about 0° to 20°, and a Conradson carbon residue content of about 2 to 40 wt. percent. (As to Conradson carbon residue see A. S. T. M. Test D-189-41.)

It is preferred to operate with solids having a particle size ranging between 100 and 1000 microns in diameter with a preferred particle size range between 150 and 400

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microns. Preferably not more than 5% has a particle size below about 75 microns, since small particles tend to agglomerate or are swept out of the system with the gases. While coke is the preferred particulate solid, other inert solids such as spent catalyst, pumice, sand, kieselguhr, Carborundum, and alumina can be employed.

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.

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.

This invention provides an improved process for improving the yields of gas oil and obtaining the same in a more efficient manner. The process comprises thermal cracking a heavy hydrocarbon oil feed under pressure. The products from the thermal cracking are flashed to remove the overhead gas oil and lighter components which are fractionated in a common coker-scrubber fractionator. The heavy residual bottoms from the thermal cracking is fed to the coker. The heavy residue from the coker is also fed to the thermal cracking zone.

This process is applicable to all the heavy hydrocarbon oils listed previously. It is particularly suitable, however, for long residua which are produced in atmospheric pipe stills with steam stripping at the bottom. Due to variations in crude oils and refining practices, the initial boiling point varies from roughly 700° to 950° F., and the Conradson carbon from 2 to 15 wt. percent. From 100 to 20 vol. percent of the feed is thus fed directly to the thermal cracking zone.

The thermal cracking zone is operated at a temperature in the range of 850° to 950° F., and a superatmospheric pressure in the range of 100 to 1000 p. s. i., although higher pressures may be used.

The cracked products are then distilled as in a flash drum to remove substantially all the gas oil present, i. e., to remove the fraction boiling below about 930° F. which are sent to a common scrubber-fractionator zone.

The heavy residual bottoms from the flash distillation zone are sent as feed to a fluid coker which operates under conventional conditions.

The effluent material from the distillation, i. e. the gas oil and lighter fraction, is sent to the coker-scrubber fractionation zone. In the fractionation zone several fractions are separated; a low boiling fraction, i. e. having a maximum boiling point of 425° F.; a medium gas oil fraction having an end point of about 1000° F.; and a heavy residual bottoms condensate fraction boiling predominantly above about 1000° F. atmosphere. This heavy residual bottoms fraction is sent to the thermal cracking step for treatment as indicated. A portion of the 1000° F. bot-

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toms also collects in the bottom of the coker-scrubber. This material contains the fine coke which passes from the coker and the mixture is returned to the coker.

In many refining operations, other heavy oils as asphalt from deasphalting are available. These and a portion of the long residuum feed may be fed directly to the coker and bypass the thermal treating step. The relative distribution of these oils, the long residuum and the recycle coker bottoms depends on their availability and relative capacities of the component units of the combination units.

This invention will be better understood by reference to an example and the flow diagram shown in the drawing.

In the drawing, the numeral 1 is a coking vessel constructed of suitable materials for operation at 950° F. A bed of coke particles preheated to a sufficient temperature, e. g., 1125° F., to establish the required bed temperature of 950° F. is made up of suitable particles of 150 to 400 microns. The bed of solid particles reaches an upper level indicated by the numeral 5. The bed is fluidized by means of a gas such as stripping steam entering the vessel at the stripping portion near the bottom thereof via pipe 3. The fluidizing gas plus vapors from the coking reaction pass upwardly through the vessel at a velocity of 1 ft./sec. establishing the solids at the indicated level. The fluidizing gas serves also to strip the vapors and gases from the hot coke from the heater which flows down through the vessel from pipe 9.

A stream of solid particles is removed from the coking vessel via line 8 and transferred to the heater not shown. The temperature of the burner solids is usually 100° F. to 300° F. higher than that of the solids in the coking vessel, e. g., 175° F. higher in this example.

Heavy residual bottoms to be converted is introduced into the bed of hot coke particles via line 2, preferably at a plurality of points in the system. The oil upon contacting the hot particles undergoes decomposition and the vapors resulting therefrom assist in the fluidization of the solids in the bed and add to its general mobility and turbulent state. The product vapors pass upwardly through the bed through cyclone 6 from which solids are returned to the bed via dipleg 7. From cyclone 6 the vapors pass into a scrubbing and fractionating tower 18 preferably mounted directly above the coking vessel although it can be located elsewhere.

The temperature at the bottom of the tower 18 is controlled by introducing a stream of quench oil, e. g. fresh feed or preferably heavy gas oil from the operations through line 21. The condensation is conducted so as to obtain a heavy residue condensate boiling predominantly above 1000° F. atmospheric. The initial boiling point will be predominantly in the range of 900° to 1100° F., and the quenching temperature accordingly adjusted.

A liquid drawoff is provided near but not at the bottom of the tower to remove the heavy oils boiling above about 1000° F. through line 24. Another liquid drawoff is placed in the bottom of the tower on which is collected unvaporized oil and fine coke which passes through cyclone 6. This mixture is recycled to the coker through line 25.

Vapors remaining uncondensed in the bottom scrubbing section of the tower pass upwardly through a series of bubble cap trays located in the top of the tower where they are subjected to fractionation to condense an additional fraction in the gas oil boiling range. The condensate formed in the upper section is withdrawn as a side stream through line 31. This gas oil has a 1000° F. end point. The low boiling products, i. e. the gases and hydrocarbons boiling to 425° F. and thus including naphtha are removed overhead through line 36.

The long residuum feed, e. g. a West Texas bottoms boiling above 950° F. is fed through lines 40 and 42 to thermal coil 44. 100% of the feed is fed to this thermal coil although as explained previously, some may be fed

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directly to the fluid coker 1. This fraction of the feed plus any other heavy oils are introduced to the coker through line 26. The heavy residual bottoms from line 24 is also fed to thermal coil 44 by lines 24 and 42. Normally, with the West Texas bottoms, about 20% of the feed to the thermal coil is recycle bottoms, although this figure is subject to wide variations. The mixture is cracked in the liquid phase at 910° F. and 500 p. s. i. pressure with a feed rate from 2 to 10 vol. of feed per vol. of coil above 800° F. per hour, preferably about 3 to 5 v./hr./v. The cracked products are removed through line 46 to flash drum 48. In flash drum 48 substantially all of the gas oil and lower fractions, i. e., those boiling below about 930° F. are removed through line 52, to scrubber-fractionator 18 where they are treated as explained previously. The resulting heavy residual bottoms comprising about 40 wt. percent based on the total feed to the thermal coil 41 in the case of the West Texas residuum is then recycled directly to fluid coker 1 by means of lines 50 and 2 where it is processed as explained previously.

The advantages of this invention will be apparent to the skilled in the art. Expense of vacuum tower equipment are eliminated. The size of fluid coking equipment is reduced because the gas oil need not be processed therein. In addition, degradation of the gas oil from vapor phase cracking in the fluid coker is eliminated. The mixing of the atmospheric bottoms with the more viscous heavy residual bottoms from fluid coking makes for better handling. Furthermore, the metals which undesirably contaminate cracking catalysts are removed from the vapor products streams and segregated eventually to the coke particles.

In addition to the mentioned equipment savings, which are greater if thermal equipment is available when a coker is installed, experiments have shown that the yield and quality of the gas oil are superior when a long residuum is processed by this invention over feeding it directly to the coker without the thermal treatment. The ° API of the 425° to 1000° F. fraction is about 2 points higher. Also, for the same metal content, the end point of this gas oil can be about 50° F. higher. Finally, the yield of the gas oil is higher due to the liquid phase cracking in the thermal coil rather than vapor phase in the coker. These advantages, which give more and higher quality raw material for heating oil and catalytic cracking, are summarized below for the same metal content from the West Texas long residuum.

	Coker Alone	Coker plus Thermal Treatment
Boiling range.....°F.	430-950	430-1,000
Gravity, °API.....	17	19
Yield, Vol. Percent Feed.....	55	60

The conditions usually encountered in a fluid coker for fuels are also listed below:

Conditions in fluid coker reactor

	Broad Range	Preferred Range
Temperature, °F.....	850-1,200	900-1,000
Pressure, Atmospheres.....	1-10	1.5-2
Superficial Velocity of Fluidizing Gas, Ft./sec.....	0.2-10	0.5-4
Coke Circulation (Solids/Oil ratio).....	2-30	7-15

Conditions in burner

	Broad Range	Preferred Range
Temperature, °F.....	1,050-1,600	1,100-1,200
Superficial Velocity of Fluidizing Gas, Ft./Sec.....	1-5	2-4

It is to be understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. A process for pyrolytically upgrading a long residuum containing appreciable amounts of 700 to 1000° F. virgin gas oil and having a Conradson carbon in the range of 2 to 15 wt. percent, obtained by the atmospheric distillation of a whole crude, which comprises the steps of: combining said long residuum with a solids free heavy residual fraction obtained as hereinafter described; thermally cracking the resulting admixture in liquid phase in a thermal cracking zone at a temperature in the range of 850 to 950° F. and a pressure in the range of 100 to 1000 p. s. i.; distilling the resulting cracked products to segregate an overhead gas oil boiling below about 930° F. and a heavy bottoms fraction; passing said overhead gas oil directly to a scrubbing-fractionation zone; injecting said heavy bottoms fraction into a body of fluidized inert particulate solids maintained at a coking temperature of 850 to 1200° F. in a separate fluid coking reaction zone; circulating said particulate solids through an external heating zone and back to said fluid coking reaction zone to maintain said coking temperature; passing the resultant vapors from said fluid coking reaction zone directly to said scrubbing-fractionation zone; recov-

ering product fractions from said scrubbing-fractionation zone and two heavy residual fractions boiling predominantly above 1000° F.; one of said heavy residual fractions containing coke fines entrained from said fluid coking reaction zone with said vapors; combining the substantially solids free heavy residual fraction with said long residuum, and recycling the other coke fine containing heavy residual fraction to said coking zone.

2. A process of claim 1 wherein said heavy bottoms fraction amounts to about 40 wt. percent based on fresh feed.

3. A process of claim 1 wherein about 0 to 80 volume percent of said long residuum by-passes said thermal cracking zone and is introduced directly into said fluid coking reaction zone.

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