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FRACTIONATION IN COKER SCRUBBER OF HEAVY GAS
OILS CONTAINING A HIGH CONCENTRATION
OF METAL CONTAMINANTS
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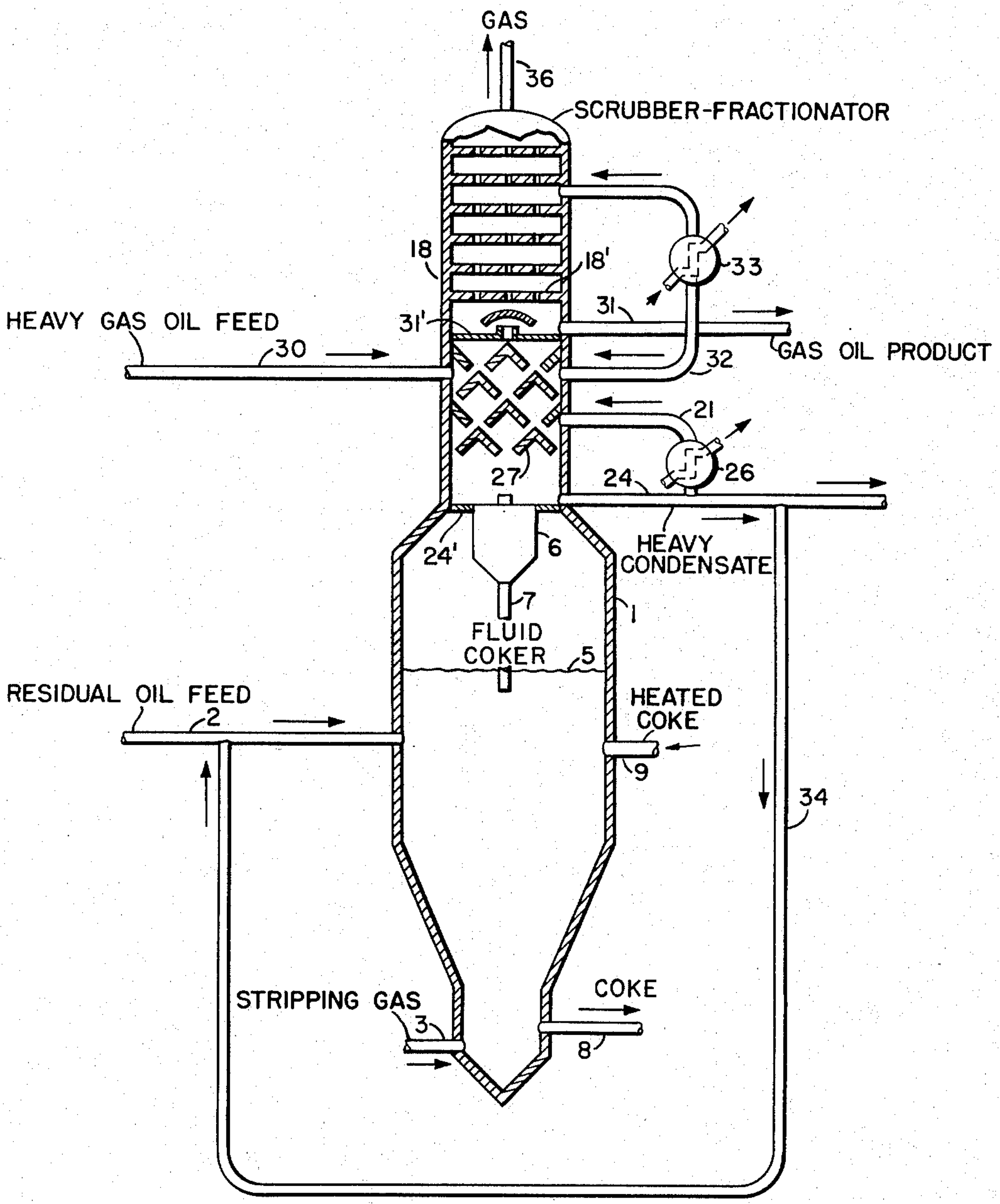

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FRACTIONATION IN COKER SCRUBBER OF HEAVY GAS OILS CONTAINING A HIGH CONCENTRATION OF METAL CONTAMINANTS

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4 Claims. (Cl. 208—82)

This invention relates to improvements in the coking of heavy hydrocarbon oils wherein heavy gas oils containing a high concentration of metal contaminants are decontaminated by fractionation in the scrubbing-fractionation zone of a fluid coker.

During recent years there has been considerable incentive for upgrading residua because of the spread of price between crude and fuel oil. The demand for heavy fuel oil relative to lighter petroleum products has been steadily decreasing with the years. Therefore, refiners have been seeking economical methods for reducing fuel-oil production based on vacuum distillation, deasphalting, and coking.

Vacuum distillation has found extensive use in maximizing the production of catalytic cracking feed stocks, although the extent to which crude can be reduced by this means is dependent on crude quality. Therefore, the quantity of the resulting residuum may vary from as little as approximately 4 percent for such crudes as South Louisiana to 40 to 50 percent for some of the heavier crudes which are now coming into the picture. The chief limitation to an increase in the amount of gas oil taken overhead in vacuum distillation is the carry-over of traces of metals which contaminate cracking catalysts. As the percentage overhead obtained by vacuum distillation of a metal-containing reduced crude is increased, the concentration of metal in the distillate increases in a regular manner.

There has recently been developed an improved process known as the fluid coking process also for the production of lower boiling distillates from heavier fractions. The fluid coking unit consists basically of a reaction vessel or coker and a heater or burner vessel. Several reactor stages can be employed. 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. 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. Product 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.

The heat for carrying out the endothermic coking reaction is generated in the heater or burner vessel. A stream of coke is transferred from the reactor to the usually extraneous burner vessel 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 or equivalent, based on

the feed, is burned for this purpose. This amounts to approximately 15% to 30% of the coke made in the process. The unburned portion of the coke represents the net coke formed in the process. This coke is preferably withdrawn from the burner, normally cooled and sent to storage.

Heavy hydrocarbon oil feeds suitable for the coking process include heavy or reduced crudes, vacuum bottoms, pitch, asphalt, other heavy hydrocarbon residua or mixtures thereof. Typically, such feeds can have an initial boiling point of about 700° F., an A.P.I. gravity of about 0° to 20°, e.g., 1.9°, and a Conradson carbon residue content of about 5 to 40 weight percent. (As to Conradson carbon residue see ASTM Test D–180–52.)

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.

A more complete description of this technique of fluid solids coking can be obtained by reference to copending application entitled, "Fluid Coking of Heavy Hydrocarbons and Apparatus Therefor," Serial No. 375,088, filed August 19, 1953, by Pfeiffer et al. The method of fluid solids circulation described above is well known in the prior art. Solids handling technique is described broadly in Packie Patent No. 2,589,124, issued March 11, 1952.

Vacuum distillation in a pipe still normally precedes the sending of the coker heavy feed to the coking system. This, of course, produces the vacuum residuum feed. The atmospheric residuum to the vacuum pipe still can be cut less deeply to avoid the obtaining of an excessively contaminated heavy gas oil distillate fraction. This, however, decreases the heavy gas oil yield from the distillation and increases the quantity of material that must be handled in the coker. Also it presents the resultant disadvantage of having to coke excessive amounts of vacuum bottoms. The other alternative is to cut deeper in the vacuum still and recover larger quantities of heavy gas oil, which can, however, be excessively contaminated with metals. Since the metal contaminants are less volatile than the gas oil, their removal can still be accomplished by improved fractionation in an auxiliary vacuum tower or towers. This represents, however, substantial increase in investment and operating costs.

This invention provides an improved process for removing the metal contaminants from the heavy gas oils. The process comprises feeding a heavy gas oil containing a high concentration of metal contaminants to the scrubbing-fractionation zone of the fluid coker. Substantially all of the metals are fractionated out in the heavy condensate and a gas oil substantially free of metal contaminants is recovered.

The heavy gas oil from which the contaminants are removed constitutes a petroleum oil having a true boiling temperature range within the range of 800° to 1350° F.

Although the problem of metal contamination is most often encountered in the heavy gas oil from the vacuum pipe still, other fractions in which the problem also occurs are atmospheric gas oil or residuum, vacuum residuum, and other contaminated heavy oils.

The contaminants most often found are nickel, vanadium and iron organic complexes. Nickel is the most objectionable component since it most deleteriously effects cracking catalysts. The concentration of metal contaminants is therefore expressed in the art as "nickel equivalents." A metal contaminant level of about 0.2 or higher pounds of nickel equivalent, per 1,000 bbls. of heavy gas oil is an undesirably high concentration. The process of this invention reduces the level of the contaminants to below 0.10 and even below 0.02 pound of nickel equivalent per 1,000 bbls. of gas oil.

This invention will be better understood by reference to an example and to the drawing which represents a vertical cross section of apparatus adapted to be used in the practice of the present invention.

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 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.

A reduced crude oil or residual oil to be converted is preferably preheated to a temperature not above its cracking temperature, e.g., 700° F. It 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.

A heavy gas oil (e.g. boiling between 850° to 1100° F., having an A.P.I. gravity of 20°, and containing 1.0 pound of nickel equivalent per 1,000 bbls. of gas oil) is fed through line **30** into scrubber-fractionator **18**. The oil may be partially vaporized by a preheat furnace prior to its introduction to tower **18**. On entering the scrubber-fractionator, further flashing or condensation will occur, depending on the boiling range of the oil and the conditions of temperature and pressure in the scrubber.

The temperature at the bottom of the tower **18** is controlled by introducing a stream of quench oil through line **21**. The condensation is conducted so as to obtain a condensate boiling predominantly above 1015° F. atmospheric pressure. The initial boiling point will be predominantly in the range of 950° to 1050° F. and the quenching temperature accordingly adjusted. For example, condensate collected in the bottom of the tower on tray **24'** may be removed through line **24**, a portion passed through cooler **26** and returned to the tower above a lower series of baffles **27**.

The temperature necessary to condense the metallic impurities will depend on the nature and amount of such impurities present in the feed. It is preferred to operate at the maximum temperature which will effect removal of impurities. Excessive temperatures at this point would result on the other hand in excessive coking and the carrying over of the metal contaminants. The exact temperatures utilized can of course be varied with the pressures. The skilled-in-the-art person will be able to select the conditions within these teachings to reduce the metal contaminants to the desired level by condensing a heavy fraction containing substantially all the metal contaminants.

Instead of cooling and recycling heavy condensate to the bottom section of the tower, other cooling mediums may be used. For example, fresh feed may be fed into this section. In this case the residual feed will be preheated by contact with hot vapors.

Vapors remaining uncondensed in the bottom scrubbing section of the tower pass upwardly through a series of bubble cap trays or perforated plates **18'** located in the top of the tower where they are subjected to fractionation to condense an additional fraction in the gas oil boiling range substantially free of metallic contaminants, e.g., 0.04 of nickel equivalents. The condensate formed in the upper section is withdrawn from trap out tray **31'** as a side stream through line **31**. A portion of this stream is pumped back to below the upper row of baffles in the lower section of the tower through line **32** as additional scrubbing and cooling medium and another portion may be pumped through cooler **33** and introduced into the top of the tower to serve as reflux. A part of the stream is withdrawn as gas oil product.

The temperature at the top of tower **18** should be kept above the dew point of steam, i.e., at a temperature of at least 200° to 225° F. This prevents condensation of steam which, if allowed to occur, might cause emulsion and corrosion problems in the top of the tower. The temperature of the vapors leaving the top of the tower may be about 300° F.

The heavy condensate fraction withdrawn from the bottom of the scrubbing tower **18**, through line **24**, and the portion not recycled for quenching and scrubbing as before described may be continuously pumped through line **34** back to the coking vessel **1** wherein the metal contaminants are deposited on the coke. This heavy condensate may be mixed with fresh feed prior to injection or may be injected through separate nozzles preferably in the lower part of the coking vessel. As an alternative, this heavy feed may be introduced into the vacuum tower for further fractionation and the bottoms from the vacuum tower may be passed to the coking vessel. The vacuum tower may be the same tower in which crude from the coking feed is distilled. The gas oil withdrawn as a side stream through line **31** constitutes a final product of the process. This oil being a condensate relatively free of residual components and metallic impurities may be subjected to catalytic cracking to form high quality gasoline.

Uncondensed vapors and gas are withdrawn from the top of tower **18** through line **36**, and passed through a water cooled condenser and then to a separating drum (not shown) in which the liquid distillate separates from uncondensed gas.

In order to express this information more fully the following conditions of operation of the various components are further set forth below.

Conditions in fluid coker 1

	Broad Range	Preferred Range
Temperature, °F	850-1, 500	900-1, 000
Pressure, Atmospheres	1-10	1. 5-2
Superficial Velocity of Fluidizing Gas, Ft./sec	0. 2-2. 0	0. 5-1. 5
Average Size of Coke Particles, Microns	100-1, 000	150-400
Coke Circulation (Solids to Oil Ratio)	5-10	7-8

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

The process of this invention avoids the necessity of constructing separate and auxiliary vacuum distillation equipment.

Liquid product loss accompanying the removal of contaminants are held to a minimum since the metals are rejected with the coke.

A very important advantage is the fact that the refiner can cut deeper in the vacuum pipe still operation because the metal contaminated heavy gas oil fraction can be economically purified.

Higher overall yields from the crude are obtained. Since the contaminated heavy gas oil is sent to the scrubber-fractionator rather than relegating a portion of it to the vacuum residuum coker, coker capacity requirements are minimized. Excessive gas oil degradation in the coker is avoided and a high quality virgin gas oil is obtained from the pipe still.

The advantage of being able to cut deeper in the vacuum pipe still operation is exemplified as follows:

Given a pipe still operated at 25 mm. Hg hydrocarbon pressure and a distillation temperature of 820° F., about 4 wt. percent, based on the crude, is obtained as a vacuum residuum. This temperature is one that avoids an excessive metals concentration in the heavy gas oil distillate. Raising the distillation temperature to 860° F. results in a greater production of the heavy gas oil and only 0.5% of vacuum residuum. The heavy gas oil is decontaminated as taught and the charge to the coker is greatly diminished.

The metal contaminants eventually are deposited on the coke particles. This represents a saving as contrasted to their being present in any of the liquid fuel components.

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 residual hydrocarbon oil by contacting the residual oil coking charge stock at a coking temperature with a body of inert particulate solids maintained in the form of a dense turbulent fluidized bed in a coking zone to produce vapors, removing vapors overhead from said coking zone and passing them to a scrubbing-fractionation zone, scrubbing and cooling said vapors therein to a temperature sufficient to condense a heavy hydrocarbon fraction and fractionating the remaining vapors to separate a lighter gas oil distillate fraction substantially free of metal contaminants, circulating the inert solids through a heating zone wherein a portion of the inert solids are heated and back to said coking zone to supply heat thereto, the improved method of removing metal contaminants from a heavy gas oil distillate fraction boiling above about 850° F. and containing a high concentration of metal contaminants which comprises the steps of feeding said heavy gas oil fraction to said scrubbing-fractionating zone to vaporize part of said heavy gas oil, scrubbing and cooling said vapors therein at a temperature in the range of 950° F. to 1050° F. to condense a heavy condensate fraction boiling predominantly above 1015° F. and containing substantially all the metal contaminants, fractionating the remaining vapors to separate a lighter gas oil fraction substantially free of metal contaminants, recycling at least a portion of said heavy condensate fraction to said coking zone and recovering a lighter gas oil product fraction, including that derived from said coking step and that derived from said contaminated heavy gas oil fraction, substantially free of metal contaminants.

2. A process according to claim 1 wherein said heavy contaminated gas oil distillate fraction has a boiling range between about 850° F. and 1100° F.

3. The process of claim 1 in which the scrubbing-fractionation zone is directly superimposed above the coking reaction zone.

4. The process of claim 1 in which the metal concentration in the heavy gas oil fraction is a minimum of 0.2 pound of about nickel equivalents per 1,000 bbls. of feed and the recovered lighter gas oil product substantially free of metal contaminants contains below about 0.10 lb. of nickel equivalents per 1,000 bbls. of product.

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