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(54) **DELAYED COKING PROCESS FOR THE PRODUCTION OF SUBSTANTIALLY FRE-FLOWING COKE FROM A DEEPER CUT OF VACUUM RESID**

DELAYED-COKING-VERFAHREN ZUR HERSTELLUNG VON WEITGEHEND FREIFLIESSENDEM KOKS AUS EINEM TIEFEREN VAKUUMRÜCKSTANDSSCHNITT

PROCEDE DE COKEFACTION DIFFEREE PERMETTANT LA PRODUCTION D'UN COKE A ECOULEMENT SENSIBLEMENT FLUIDE A PARTIR D'UNE FRACTION PLUS PROFONDE DE RESIDUS SOUS VIDE

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Description**FIELD OF THE INVENTION**

5 **[0001]** The invention relates to a modified vacuum distillation and delayed coking process for making substantially free-flowing coke, preferably free-flowing shot coke. A vacuum resid feedstock is used which contains less than 10 wt. % material boiling between 900°F and 1040°F (482.22°C to 560°C) as determined by HTSD (High-temperature Simulated Distillation). The use of such a high boiling resid favors the formation of shot coke. Use of distillate recycle in the feed reduces coker furnace fouling potential of the heavier feedstock.

DESCRIPTION OF RELATED ART

10 **[0002]** Delayed coking involves thermal decomposition of hydrocarbonaceous feedstocks (HFs) including petroleum residua (resids) and deasphalter bottoms etc. to produce gas, liquid streams of various boiling ranges, and coke. Delayed coking of HFs from heavy and heavy sour (high sulfur) crude oils is carried out primarily as a means of disposing of these low value feedstocks by converting part of the HFs to more valuable liquid and gas products.

15 **[0003]** In the delayed coking process, a resid feedstock is rapidly heated in a fired heater or tubular furnace at from 480°C to 520°C and pressures of 50 to 550 psig (344.74 to 3792.12 kPag) . The heated feedstock is then passed to a coking drum that is maintained at conditions under which coking occurs, generally at temperatures above 800°F (426.6 °C), typically between 480°C to 520°C (895°F to 970°F), under super-atmospheric pressures of 15 to 80 psig (103.42 to 551.58 kPag) to allow volatiles that form in the coker drum to be removed overhead and passed to a fractionator, leaving coke behind. When the coker drum is full of coke, the heated feed is switched to another drum and additional hydrocarbon vapors are purged from the coke drum with steam. The drum is then quenched with water to lower the temperature to below 300°F (148.89°C) after which the water is drained. When the cooling step is complete, the drum is opened and the coke is removed after drilling and/or cutting using high velocity water jets.

20 **[0004]** US-A-4,549,934 discloses delayed coking of heavy hydrocarbons.

25 **[0005]** For example, a high speed, high impact water jet is used to cut the coke from the drum. A hole is typically bored in the coke from water jet nozzles located on a boring tool. Nozzles oriented horizontally on the head of a cutting tool then cut the coke from the drum. The coke removal step adds considerably to the throughput time of the overall process. Thus, it would be desirable to be able to produce a free-flowing coke, in a coker drum, that would not require the expense and time associated with conventional coke removal, i.e., it could be drained out of the bottom of the drum.

30 **[0006]** Even though the coking drum may appear to be completely cooled, some volumes of the bed may have been bypassed by the cooling water, leaving the bypassed coke very hot (hotter than the boiling point of water). This phenomenon, sometimes referred to as "hot spots" or "hot drums", may be the result of a combination of morphologies of coke being present in the drum, which may contain a combination of more than one type of solid coke product, i.e., sponge coke and shot coke. Since unagglomerated shot coke may cool faster than other coke morphologies, such as large shot coke masses or sponge coke, it would be desirable to predominantly produce free-flowing shot coke in a delayed coker, in order to avoid or minimize hot drums.

SUMMARY OF THE INVENTION

35 **[0007]** In an embodiment, there is provided a delayed coking process comprising:

40 a) preparing a vacuum resid that has less than 10wt.% 900 to 1040°F (482.22°C to 560°C) boiling material as measured by HTSD (High-Temperature Simulated Distillation) and combining with a distillate recycle stream wherein the distillate recycle stream has boiling range within the interval of 450°F to 750°F (232.22°C to 398.89°C) and is in the range of 0 to 7 volume percent ;

45 b) conducting said mixture to a heating zone wherein it is heated to an effective coking temperature; and

50 c) conducting said heated mixture from said heating zone to a coking zone wherein vapor products are collected overhead and whereby coke with reduced incidence of hot drums and of a relatively free-flowing nature is formed.

[0008] In a preferred embodiment, the coking zone is in a delayed coker drum, and a substantially free-flowing shot coke product is removed from the coker drum.

55 **[0009]** In still another preferred embodiment an additive is introduced into the feedstock either prior to heating or just prior to it being introduced in the coker vessel, which additive can be a metals-containing or metals-free additive. If a metals containing it is preferably an organic soluble, organic insoluble, or non-organic miscible metals-containing additive that is effective for the formation of substantially free-flowing coke.

[0010] In yet another preferred embodiment of the present invention the metal of the additive is selected from the

group consisting of sodium, potassium, iron, nickel, vanadium, tin, molybdenum, manganese, aluminum, cobalt, calcium, magnesium, and mixtures thereof.

[0011] In another embodiment, the metals-containing additive is a finely ground solid with a high surface area, a natural material of high surface area, or a fine particle/seed producing additive. Such high surface area materials include fumed silica and alumina, catalytic cracker fines, FLEXICOKER cyclone fines, magnesium sulfate, calcium sulfate, diatomaceous earth, clays, magnesium silicate, vanadium-containing fly ash and the like. The additives may be used either alone or in combination.

[0012] In another embodiment substantially metals-free additives can be used in the practice of the present invention. Non-limiting examples include elemental sulfur, high surface area substantially metals-free solids, such as rice hulls, sugars, cellulose, ground coals, ground auto tires and mineral acids such as sulfuric acid, phosphoric acid, and their acid anhydrides. It is to be understood that before or after the resid is treated with the additive, a caustic species, preferably in aqueous form, may optionally be added. The caustic can be added before, during, or after the resid is passed to the coker furnace and heated to coking temperatures. Spent caustic obtained from hydrocarbon processing can be used. Such spent caustic can contain dissolved hydrocarbons, and salts of organic acids, e.g., carboxylic acids, phenols, naphthenic acids and the like.

[0013] In another embodiment, the process is used in conjunction with automated coke drum bottom deheading valves, and the product coke plus cooling water mixture is throttled out the bottom of the coke drum through the bottom valve.

[0014] If an additive is used, it is desirable to avoid heterogeneous areas of coke morphology formation. That is, one does not want locations in the coke drum where the coke is substantially free flowing and other areas where the coke is substantially non-free flowing. Dispersing of the additive is accomplished by any number of ways, preferably by introducing a side stream of the additive into the feedstream at the desired location. The additive can be added by solubilization of the additive into the vacuum resid, or by reducing the viscosity of the vacuum resid prior to mixing in the additive, e.g., by heating, solvent addition, etc. High energy mixing or use of static mixing devices may be employed to assist in dispersal of the additive agent, especially additive agents that have relatively low solubility in the feedstream.

[0015] Preferably, all or substantially all of the coke formed in the process is substantially free-flowing coke, more preferably, free-flowing shot coke. It is also preferred that at least a portion of volatile species present in the coker drum during and after coking be separated and conducted away from the process, preferably overhead of the coker drum.

BRIEF DESCRIPTION OF THE FIGURES

[0016]

Figure 1 is a simplified process flow diagram of one preferred method of obtaining a deep cut heavy oil stream for use in the present invention. This figure shows the vacuum distillation system modified with a steam side stripper, as well as a distillate recycle stream from the coker main fractionator.

Figure 2 is another simplified process flow diagram of another preferred method for obtaining a deep cut heavy oil stream for use in the present invention. This figure is similar to that of Figure 1 hereof except that there is an intermediate resid reheating furnace for reheating the stream upstream of the stripper.

Figure 3 is a cross polarized light optical micrograph showing coke formed from a transition coke-forming heavy Canadian vacuum resid containing 12 wt.% 1000°F (537.78°C) boiling material as determined by HTSD. The figure shows small domains ranging in size from 10 to 20 micrometers with some coarse mosaic ranging from 5 to 10 micrometers (this microstructure is associated with bulk coke beds having transition coke morphology).

Figure 4 shows the effect of further distilling the feed so that it contains only 2 wt.% 1000°F (537.78°C) boiling material. The figure is a cross polarized light optical micrograph showing coke resid formed from the deeper cut resid and shows a medium/coarse mosaic structure ranging in size from 2 to 10 micrometers (this microstructure is associated with bulk coke beds having shot coke morphology).

DETAILED DESCRIPTION OF THE INVENTION

[0017] Petroleum vacuum residua ("resid") feedstocks are suitable for delayed coking. Such petroleum residua are frequently obtained after removal of distillates from crude feedstocks under vacuum and are characterized as being comprised of components of large molecular size and weight, generally containing: (a) asphaltenes and other high molecular weight aromatic structures that would inhibit the rate of hydrotreating/hydrocracking and cause catalyst deactivation; (b) metal contaminants occurring naturally in the crude or resulting from prior treatment of the crude, which contaminants would tend to deactivate hydrotreating/hydrocracking catalysts and interfere with catalyst regeneration;

and (c) a relatively high content of sulfur and nitrogen compounds that give rise to objectionable quantities of SO₂, SO₃, and NO_x upon combustion of the petroleum residuum. Nitrogen compounds present in the resid also have a tendency to deactivate catalytic cracking catalysts.

[0018] Coke bed morphology is typically described in simplified terms such as sponge coke, shot coke, transition coke, and needle coke.

[0019] As previously mentioned, there are generally three different types of solid delayed coker products that have different values, appearances and properties, i.e., needle coke, sponge coke, and shot coke. Needle coke is the highest quality of the three varieties. Needle coke, upon further thermal treatment, has high electrical conductivity (and a low coefficient of thermal expansion) and is used in electric arc steel production. It is relatively low in sulfur and metals and is frequently produced from some of the higher quality coker feedstocks that include more aromatic feedstocks such as slurry and decant oils from catalytic crackers and thermal cracking tars. Typically, it is not formed by delayed coking of resid feeds.

[0020] There are additional descriptors of coke too, although they're less common. For example, a sandy coke is a coke that after cutting looks to the naked eye much like coarse black beach sand.

[0021] In an embodiment, resid feedstocks include but are not limited to residues from the atmospheric and vacuum distillation of petroleum crudes or the atmospheric or vacuum distillation of heavy oils, visbroken resids, tars from deasphalting units, coal liquids, shale oil or combinations of these materials. Atmospheric and vacuum topped heavy bitumens can also be employed. Feedstocks typically used in delayed coking are high-boiling hydrocarbonaceous materials with an API gravity of 20° or less, and a Conradson Carbon Residue content of 0 to 40 weight percent.

[0022] Vacuum resids are characterized by a number of parameters, including their boiling point distributions. The boiling point distribution can be obtained by a physical distillation in a laboratory, but it is costly to perform this type of analysis. Another method for determining the boiling point distribution is to use specialized gas chromatographic techniques that have been developed for the petroleum industry. One such GC method is High-temperature Simulated Distillation (HTSD). This method is described by D.C. Villalanti, et al. in "High-temperature Simulated Distillation Applications in Petroleum Characterization" in Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.), pp. 6726-6741 John Wiley, 2000, and has been found to be effective for characterizing the boiling point distributions of vacuum residua. Boiling point distributions are reported as wt.% off versus atmospheric equivalent boiling point (AEBP) and are report in increments of 1 wt.%.

[0023] Vacuum distillation is well known in the industry. A number of variables affect the boiling point distribution of the vacuum distillation unit bottoms. As refiners tend to try to push ever more flow through existing units, however, the boiling point distributions of the vacuum bottoms tend to pick up a higher percentage of the lowest boiling components.

[0024] It has unexpectedly been found by the inventors hereof that the components that are contained a virgin resid which boil between 900°F (482.22°C) and 1040°F (560°C) can have a significant influence on delayed coker coke morphology is they are present in an abundance in excess of 10 wt.% of the entire virgin feed. Specifically, it has been found that when a resid that otherwise would make shot coke has the 900°F to 1040°F (482.22°C to 560°C) fraction in excess of 10 wt.%, it will make a transition coke, or a bonded shot, and can have appreciable percentage of hot drums when coked under "typical" delayed coker conditions, e.g., DOT = 820°F, DOP = 15 to 35 psig (103.42 to 241.32 kPag) , and recycle ratio of under 10%, where DOT is drum outlet temperature and DOP is drum outlet pressure.

[0025] It has been found that by reducing the fraction of 900°F to 1040°F (482.22°C to 560°C) AEBP material to under 10 wt.% pushes coke morphology back to a less bonded and less self-supporting coke morphology.

[0026] Such deeper cuts of resids can be obtained by any means available in a petroleum refinery. One means is represented in Figure 1 hereof wherein atmospheric resid bottoms is conducted via line **19** through a furnace 1 wherein it is heated to a temperature of 700°F to 800°F (371.11°C to 426.67°C) then sent via line **20** to vacuum distillation tower **2** wherein non-condensable material, such as steam and any small amount of remaining light ends are collected overhead via line **6** preferably by use of an ejector system (not shown). A heavy vacuum gas oil cut is removed via line **5** . An intermediate cut is removed via line **4** where it is combined with vacuum bottoms of line **3** and conducted to outboard stripper **7** where a lighter stream, such as one containing at least a fraction of any remaining gas oil, is stripped by use of steam injected via line **8** and sent back to the vacuum distillation tower via line **80**. The stripped vacuum resid bottoms is then conducted via line **9** to a delayed coker where it is typically introduced near the bottom of the main fractionator **10'** although it can be fed directly to the coker furnace **11** . The bottoms of the main fractionator line **100** are fed to the coker furnace wherein recycle distillate is introduced via line **12** . Any additives to aid in the desired coking reaction can be introduced via line **13** . The resid stream is heated in coker furnace **11** to coking temperatures then sent via line **14** to one or more coker drums (not shown).

[0027] Figure 2 hereof shows another preferred process scheme for obtaining a deep cut vacuum resid feed for producing substantially free-flowing shot coke in a delayed coker. The process scheme is similar to that shown in Figure 1 hereof except the intermediate cut removed from distillation tower **2** is conducted via line **50** and combined with vacuum distillation bottoms on line **55** and sent through outboard stripper furnace **15** for reheating to substantially the same temperature as that of furnace **1**. The reheated vacuum bottoms/intermediate cut stream is conducted via line **60** to

outboard stripper 7.

[0028] The drawback of the deeper cut resids, however, is that they tend to foul the coker furnace more rapidly than less deeply cut resids, and this a potential economic debit because this can increase frequency of furnace cleanout, which in turn reduces overall throughput of the coker unit. To mitigate the higher fouling tendency of the deeper cut vacuum resid, a distillate stream can be added to the coker feed. The boiling point distribution of the distillate recycle stream is such that it is an effective mitigator of furnace fouling yet its endpoint is low enough that it does not affect the coke morphology. An example of this would be a coker distillate stream with a boiling range of 450°F to 750°F (232.22°C to 398.89°C).

[0029] The resid feed pumped to a heater at a pressure of 50 to 550 psig (344.74 to 3792.12 kPag) , where it is heated to a temperature from 480°F (248.89°C) to 520°F (271.11°C). It is then discharged into a coking zone, typically a vertically-oriented, insulated coker drum through an inlet at the base of the drum. Pressure in the drum is usually relatively low, such as 15 to 80 psig (103.42 to 551.58 kPag) to allow volatiles to be removed overhead. Typical operating temperatures of the drum will be between 410°C and 475°C. The hot feedstock thermally cracks over a period of time (the "coking time") in the coker drum, liberating volatiles composed primarily of hydrocarbon products, that continuously rise through the coke mass and are collected overhead. The volatile products are sent to a coker fractionator for distillation and recovery of coker gases, gasoline, light gas oil, and heavy gas oil. In an embodiment, a portion of the heavy coker gas oil present in the product stream introduced into the coker fractionator can be captured for recycle and combined with the fresh feed (coker feed component), thereby forming the coker heater or coker furnace charge. In addition to the volatile products, delayed coking also forms solid coke product.

[0030] Coke bed morphology is typically described in simplified terms such as sponge coke, shot coke, transition coke, and needle coke. Sponge coke, as the name suggests, has a sponge-like appearance with various sized pores and bubbles "frozen into" a solid coke matrix. One key attribute of sponge coke produced by routine coker operating conditions is that the coke is self-supporting, and typically will not fall out of the bottom of an un-headed coker drum, which typically has a head diameter of 6 feet (1.83 m) . The head of the coker drum can be removed either manually or by use of a throttled slide valve. Needle coke refers to a specialty coke that has a unique anisotropic structure. Preparation of coke whose major component is needle coke is known to those skilled in the art and is not the subject of this invention.

[0031] Shot coke is a distinctive type of coke. It is comprised of individual substantially spherical particles that look like BBs. These individual particles range from substantially spherical to slightly ellipsoidal with average diameters of 1 mm to 10 mm. The particles may be aggregated into larger-sized particles, e.g., from tennis-ball size to basketball or larger sizes. The shot coke can sometimes migrate through the coke bed and to the bottom drain lines of the coke drum and slow, or even block, the quench water drain process. While shot coke has a lower economic value than sponge coke, it is the desired product coke for purposes of this invention because its ease of removal from the coker drum results in effectively increasing the process capacity which more than offsets its reduced economic value.

[0032] At times there appears to be a binder material present between the individual shot coke particles, and such a coke is sometimes referred to as "bonded shot" coke. Depending upon the degree of bonding in the bed of shot coke, the bed may not be self-supporting, and can flow out of the drum when the drum is opened. This can be referred to as "fall-out" or "avalanche" and if unexpected it can be dangerous to operating personnel and it can also damage equipment.

[0033] The term "transition coke" refers to coke that has morphology between that of sponge coke and shot coke. For example, coke that has a mostly sponge-like physical appearance, but with evidence of small shot spheres that are just beginning to form as discrete particles in one type of transition coke.

[0034] Coke beds are not necessarily comprised of all of one type of coke morphology. For example, the bottom of a coke drum can contain large aggregates of shot, transitioning into a section of loose shot coke, and finally have a layer of sponge-rich coke at the top of the bed of coke. There are additional descriptors for coke, although less common. Such additional descriptors include: sandy coke which is a coke that after cutting looks to the naked eye much like coarse black beach sand; and needle coke that refers to a specialty coke that has a unique anisotropic structure. Preparation of coke whose major component is needle coke is well known to those having ordinary skill in the art and is not a subject of this invention.

[0035] The term "free-flowing" as used herein means that 500 tons (508.02 Mg) of coke plus its interstitial water in a coker drum can be drained in less than 30 minutes through a 60-inch (152.4 cm) diameter opening .

[0036] It has been discovered that substantially free-flowing shot coke can be produced by the practice of the present invention by insuring that the resid feed is one having a substantially higher initial boiling point than residues conventionally used for delay coking. As previously mentioned, conventional delayed coking resid feeds typically have an initial boiling point from 500°C to 526°C, but the resid feeds of the present invention having an initial boiling point from 549°C to 566°C will unexpectedly produce shot coke over sponge coke.

[0037] Conventional coke processing aids, including an antifoaming agent, can be employed in the process, for example, delayed coking wherein a resid feedstock is air-blown to a target softening point as described in U.S. Patent No. 3,960,704. While shot coke has been produced by conventional methods it is typically agglomerated to such a degree that water-jet technology is needed for its removal. Additives are employed to provide for the formation of the desired,

substantially free-flowing shot coke.

[0038] It is within the scope of this invention to use a suitable additive to aid in the formation of shot coke, preferably substantially free-flowing shot coke. In an embodiment, the additive is an organic soluble metal, such as a metal naphthenate or a metal acetylacetonate, including mixtures thereof. Preferred metals are potassium, sodium, iron, nickel, vanadium, tin, molybdenum, manganese, aluminum, cobalt, calcium, magnesium and mixtures thereof. Potassium, sodium, iron, aluminum and calcium are preferred. Additives in the form of species naturally present in refinery stream can be used. For such additives, the refinery stream may act as a solvent for the additive, which may assist in the dispersing the additive in the resid feed. Additives naturally present in refinery streams include nickel, vanadium, iron, sodium, and mixtures thereof naturally present in certain resid and resid fractions (i.e., certain feed streams). The contacting of the additive and the feed can be accomplished by blending a feed fraction containing additive species (including feed fractions that naturally contain such species) into the feed.

[0039] In another embodiment, the metals-containing additive is a finely ground solid with a high surface area, a natural material of high surface area, or a fine particle/seed producing additive. Such high surface area materials include fumed silica and alumina, catalytic cracker fines, FLEXICOKER cyclone fines, magnesium sulfate, calcium sulfate, diatomaceous earth, clays, magnesium silicate, vanadium-containing fly ash and the like. The additives may be used either alone or in combination.

[0040] It is within the scope of this invention that a metals-free additive be used. Non-limiting examples of substantially metals-free additives that can be used in the practice of the present invention include elemental sulfur, high surface area substantially metals-free solids, such as rice hulls, sugars, cellulose, ground coals, ground auto tires. Other additives include inorganic oxides such as fumed silica and alumina; salts of oxides, such as ammonium silicate and mineral acids such as sulfuric acid and phosphoric acid, and their acid anhydrides.

[0041] Preferably, a caustic species is added to the resid coker feedstock. When used, the caustic species may be added before, during, or after heating in the coker furnace. Addition of caustic will reduce the Total Acid Number (TAN) of the resid coker feedstock and also convert naphthenic acids to metal naphthenates, e.g., sodium naphthenate.

[0042] Uniform dispersal of the additive into the vacuum resid feed is desirable to avoid heterogeneous areas of shot coke formation. Dispersing of the additive is accomplished by any number of ways, for example, by solubilization of the additive into the vacuum resid, or by reducing the viscosity of the vacuum resid prior to mixing in the additive, e.g., by heating, solvent addition, use of organometallic agents, etc. High energy mixing or use of static mixing devices may be employed to assist in dispersal of the additive agent.

[0043] Polarizing light microscopy was used in the examples (illustrated in Figures 1 and 2) for comparing and contrasting structures of green coke (i.e., non-calcined coke) samples.

[0044] At the macroscopic scale, i.e., at a scale that is readily evident to the naked eye, petroleum sponge and shot green cokes are quite different--sponge has a porous sponge-like appearance, and shot coke has a spherical cluster appearance. However, under magnification with an optical microscope, or polarized-light optical microscope, additional differences between different green coke samples may be seen, and these are dependent upon amount of magnification.

[0045] For example, utilizing a polarized light microscope, at a low resolution where 10-micrometer features are discernable, sponge coke appears highly anisotropic, the center of a typical shot coke sphere appears much less anisotropic, and the surface of a shot coke sphere appears fairly anisotropic.

[0046] At higher resolutions, e.g., where 0.5-micrometer features are discernable (this is near the limit of resolution of optical microscopy), a green sponge coke sample still appears highly anisotropic. The center of a shot coke sphere at this resolution is now revealed to have some anisotropy, but the anisotropy is much less than that seen in the sponge coke sample.

[0047] It should be noted that the optical anisotropy discussed herein is not the same as "thermal anisotropy", a term known to those skilled in the art of coking. Thermal anisotropy refers to coke bulk thermal properties such as coefficient of thermal expansion, which is typically measured on cokes which have been calcined, and fabricated into electrodes.

[0048] It is within the scope of this invention that a metals-free additive be used to encourage the production of free-flowing coke, preferably free-flowing shot coke. Non-limiting examples of metals-free additives include elemental sulfur, high surface area substantially metals-free solids, such as rice hulls, sugars, cellulose, ground coals, ground auto tires; inorganic oxides such as fumed silica and alumina; salts of oxides, such as ammonium silicate and mineral acids such as sulfuric acid, phosphoric acid, and acid anhydrides.

[0049] The present invention will be better understood by reference to the following non-limiting examples that are presented for illustrative purposes.

EXAMPLE

[0050] A vacuum resid is produced in a refinery and has had the vacuum overflash reincorporated into it. The refinery is pushing throughput, and consequently the resid boiling point distribution is having an increased amount of the lightest portion. The vacuum resid has an API gravity of 3.7, contains 5.4 wt.% S, and 10.0 wt.% hydrogen. The boiling point

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distribution of the front end as determined by HTSD is as follows in the column labeled "base case vacuum resid" in the table below.

TABLE

	Base Case Vacuum Resid	Resid with second stage vacuum distillation
HTSD Wt.% Off	AEBP, Deg. F (Deg. C)	AEBP, Deg. F (Deg. C)
IBP	554 (290)	910 (487.78)
1	698 (370)	954 (512.22)
2	813 (433.89)	986 (530)
3	858 (458.89)	1003 (539.44)
4	888 (475.56)	1016 (546.67)
5	911 (488.33)	1027 (552.78)
6	929 (498.33)	1036 (557.78)
7	944 (506.67)	1045 (562.78)
8	957 (513.89)	
9	969 (520.56)	
10	980 (526.67)	
11	990 (532.22)	
12	999 (537.22)	
13	1007 (541.67)	
14	1016 (546.67)	
15	1024 (551.11)	
16	1032 (555.56)	
17	1039 (559.44)	
Wt.% 1382 - Deg. F (750°C)	79.9	73.6

[0051] The resid contains 12 wt.% 900°F to 1040°F (482.22°C to 560°C) material. The base case resid is coked in a pilot plant coker with a drum overhead temperature of 820°F (437.78°C), drum overhead pressure of 15 psig (103.42 kPag) and zero recycle. The product coke has a bonded morphology which appears highly fused throughout the bed. Microscopic examination of the coke under cross polarized light reveals mostly small domains (10-20 microns) with coarse mosaic (5-10 micron). Percentage shot coke by the micrographic technique is estimate to be 25%. By a known relationship with a commercial-scale coker, it is projected that this coke would yield a bonded shot that would be self-supporting in the commercial scale coke drum.

[0052] The base case resid then has a second stage vacuum distillation which removes a portion of the lightest components. The boiling point distribution of the resid after distillation is shown in the right column of the table, i.e., after the second stage vacuum distillation, the resid contains 7 wt.% 900°F to 1040°F (482.22°C to 560°C) material.

[0053] The deeper cut resid is coked in the pilot plant coker with a drum overhead temperature of 820°F (437.78°C), a drum overhead pressure of 15 psig (103.42 kPag) , and zero recycle. The product coke is 80% shot coke. Microscopic examination of the coke under cross-polarized light reveals mostly medium/coarse mosaic (2-10 microns). Percentage shot coke by the micrographic technique is estimate to be 75%. By a known relationship with a commercial-scale coker, it is projected that this coke would yield a relatively loose shot that would be non-self supporting in the commercial scale coke drum.

Claims

1. A delayed coking process comprising:

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- preparing a vacuum resid and combining the vacuum resid with a distillate recycle stream;
- conducting said mixture to a heating zone wherein it is heated to an effective coking temperature; and
- conducting said heated mixture from said heating zone to a coking zone wherein vapor products are collected overhead and whereby coke with reduced incidence of hot drums and of a relatively free-flowing nature is formed,

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wherein the vacuum resid has less than 10 wt.% 900°F to 1040°F (482.22°C to 560°C) boiling material as measured by HTSD (High-Temperature Simulated Distillation) and the distillate recycle stream has boiling range within the interval of 450°F (232.22°C) to 750°F (398.89°C) and is in the range of 0 to 7 volume percent.

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2. The process of claim 1, wherein an additive is introduced into the feedstock either prior to heating or just prior to introduction into the coker vessel, which additive is one or more organic soluble, organic insoluble, or non-organic miscible metals-containing additive that is effective for the formation of substantially free-flowing coke.
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3. The process of claim 2, wherein the metal of the additive is selected from potassium, sodium, iron, nickel, vanadium, tin, molybdenum, manganese, cobalt, calcium, magnesium, aluminum and mixtures thereof.
4. The delayed coking process of any preceding claim wherein the distillation recycle is in the range of 0 to 3.5 volume percent.
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5. The process of any preceding claim wherein a manual or automated slide valve is located at the bottom of the coking zone.

Patentansprüche

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1. Verzögertes Verkokungsverfahren, bei dem

- ein Vakuumrückstand hergestellt wird und der Vakuumrückstand mit einem Destillatrückführungsstrom kombiniert wird;
- die Mischung in eine Heizzone geleitet wird, in der sie auf eine effektive Verkokungstemperatur erhitzt wird, und
- die erhitzte Mischung aus der Heizzone in eine Verkokungszone geleitet wird, wo Dampfprodukte als Kopfprodukt aufgefangen werden und wodurch Koks mit reduzierter Häufigkeit von heißen Trommeln und mit relativ freifließender Beschaffenheit gebildet wird,

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wobei der Vakuumrückstand weniger als 10 Gew. % bei 482,22°C bis 560°C (900°F bis 1040°F) siedendes Material aufweist, gemessen durch HTSD (High-Temperature Simulated Distillation; simulierte Hochtemperaturdestillation) und der Destillatrückführungsstrom einen Siedebereich innerhalb des Intervalls von 232,22°C bis 398,89°C (450°F bis 750°F) aufweist und im Bereich von 0 bis 7 Vol.% liegt.

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2. Verfahren nach Anspruch 1, bei dem entweder vor dem Erhitzen oder unmittelbar vor Einbringung in den Verkokungskessel ein Additiv in das Einsatzmaterial eingebracht wird, wobei das Additiv ein oder mehrere organisch lösliches, organisch unlösliches oder nicht-organisch mischbares, Metalle enthaltendes Additiv ist, das zur Bildung von im Wesentlichen freifließendem Koks wirksam ist.

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3. Verfahren nach Anspruch 2, bei dem das Metall des Additivs ausgewählt ist aus Kalium, Natrium, Eisen, Nickel, Vanadium, Zinn, Molybdän, Mangan, Kobalt, Calcium, Magnesium, Aluminium und Mischungen davon.

4. Verzögertes Verkokungsverfahren nach einem der vorhergehenden Ansprüche, bei dem die Destillationsrückführung im Bereich von 0 bis 3,5 Vol.% liegt.

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5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem sich unten in der Verkokungszone ein manueller oder automatischer Schieber befindet.

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Revendications

1. Procédé de cokéfaction retardée, comprenant :

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- la préparation d'un résidu sous vide et la combinaison du résidu sous vide avec un courant de recyclage de distillat ;
- la conduction dudit mélange dans une zone de chauffage où il est porté à une température de cokéfaction efficace ; et
- la conduction dudit mélange chauffé de ladite zone de chauffage dans une zone de cokéfaction où les produits sous forme vapeur sont recueillis à la tête et où un coke présentant une incidence réduite de tambours chauds et d'une nature relativement fluide est formé,

dans lequel le résidu sous vide contient moins de 10 % en poids de matériau d'un point d'ébullition de 900 °F à 1 040 °F (482,22 °C à 560 °C) tel que mesuré par HTSD (High-Temperature Simulated Distillation) et le courant de recyclage de distillat présente un intervalle d'ébullition dans la plage allant de 450 °F (232,22 °C) à 750 °F (398,89 °C) et est dans la plage allant de 0 à 7 pour cent en volume.

2. Procédé selon la revendication 1, dans lequel un additif est introduit dans la matière première avant le chauffage ou juste avant l'introduction dans la cuve de cokéfaction, ledit additif étant un ou plusieurs additifs contenant des métaux, solubles dans les composés organiques, insolubles dans les composés organiques ou non miscibles avec les composés organiques, qui sont efficaces pour la formation de coke essentiellement fluide.
3. Procédé selon la revendication 2, dans lequel le métal de l'additif est choisi parmi le potassium, le sodium, le fer, le nickel, le vanadium, l'étain, le molybdène, le manganèse, le cobalt, le calcium, le magnésium, l'aluminium et leurs mélanges.
4. Procédé de cokéfaction retardée selon l'une quelconque des revendications précédentes, dans lequel le recyclage de distillation est dans la plage allant de 0 à 3,5 pour cent en volume.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel un distributeur à tiroir manuel ou automatisé est situé au fond de la zone de cokéfaction.

FIGURE 1

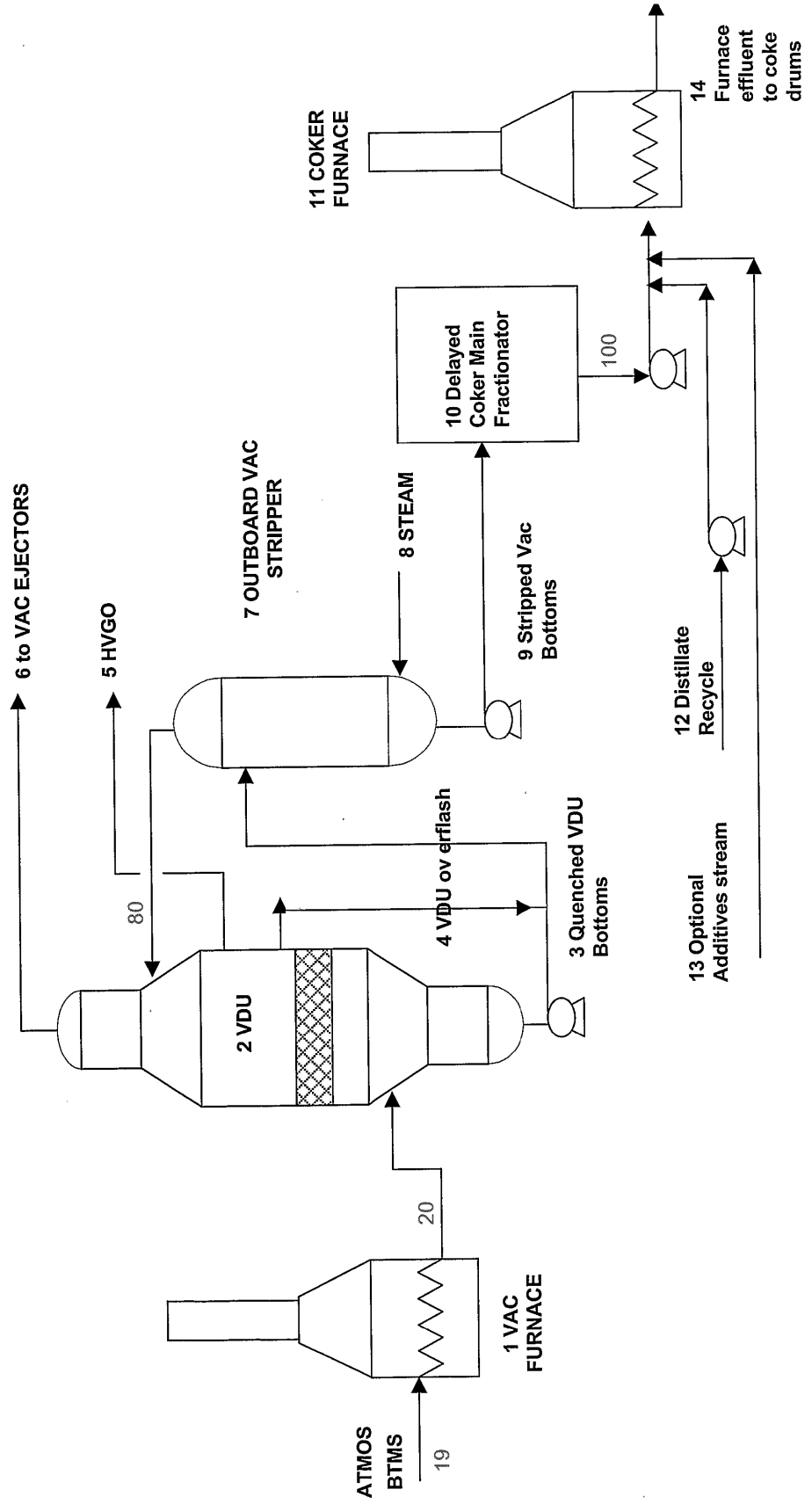


FIGURE 2

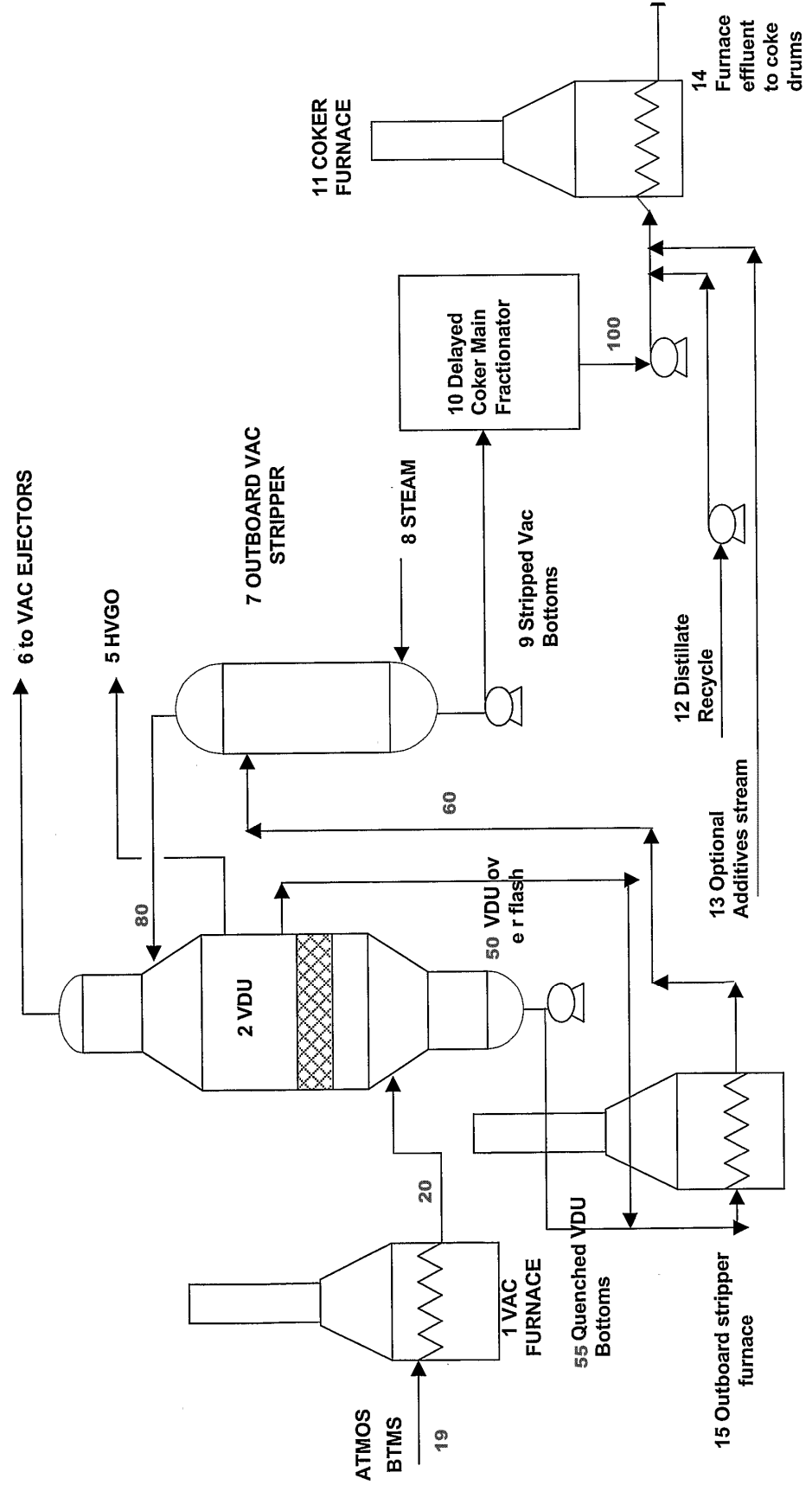


FIGURE 3

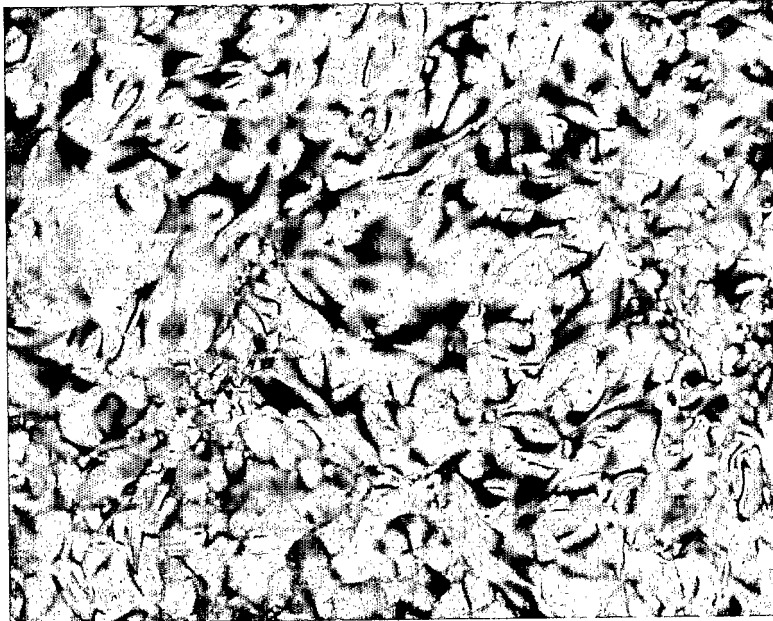
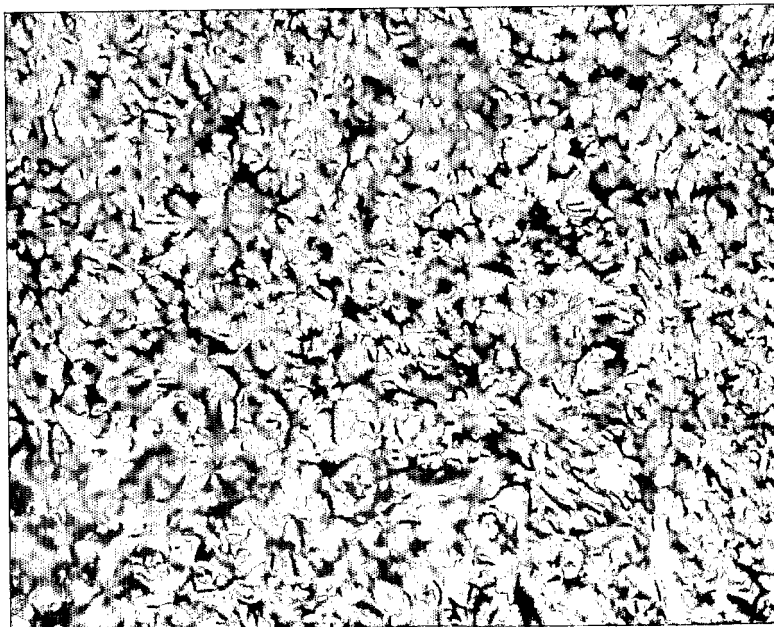


FIGURE 4



REFERENCES CITED IN THE DESCRIPTION

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