

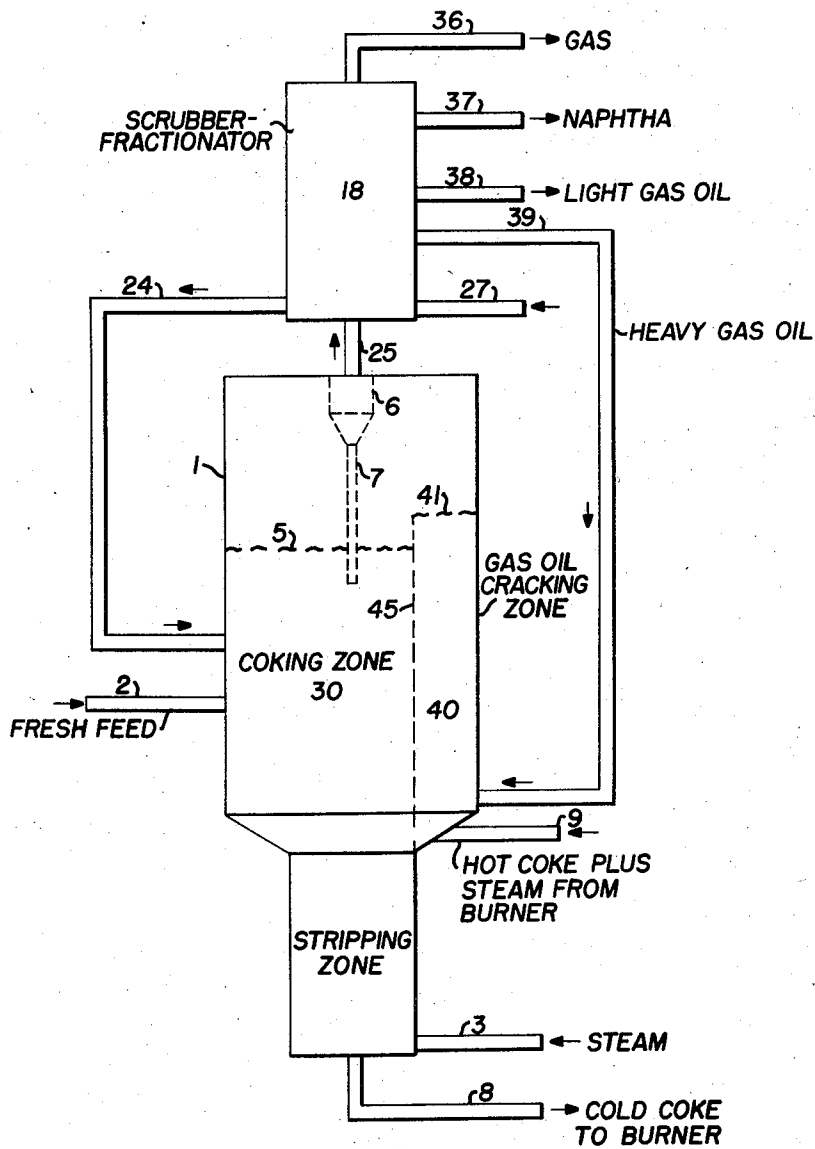
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TWO STAGE COKING OF RESIDUA FEEDS IN UNITARY REACTOR

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TWO STAGE COKING OF RESIDUA FEEDS IN UNITARY REACTOR

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This invention relates to improvements in the pyrolytic upgrading of heavy hydrocarbon oils. More particularly, it relates to an improved staged process for upgrading by coking heavy hydrocarbon oils which normally yield gas oils of inferior quality for catalytic cracking.

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, principally gas oils for catalytic cracking, e. g., see U. S. Patent No. 2,725,349 and U. S. Patent No. 2,721,169. 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. 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 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 can be 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 made less the 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 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.

Certain of these heavy oils upon being pyrolytically upgraded yield a heavy gas oil which, by reason of its high nitrogen content, ash content, or aromaticity, is decidedly unsuitable as a catalytic cracking feed stock. As examples of typical heavy oil feed stocks, there may be mentioned California residua such as Zaca, Santa Maria and Los Angeles Basin, shale oils and coal tars, etc. Typical of these are reduced crudes, a major portion of which boil above 900° F., characterized by A. P. I. gravities of -10° to 20°, Conradson carbons of 5 to 50 wt. percent, and nitrogen contents of about 0.6 wt. percent. Converting these heavy gas oils to lighter gas oils in most cases simply increases the aromatic content of the light gas oils and even worsens their catalytic cracking quality.

This invention provides an improved process for increasing the yields of high octane gasoline and unsaturated low molecular weight normally gaseous hydrocarbons from these heavy hydrocarbon oil feed stocks and minimizing the production of gas oils unsuited for catalytic cracking. The process comprises coking the heavy hydrocarbon oil feed in the first of two stages contained in a unitary reactor, each stage containing a dense turbulent fluidized bed of particulate solids. The oil is coked at conventional conditions in the first stage and the vapors taken overhead. The vaporous products are segregated to obtain a heavy gas oil fraction and a heavier residual fraction. The residual fraction is recycled to the first stage for further conversion therein. The heavy gas oil is recycled to the second stage for further conversion at higher temperatures and for longer vapor holding times to convert it predominantly to a lighter fraction boiling in the naphtha range and below.

The staging in the reactor is preferably obtained by a vertical partition and the second stage occupies a smaller volume than the first.

The heavy gas oil segregated from the vaporous products boils within the limits of about 650° to 1000° F. as distinguished from lower boiling light gas oils which boil within the limits of about 430° to 750° F. The actual boiling points depend upon specific feeds and there is no overlapping. The light gas oil taken off from the vaporous products is of good quality, either as a heating oil or a catalytic cracking feed stock. The heavy residual fraction recycled to the first stage boils predominantly above about 1000° F. atmospheric equivalent.

The conversion of the heavy gas oil in the second stage results in the obtaining therefrom of predominantly, i. e., at least 80 wt. percent, products boiling below about 430° F. made up principally of high octane gasoline and unsaturated hydrocarbons such as ethylene, propylene and butadiene.

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

In the drawing, 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 in the first stage 30 of the coker. 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

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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. A stream of solid particles is removed from the coking vessel via line 8 and transferred to the heater not shown.

A reduced crude to be converted is introduced into the bed of hot coke particles in the first stage 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 dip leg 7. From cyclone 6 the vapors pass into a scrubbing and fractionating tower 18, via line 25, 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 or bottoms from the operations through line 27. The condensation is conducted so as to obtain a heavy residual condensate fraction boiling predominantly above 1000° F. The quenching temperature is accordingly adjusted. The heavy residual fraction is recycled through line 24 back to the first stage 30 of the coking vessel.

Unsaturated hydrocarbons and other normally gaseous materials are taken overhead from the scrubber 18 through line 36. A naphtha fraction is removed as a side stream through line 37 and a light gas oil through line 38.

The heavy gas oil, e. g., one boiling in the range of 650°–1000° F. is recycled by means of line 39 to the dense turbulent fluidized bed of particles in the second stage 40 of the reactor. The heavy gas oil is contacted at higher temperature, e. g., 1125° F. for a vapor holding time of 20 seconds and is thus converted to a lighter fraction boiling below 430° F. This is removed and recovered in the same manner as the overhead from the first stage. Hot particles at 1125°–1200° F., plus steam from the burner, enter the second stage through line 9. The coke is fluidized by the steam plus evolved vapors. The solids overflow the partition 45 into the bed contained in the first stage and the system is thus maintained in heat balance.

The following example demonstrates how increased yields of gasoline and low molecular unsaturates are obtained by this invention. Column I represents the results obtained by a one stage coking and column II, the results of a two stage treatment as taught herein of a Hawkins residuum.

Yields on Residuum	I	II
Coke, Wt. Percent.....	26.4	28.2
C ₂ -, Wt. Percent.....	6.6	15.1
Propylene, Vol. Percent.....	3.2	10.2
Propane, Vol. Percent.....	2.9	4.6
Total C ₄ , Vol. Percent.....	3.4	6.5
C ₅ -430° F., Vol. Percent.....	20.0	46.1
430-650, Vol. Percent.....	13.1	13.1
650+ Gas Oil, Vol. Percent.....	38.8	0

This improvement is especially significant in view of the poor quality of the 650+ cut for catalytic cracking.

The conditions utilized in this invention are listed below:

Conditions in fluid coker reactor—stage I

	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

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Conditions in fluid coker reactor—stage II

	Broad Range	Preferred Range
Temperature, °F.....	1,000-1,200	1,050-1,150
Pressure, Atmospheres.....	1-10	1.5-2.0
Superficial Velocity of Fluidizing Gas, Ft./sec.....	0.1-5	0.2-1.0
Coke Circulation (Solids/Oil Ratio).....	4-60	14-30
Vapor contact time, seconds.....	1-40	10-25

Conditions in burner

	Broad Range	Preferred Range
Temperature, °F.....	1,050-1,600	1,125-1,200
Superficial Velocity of Fluidizing Gas, Ft./Sec.....	1-5	2-4

The advantages of this invention are apparent to those skilled in the art.

Excess recycle rates are reduced since the heavy gas oil is cracked to extinction in essentially one pass. This is done with the production of gasoline and lighter components and with the production of little or no aromatic light gas oils, of especial advantage to the small refiner. The high temperature and long time contact of the fluid bed treatment in the second stage is necessary to obtain the indicated results. Neither high temperature and short time (transfer line operation) nor low temperature and long time (return of heavy gas oil to stage 1) operation accomplishes these results. The light gas oil obtained is of good quality and is completely suited for catalytic cracking or heating oil since it is not contaminated with inferior products. All this is produced with an efficient apparatus that does not require excessive burner temperatures.

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 heavy hydrocarbon oil which upon coking yields heavy gas oil of unsuitable catalytic cracking quality which comprises the steps of providing a unitary reaction zone containing two stages, each stage containing a dense turbulent fluidized bed of inert particulate solids, contacting the oil charging stock with the dense turbulent fluidized bed in the first stage at a temperature in the range of 850° to 1200° F. to produce vaporous conversion products and coke, separating the vaporous products to segregate a heavy gas oil fraction boiling within the limits of about 650° F. to 1000° F. and a heavy residual fraction boiling above about 1000° F., recycling the heavy residual fraction to the first stage of the reactor for further conversion to light gas oil therein and recycling only the heavy gas oil to the second stage where it is contacted with the dense turbulent fluidized bed contained therein at a higher temperature than in the first stage, one in the range of about 1000° to 1200° F. for a vapor holding time of about 1 to 40 seconds so as to convert it predominantly to a lighter fraction boiling below about 430° F.

2. The process of claim 1 wherein the reaction zone is vertically partitioned to provide the staging.

3. The process of claim 2 including the additional step of circulating the solids from the first stage to an external heating zone where they are reheated by partial combustion, back to second stage and then sending the solids from the second high temperature stage to the first stage.

4. The process of claim 3 wherein the heavy oil charging stock comprises a reduced crude that upon being coked produces a heavy gas oil of unsatisfactory catalytic cracking quality, said reduced crude being typified by inspections in the following ranges: 10 to 20° A. P. I. gravity,

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5 to 50 wt. percent Conradson carbon, and nitrogen content of about 0.6 wt. percent.

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