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REMOVAL OF CONTAMINANTS FROM GAS OILS PRODUCED BY FLUID COKING

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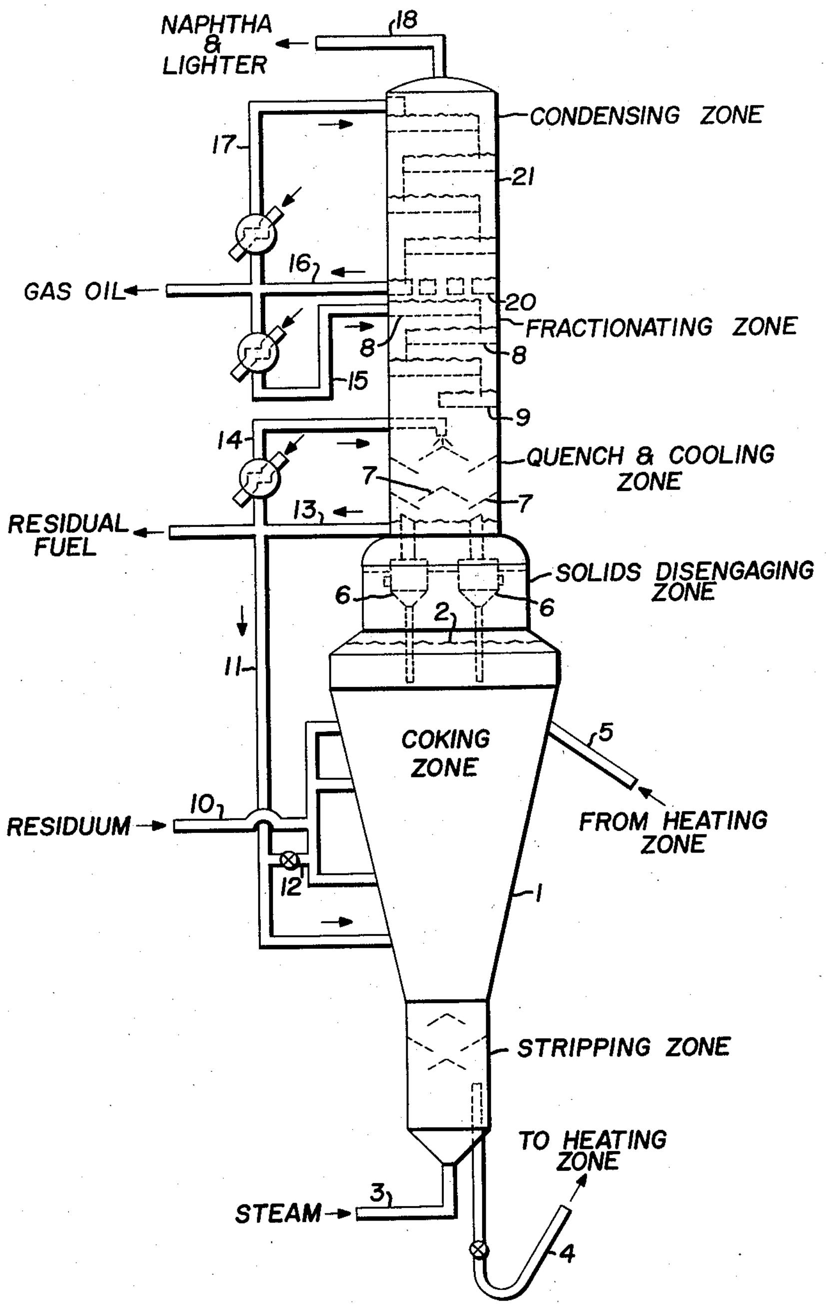

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REMOVAL OF CONTAMINANTS FROM GAS OILS PRODUCED BY FLUID COKING

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This invention relates to improvements in the fluid coking of hydrocarbon oils. It is concerned with a method and apparatus for securing increased yields and improving product quality from the conversion of petroleum residua in fluidized solids systems.

In essence, this invention proposes to reduce the metal catalyst contaminants in the product gas oils from a fluid coking process whereby increased yields of gas oils can be obtained at constant contamination rates, or higher quality gas oils can be obtained at constant yields.

The charging stock which is to be converted, according to the present invention comprises, preferably, low value, high boiling petroleum residua having an API gravity between about −10 and 20°, a Conradson carbon content between about 5 and 50 wt. percent and an initial boiling point between 850° and 1200° F. Broadly the present invention may find applicability in the converting of other charging stocks comprising shale oils, synthetic oils, pitchs, tars, coal tars, asphalts, cycle stocks, and extracts.

The prior art is familiar with residual oil coking processes wherein a charging stock is upgraded by contact with a dense turbulent bed of fluidized solids maintained at a coking temperature in a coking zone. The oil, upon contact with the solids, undergoes vaporization and pyrolysis, evolving relatively lighter, normally liquid hydrocarbon vapors and depositing carbonaceous residue or coke on the solids. The necessary heat for the pyrolysis is usually supplied by circulating a stream of the solids through an external heating zone, generally a combustion zone wherein about 15 to 30% of the coke make is consumed, and back to the coking vessel. Steam, or another relatively inert gasiform medium is used to fluidize the solids in the coking zone and to effect circulation of the solids. The excess coke produced is withdrawn either continuously or intermittently.

The heat-carrying particulate solids that form the high temperature fluidized coking bed may comprise any suitable, finely divided, substantially catalytically inert refractory solids such as sand, metal particles, spent catalyst, glass beads, and ceramics. Preferably, however, coke particles produced by the process are solids used. This permits the withdrawing of coke product free from extraneous foreign matter. As this is a fluidized solids process, these coke particles have a size preferably in the range of 40 to 500 microns by screen analysis, although the size in some applications may vary considerably beyond this range, e.g., from 10 to 1000 microns.

The coking temperatures used may vary from 850° to 1200° F. Low temperatures in the range of 850° to 1000° F. are preferred when heavier distillates, e.g., gas oils are desired as the primary product and higher temperatures in the range of 1000° to 1200° F. are preferred when lighter distillates, e.g., gasolines, are primarily desired.

The coking process of the type described has found application principally in upgrading heavy oils containing constituents nonvaporizable at ordinary pressures without cracking, such as vacuum residua, to materials suitable as charging stocks to catalytic cracking units. Generally, the heavy oil is treated to an extent sufficient only to deash and decarbonize the oil to convert it into a proper feed stock for catalytic cracking, as this catalytic method of conversion still remains the best means of upgrading oils. Undue thermal conversion of the heavy oils is desirably avoided in the coking zone because of the loss of potential products to coke and gas.

According to prior practices, the vaporous conversion products, after having entrained solids removed, are passed from the coking zone to a scrubbing-fractionating zone. The vapors are first quenched by refluxed oils in the scrubbing zone of the scrubber-fractionator, and heavy ends containing highly refractory materials and catalyst contaminants are separated. The quenched vapors then enter the fractionation zone, the first plate of which consists of a drawoff plate for removing the highest boiling gas oil product and reflux stocks. The heavy ends removed in the scrubbing zone are recycled to the coking zone substantially to extinction. To obtain high yields, the initial boiling point of the heavy ends is desirably maintained at the highest temperature possible consistent with securing a gas oil meeting minimum quality standards. Conversely stated, the end boiling point or cut point of the highest boiling gas oil removed as product is maintained as high as possible without exceeding the permissible content of metal or other contaminants in the gas oil. This is done not only to secure higher yields of gas oils but also to decrease the amount of material that must be recycled. A high recycle rate is to be avoided, not only because it is uneconomical per se, but also because a high recycle rate leads to poorer product qualities and yields.

The metal contaminants that prescribe this limitation on the coker gas oil cut point are primarily nickel, vanadium, and iron. They exist as organic complexes. Nickel is the most objectionable because it has the most deleterious effect on cracking catalysts. For this reason, the total concentration of metal contaminants in a gas oil is usually expressed in the art as "nickel equivalents." A contamination level above about 0.3 pound nickel equivalents per 1,000 bbls. in a catalytic cracking charge stock has been found to be undesirable. Also, it is desirable to have the Conradson carbon content, a measure of the coke forming propensity of the oil, below about 3 wt. percent.

It has now been discovered that metal contaminants can be effectively separated from gas oils by improved fractionation. According to the present invention, through proper fractionation in separating the heavy ends from the coker effluent, higher yields of gas oils may be obtained at a constant contamination level or, alternatively, gas oil contamination can be greatly reduced at a constant cutpoint. The contaminants removed from the gas oil are carried down within the scrubbing zone to the heavy ends and removed therewith.

This invention will become clear as the drawing, attached to and forming a part of this description, is described in detail. The drawing depicts one preferred embodiment of this invention wherein in a coking system additional fractionation plates or their equivalent have been added in the product separation zone below the gas oil drawoff plate.

Referring to the attached drawing, there is shown a fluid coking vessel **1** with an integral superposed combination scrubbing-fractionating tower **21**. The coker **1** contains a fluidized bed of particulate coke maintained at a coking temperature. The bed has a definite upper level **2** with a dilute or disperse phase thereabove. Fluidization gases, e.g., steam or light hydrocarbon gases, are admitted to the base of the vessel by line **3** and serve first to strip coke particles in the lower portion of the vessel and then pass upwardly, fluidizing the solids therein. The fluidizing gas plus the vaporous conversion products pass upwardly through the vessel at a velocity in the range of 0.5 to 5 ft./sec.

To maintain the coking temperature, solids are preferably continuously circulated via line **4** to an external heating zone and back via line **5**. In the heating zone, the solids are heated to a temperature 100° to 300° F. above the coking temperature. The external heating zone comprises preferably a fluid bed unit wherein the circulated coke particles are partially combusted by contacting a free oxygen-containing gasiform medium, e.g., air. Other means of supplying heat to the coker may, of course, be used. Thus transfer line burners, gravitating bed burners or shot circulation heating systems may also be used.

The oil to be converted, which may be suitably preheated, is introduced into the coking vessel at a plurality of horizontal and vertical points via line **10**. Upon contact with the high temperature solids, the injected oil undergoes pyrolysis and vaporization depositing carbonaceous residue on the solids and evolving vaporous conversion products. Recycled heavy ends separated from the conversion products can be introduced into the coker either with the fresh feed via line **12**, or lower down in the coker via line **11**. The latter is preferred as the recycled material is usually more volatile than the original feed and will, by being injected into the base of the coker, serve to supplant some of the fluidization steam used.

The conversion products pass through the solids disengaging zone into cyclone system **6** wherein entrained solids are removed and returned to the bed. To inhibit or prevent coking of the cyclone system, additional diluent gas or extraneous hot solids can be introduced into the cyclone inlet or thereabouts. It is desirable not to remove all entrained solids from the conversion products as passage of entrained solids through the cyclone to the outelt will prevent or inhibit coke deposits in the lines leading from the cyclones.

The vaporous conversion products emerging from the cyclones will have a vapor temperature in the range of about 850° to 1200° F. These vapors contain catalysts contaminants either because of vaporization of the contaminant materials or because of entrainment. For normal feed stocks, the contamination level will be about 20 nickel equivalents/1000 bbls. For extremely poor feed stocks, this contamination level may run as high as 30 nickel equivalents. The higher boiling ends of the vapors comprise largely refractory highly aromatic constituents of unsatisfactory catalytic cracking quality.

The vapors emerging from the cyclones are immediately met with a refluxed cooling or quench medium. In cases where the scrubber-fractionator is not superposed on the coking unit, this quench medium can be injected into the conduit conveying the vapors to the separation tower. In this manner, the vapors are rapidly cooled to a temperature below incipient cracking temperatures, i.e., below about 850° F. The quench medium removes from the vapors the heavier high boiling ends. Depending upon the charging stock to the coker, operating conditions, etc., these condensed ends having a nominal initial boiling point in the range of 700° to 1000° F.

The condensed ends collect in the bottom portion of the tower and are removed from the tower by line **13**. The maximum liquid temperature at the bottom of the tower should not exceed about 700° to 800° F. in order to prevent coking in this section. The ends will contain a major proportion of the contaminants and substantially all of the entrained solids in the vapors. A portion of these ends is cooled and recycled via line **14** to serve as a scrubbing or reflux oil. The reflux ratio of the heavy ends can be in the range of 1/1 to 10/1, based on recycle to coker, and the recycled oil may be cooled to a temperature in the range of 300° to 650° F. This reflux oil descends in the scrubbing zone countercurrently to the vapors, falling over liquid-gas contacting means, e.g., disc and doughnut baffles **7**.

Substantially all of the heavy ends are recycled to the coker via line **11** as previously described. This permits depositing of the metal contaminants on the solids whereby they can be conveniently removed from the process. With some charging stocks, the recycled material may be extremely refractory. For this reason, it may be desired to bleed a portion of the recycled ends from the process as a residual fuel product via line **13** to prevent undue build-up of these refractory constitutents.

The material recycled via line **11** may be processed in the vacuum distillation unit preparing fresh charging stock for the coker if a vacuum distillation unit be used. If so, the recycled ends enter the coker in intimate admixture with the fresh feed.

It has been previously proposed to use fresh feed to the process as the scrubbing oil instead of using recycled ends and such a variation is applicable to the present invention. Specifically, fresh feed can be introduced into the scrubbing zone via line **14**, can be collected into the bottom portion of the zone and then can be introduced into the coker via lines **11** and **12**.

The vapors after quenching pass upwardly through the tower and enter a fractionation or continuous rectification zone. A heavy gas oil that contains a major proportion of the metal contaminants remaining in the vapors is initially condensed. Preferably, this zone comprises at least 2 actual fractionation plates or their equivalent, e.g., perforated or slotted plates, or plates with bubble caps. Preferably, 2 to 4 equivalent fractionation plates are used. As illustrated, perforated plates **8** with suitable downcomers and a collection well **9** are used. The condensed material in collection well **9** overflows into the scrubbing section. This overflow material should be a minimum of 5 or 10 percent on gas oil product. This heavy gas oil preferably has a final boiling point in the range of 1000° to 1300° F., e.g., 1100° F., and an initial boiling point in the range of 700° to 900° F., e.g., 800° F. It is to be observed that this separation of the contaminant-containing gas oil is made prior to the withdrawal of any distillate product streams.

Immediately above the fractionation plates **8** there is a drawoff plate **20** from which the condensed gas oils designated as catalytic cracking feed stock are withdrawn via line **16**. Preferably, a portion of these withdrawn gas oils are cooled and returned to the lower portion of the fractionation zone via line **15** as shown, to increase the efficiency of separation. The reflux ratio used may be in the range of 0.3 to 5 based on gas oil product, and the recycled material may be cooled to a temperature in the range of 400° to 700° F. As is customary, another portion of this gas oil product may be cooled and recycled further up to the tower via line **17**.

The portion of the tower above the drawoff plate **20** is of conventional design and may comprise as many fractionation steps and side streams as desired. As illustrated, no further product streams are withdrawn from the tower. The gas oil product obtained via line **16** has an initial boiling point in the range of 200° to 500° F. Preferably, the temperature at the top of the tower **2** is kept above the dew point of steam, i.e., at a temperaure of a least 200° to 225° F., depending upon the pressure. This prevents condensation of the steam which, if allowed to occur might cause corrosion problems at the top of the tower and later emulsion difficulties. The temperature of the vapor leaving the top of the tower via line **18** may be about 200° to 400° F. The vapors can be further separated in conventional equipment as desired.

Staged heat removal may conveniently be used in the fractionator-scrubber. Thus the various coolers illustrated may exchange heat with other pump-around streams or with the feed stocks to the process.

Table I presents a specific example of operating conditions applicable to the present invention. Table II presents an example of the product attainable when the process is operated in accordance with the example of Table I, using the charging stock indicated.

Table I

Coking zone:	
Pressure @ cyclone inlet	6 p.s.i.g.
Temperature	950° F.
Fresh feed rate	0.7 lbs./hr./lb. fluidized solids (w./hr./w.).
Solids/oil ratio (wt.)	10.
Temperature of reheated solids	1125° F.
Fluidizing and stripping stream	5 wt. percent of fresh feed.
Vapor temperature @ cyclone outlet	950° F.
Vapor volume @ cyclone outlet	3000 ft.³/bbl. fresh feed.
Scrubbing and fractionation zone (3 actual plates below gas oil drawoff):	
Pressure @ tower top	4 p.s.i.g.
Vapor temperature @ tower top	230° F.
Vapor temperature @ gas oil drawoff plate	780° F.
Side streams:	

	Via Line	Liquid Temp., ° F.	Rate, Vol. Percent Fresh Feed
Recycle to coking zone, 1,015° F.+	11	700	20
Bottoms pump-around	14	500	115
Gas oil pump-around to upper plates	17	215	250
Gas oil pump-around to lower plates	15	400	30
Gas oil product	16	500	60

Table II

Charging stock inspections:	
API gravity	8.5°
Conradson carbon	19.1 wt. percent.
Initial boiling point	900° F.
Sulfur	4 wt. percent.
Viscosity	627 SSF @ 210° F.
Ash	0.15 wt. percent.
Products, percent on fresh feed:	
C_3—	7.7 wt. percent.
C_4/430	22.4 vol. percent.
430/650	14 vol. percent.
650/900	30 vol. percent.
900/1050	11 vol. percent.
Gross coke make	20 wt. percent.
Net product coke	14 wt. percent.
10# RVP gasoline 76 Research clear octane	20 vol. percent.
Gas oil inspections:	
IBP	430° F.
FBP	1050° F.
Nickel equivalents, pounds/1000 bbl.	0.2.
Aniline pt., ° F.	125.
Aromatic rings, wt. percent	19.
Naphthenic rings, wt. percent	46.

Various modifications of this invention will be apparent to those skilled in the art. For example, the combination scrubber-fractionator need not be superposed on the coking vessel as illustrated. If it is not, then external cyclones may be used to remove solids from the vaporous conversion products. Further, although the scrubbing-fractionating zones have been described as being integral, they also may be separate and the vapors and liquids may be transferred between the zones by suitable piping arrangements.

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. In a fluid coking process wherein a contaminants-containing charging stock is injected into a fluidized bed of particulate solids maintained at a coking temperature, vaporous products being thereby produced, said vapors being withdrawn overhead through a solids separation zone and introduced into a scrubbing zone directly over which is positioned a fractionation zone, wherein vapors are cooled in said scrubbing zone to below about 850° F. to condense out heavy ends having a nominal initial boiling point above 700° F., the heavy ends collecting in the bottom of said scrubbing zone, and wherein at least a portion of the heavy ends are removed, cooled and returned to the upper portion of said scrubbing zone to serve as reflux oil, the improvement which comprises fractionally distilling in the fractionation zone immediately above said scrubbing zone the remainder of said vapors to obtain a contaminant-containing heavy gas oil having an initial boiling point above 700° F. and a final boiling point below 1300° F. and to obtain a lower boiling gas oil having an initial boiling point in the range of 300–500° F. and a contaminant level below 0.3 pound nickel equivalent per barrel of charging stock, internally returning all of said heavy gas oil as reflux to said scrubbing zone, withdrawing a portion of said lower boiling gas oil from said fractionation zone as product, and returning the remainder of said lower boiling gas oil to said fractionation zone below the point of lower boiling gas oil drawoff.

2. The process of claim 1 wherein the reflux ratio of said lower boiling gas oil to said fractionation zone is in the range of 0.3 to 5.0 based on gas oil product.

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