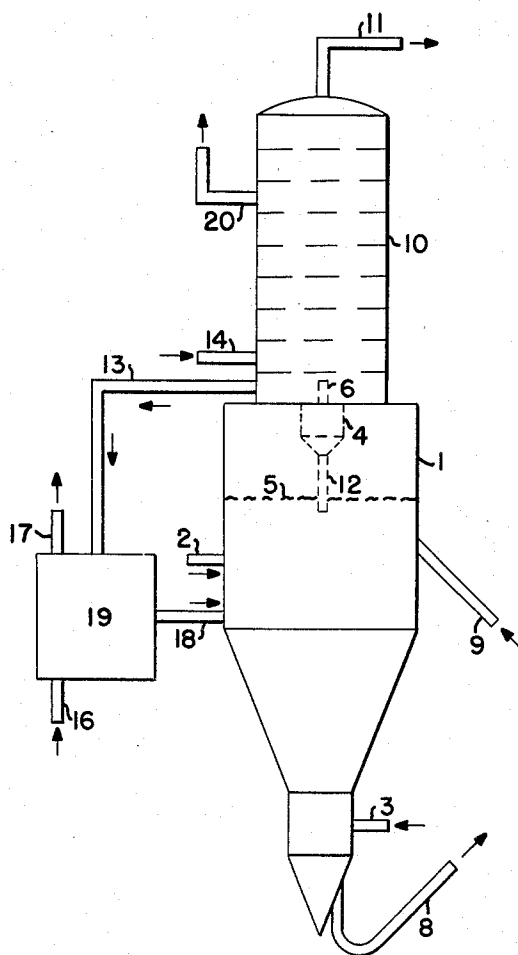


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FLUID COKING RECYCLE OPERATION

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The present invention relates to an improved method of increasing conversion and reducing recycle rates in the fluid coking for fuels. More particularly it relates to a method of accomplishing the latter by oxidizing the residual bottoms fraction from the product vapor recovery system prior to its normal recycle to the fluid coking zone.

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 U.S. Patents 2,735,349 and 2,735,806.

The fluid coking process itself is not part of this invention but will be described for completeness. The fluid coking process 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 fluidized particles, e.g. a dense, turbulent, fluidized bed or transfer line. A staged reactor 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 scrubber-fractionator for the recovery of gas oil and lighter 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 or heater vessel, usually separate. A stream of all or a portion of the coke is thus transferred from the reactor to the burner vessel, e.g., a fluid bed or transfer line 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. Coke, equivalent to about 5%, 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 burned, is withdrawn and the remaining portion recycled to the reactor to supply heat thereto.

Heavy hydrocarbon oil feeds suitable for the coking process include heavy crudes, atmospheric and vacuum bottoms from crude, pitch, asphalt, other heavy hydrocarbon petroleum residua or mixtures thereof. Typically such feeds 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

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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 particulate solids such as spent catalyst, pumice, sand, kieselsguhr, Carborundum, and alumina can be employed.

The product vapors from the coking are sent to a scrubber-fractionation zone. In the scrubber-fractionation zone several fractions are separated; a low boiling fraction, i.e., having a maximum boiling point of 425° F.; a gas oil fraction having an end point of about 1000° F. or lower; and a heavy residual bottoms condensate fraction boiling predominantly at a higher temperature.

It is normally desired to recycle a residual bottoms fraction boiling above about 1000° F. In practice, however, because of fractionation limitations, in order to minimize catalytic cracking metal contaminants in the gas oil and coke formation in the fractionator, a cut point as low as 850° F. is used to separate the gas oil from the residual bottoms fraction. A low cut point may also be desired where there is limited catalytic cracking capacity for cracking the heavy coker gas oil. The resulting bottoms fraction, because of its low boiling point, immediately flashes upon entering the coking reaction vessel thus undergoing virtually no conversion in the liquid phase. Because of this low conversion a high recycle rate becomes necessary, increasing equipment sizes. It is therefore desirable to improve this recycle operation.

This invention provides an improved method of increasing the conversion per pass in the liquid phase of the residual bottoms fraction. The method comprises contacting the residual bottoms fraction with an oxygen containing gas at a temperature below its cracking temperature, i.e., one in the range of 450° to 700° F. in an oxidation zone, preferably extraneous. The oil is thus oxidized to a combined oxygen content of about 2 to 6 wt. percent. This oxidation increases the average molecular weight and average boiling point. The oxidized bottoms fraction is then fed to the coker. Further details follow.

The recycle fraction is treated as stated previously with an oxygen containing gas. Because of cost considerations air is preferred. Pressure and oxygen concentration can be varied also to produce a smooth operation.

The oxidation treatment is carried out while the oil is in the liquid phase, preferably in a reactor extraneous to the coking reactor. Excess gas is vented from the oxidizer. The use of the extraneous reactor with the venting of the oxygen containing gas results in the sending of the oxidized oil to the fluid coker free of extraneous gas. In this manner product degradation and dilution are avoided. Coking in the pretreating oxidizing step is avoided by staying below cracking temperatures.

It has been found that the water produced during this air blowing step was only about 2.5 wt. percent of the feed, this holding true for a considerable variety of feedstocks, temperatures and air-to-feed ratios. Corresponding decrease in the hydrogen content of the feed is less than 0.3 wt. percent, which is not enough to decrease the quality of the stock as a coker feed significantly.

There is no need to oxidize the fresh feed to the coker because this usually consists of material boiling almost entirely above 1000° F. Such material is high boiling enough so that relatively little of it will flash off at typical coker temperatures of 950° to 1000° F. and thus good conversion per pass is obtained without doing anything to increase the average boiling point. However, it may occasionally be desirable to feed lower boiling stocks,

such as catalytic cracking cycle stock, to the coker. In this case, the low boiling part of the fresh feed may be advantageously oxidized prior to coking.

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. Cyclone 4 is located at the upper portion of the disperse phase; several stages of cyclones can, of course, be used. 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 coke which flows down through the vessel to the heater. A stream of solid particles is removed from the coking vessel via line 8 and transferred to the heater not shown.

A reduced crude oil to be converted is introduced into the bed of hot coke particles via line 2, but 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 leave through cyclone 4 and line 6. The solids separated are returned to the bed through dipleg 12. Hot coke solids at a temperature of about 100° to 300° F. higher than the coker, e.g. 1125° F., are recycled from the heater not shown through line 9.

The product vapors pass through line 6 into scrubbing-fractionating tower 10, preferably mounted directly above the coking vessel, although it can be located elsewhere. The temperature at the bottom of the tower 10 is controlled by introducing a stream of quench oil, e.g., fresh feed or preferably heavy gas oil from the operation, through line 14. The condensation is conducted so as to obtain a heavy residue fraction condensate boiling predominantly above about 850° F. atmospheric. The nominal cut point will be predominantly in the range of 850° to 950° F. and the quenching temperature accordingly adjusted. A liquid drawoff is provided to remove the bottoms boiling above about 850° F. through line 13.

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 take off an additional fraction in the gas oil boiling range. This gas oil has an 850° F. end point and is withdrawn as a side stream through line 20. The low boiling products, i.e., the gases and hydrocarbons boiling to 425° F. and thus including naphtha, are removed overhead through line 11.

The residual bottoms fraction withdrawn through line 13 is sent into tower 19 wherein it is oxidized by treatment with air while the fraction is in the liquid phase. Air is injected through line 16 and excess gas vented through line 17. The temperature of the treatment utilized is 550° F. and the oil is thus oxidized to a combined oxygen content of 4 wt. percent. Cracking is thereby avoided. The thus oxidized fraction, free of extraneous gas, is fed through line 18 into the fluid bed in coker 1. If desired the bottoms fraction from the scrubber can be segregated into a lighter and heavier fraction and the latter, e.g., boiling above 1000° F., sent directly to the coker bypassing the oxidation step.

The advantages of this invention are illustrated in the following example.

Example

A fluid coker is operated as shown. In column I are listed results that are obtained in conventional operation. Column II shows results that are obtained when oxidizing the recycle as taught herein, e.g., at a temperature of 550° F. to a combined oxygen content of 4 wt. percent.

COKING SOUTH LOUISIANA RESIDUUM,¹ RECYCLING TO EXTINCTION OF 1015° F.+

	I	II
Treatment of Feed:		
Fresh.....	None	None
Recycle.....	None	Oxidized
Coking Conditions:		
Temperature, ° F.....	955	955
Pressure, p.s.i.g.....	10	10
Fresh Feed Rate, w./hr./w.....	0.3	0.3
Wt. Percent Steam Diluent on FF.....	11	11
Total Feed/Fresh Feed, Vol. Ratio.....	1.75	1.27
Products, Available Yields on Fresh Feed, Wt. Percent:		
Gas, C ₃ and lighter.....	7.6	7.7
C ₄	1.3	1.3
C ₅ -430°.....	15.0	14.8
430°-1,015°.....	58.7	57.2
Coke.....	17.4	19.0

¹ 14 vol. percent on crude.

It should be noted that oxidizing the recycle decreases considerably the total feed to the coker and concomitantly the load to the scrubber with little change in yields.

The advantages of this invention will be apparent to those skilled in the art. Increased conversion in the liquid phase is obtained with decreased recycle rates and consequent savings in equipment requirements. It makes it possible to economically obtain a lower end point on the gas oil product, if such is desired.

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

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	0.5-5
Coke Circulation (solids/oil ratio).....	2-30	7-15

CONDITIONS IN HEATER

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. In a process for coking a heavy hydrocarbon oil charge stock by contacting the oil charge stock at a coking temperature with fluidized coke particles in a coking zone at a temperature in the range of about 900° F. to 1200° F. wherein the oil is converted to product vapors and carbonaceous material is continuously deposited on the coke particles, passing product vapors from the coking zone to a scrubbing-fractionation zone, fractionating the product vapors in the scrubbing-fractionation zone to separate a heavy residual bottoms fraction to be recycled to the coking zone from more volatile gas oil and lighter fractions, sending a portion of the coke particles from the coking zone to a heating zone to increase the temperature of the particles and returning a portion of the heated particles from the heating zone to the coking zone, the improvement for increasing conversion per pass and for increasing the average boiling point of said recycle heavy residual bottoms fraction when the initial boiling point of said recycle heavy residual bottoms fraction is

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between about 850° F. and 950° F. which comprises contacting said recycle heavy residual bottoms fraction in the liquid phase with air at a temperature below its cracking temperature and in the range of about 550° F. to 700° F. in an oxidation zone to oxidize said recycle heavy bottoms fraction to a combined oxygen content of about 4 to 6 wt. percent and feeding the entire oxidized fraction substantially free of extraneous air to the coking zone.

2. A process as defined in claim 1 wherein the temperature in said oxidation zone is about 550° F. and the combined oxygen content of said oxidized recycle heavy residual bottoms fraction is about 4% by weight and the total oil feed to the coking zone including oxidized recycle heavy residual bottoms and the load on the scrubbing fractionation zone are decreased for substantially the same yield of products.

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3. The process of claim 1 in which said recycle heavy residual bottoms fraction is segregated into a lower boiling fraction boiling below about 1000° F. and a higher boiling fraction boiling above about 1000° F. and only said lower boiling fraction is oxidized with air in said oxidation zone before being recycled to said coking zone, the higher boiling fraction being recycled directly to said coking zone without any oxidizing treatment.

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