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**DELAYED COKING PROCESS FOR PRODUCING FREE-FLOWING
COKE USING AN OVERBASED METAL DETERGENT ADDITIVE**

FIELD OF THE INVENTION

[0001] The present invention relates to a delayed coking process for making substantially free-flowing coke, preferably shot coke. A coker feedstock, such as a vacuum residuum, is heated in a heating zone to coking temperatures then conducted to a coking zone wherein volatiles are collected overhead and coke is formed. An overbased alkaline earth metal detergent additive is added to the feedstock prior to it being heated in the heating zone, prior to its being conducted to the coking zone, or both.

DESCRIPTION OF RELATED ART

[0002] Delayed coking involves thermal decomposition of petroleum residua (resids) to produce gas, liquid streams of various boiling ranges, and coke. Delayed coking of resids 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 resids to more valuable liquid and gaseous products. Although the resulting coke is generally thought of as a low value by-product, it may have some value, depending on its grade, as a fuel (fuel grade coke), electrodes for aluminum manufacture (anode grade coke), etc.

[0003] In the delayed coking process, the feedstock is rapidly heated in a fired heater or tubular furnace. The heated feedstock is then passed to a coking drum that is maintained at conditions under which coking occurs, generally at temperatures above 400°C under super-atmospheric pressures. The heated residuum feed in the coker drum also forms volatile components that are removed

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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 hydrocarbon vapors are purged from the coke drum with steam. The drum is then quenched with water to lower the temperature to less than 300°F (149°C) after which the water is drained. When the cooling and draining steps are complete, the drum is opened and the coke is removed after drilling and/or cutting using high velocity water jets.

[0004] For example, a hole is typically bored through the center of the coke bed using 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.

[0005] Even though the coker drum may appear to be completely cooled, areas of the drum do not completely cool. This phenomenon, sometimes referred to as "hot drum", 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., needle coke, 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 produce predominantly substantially free flowing shot coke in a delayed coker, in order to avoid or minimize hot drums.

SUMMARY OF THE INVENTION

[0006] In an embodiment, there is provided a delayed coking process comprising:

- (a) heating a petroleum resid in a first heating zone, to a temperature below coking temperatures but to a temperature wherein the resid is a pumpable liquid;
- (b) conducting said heated resid to a second heating zone wherein it is heated to coking temperatures;
- (c) conducting said heated resid from said second heating zone to a coking zone wherein vapor products are collected overhead and a coke product is formed;
- (d) introducing into said resid at least one overbased alkaline earth metal detergent additive that is effective for the formation of substantially free-flowing coke, wherein said metals-containing additive is introduced into said resid at a point upstream of the second heating zone, upstream of said coking zone, or both.

[0007] In a preferred embodiment, the coking zone is in a delayed coker drum, and a substantially free-flowing shot coke product is formed.

[0008] In another embodiment, there is provided a delayed coking process comprising:

- (a) contacting a vacuum resid with an effective amount of at least one overbased metal detergent additive at a temperature from 70°C to

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370°C for a time sufficient to disperse the agent uniformly into the feed;

- (b) heating the treated resid to a temperature effective for coking said feed;
- (c) charging said heated treated resid to a coking zone at a pressure from 15 to 80 psig (103.42 to 551.58 kPa) for a coking time to form a bed of hot coke; and
- (d) quenching at least a portion of the bed of hot coke with water.

[0009] In another embodiment a substantially free-flowing shot coke product is formed and removed from the coking zone. The coking zone is preferably a delayed coker drum. The additive can be incorporated and combined with the feed either before the feed is introduced into the heating zone, which is a coker furnace, or it can be introduced into the feed between the coker furnace and coker drum. It is also within the scope of this invention that the additive be introduced into the feed in both locations. The same additive, or additives, can be added independently at each location or a different additive or additives can be added at each location.

[0010] Use of the term "combine" and "contact" are meant in their broad sense, i.e., that in some cases physical and/or chemical changes in the additive and/or the feed can occur in the additive, the feed, or both when additive is present in the feed. In other words, the invention is not restricted to cases where the additive and/or feed undergo no chemical and/or physical change following or in the course of the contacting and/or combining. An "effective amount" of additive is the amount of additive(s) that when contacted with the feed would result in the formation of shot coke in the coking zones, preferably substantially free-flowing shot coke. An

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effective amount typically ranges from 100 to 100,000 ppm (based on the total weight of the metal in the additive and feed), but would depend on the species of additive and its chemical and physical form. While not wishing to be bound by any theory or model, it is believed that the effective amount is less for additives species in a physical and chemical form that lead to better dispersion in the feed than for additive species that are more difficult to disperse. This is why additives that are at least partially soluble in organics, more preferably in the resid feed, are most preferred.

[0011] Uniform dispersal of the additive into the resid feed 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 resid feed, or by reducing the viscosity of the 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.

[0012] Preferably, all or substantially all of the coke formed in the process is substantially free-flowing coke, more preferably, substantially 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

[0013] Figure 1 hereof is an optical micrograph showing coke formed from a sponge coke making resid feed (Heavy Canadian Resid) that contained no additive. The figure shows flow domains ranging in size from 10 to 15 micrometers (typical of sponge coke), and a medium/coarse mosaic ranging from 3 to 10 micrometers (typical of shot coke).

[0014] Figure 2 shows the effect of the use of calcium on coke morphology. The figure is also an optical micrograph, but showing coke formed from a Heavy Canadian Resid containing 500 ppm (0.05 wt.%) calcium in the form of calcium sulfonate overbased detergent. The figure shows a very only a medium/coarse mosaic in the range of 1 to 8 micrometers.

[0015] Figure 3 shows the effect of the use of calcium on coke morphology. The figure is also an optical micrograph, but showing coke formed from a Heavy Canadian Resid containing 500 ppm (0.05 wt.%) calcium in the form of calcium salicylate overbased detergent. The figure shows a very only a medium/coarse mosaic in the range of 1 to 9 micrometers.

[0016] All photomicrographs in these Figures used cross-polarized light, with a viewing area of 170 by 136 micrometers.

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] 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, coal liquids, shale oil, tars from deasphalting units or combinations of these materials. Atmospheric and vacuum topped heavy bitumens can also be employed. Typically, such feedstocks are high-boiling hydrocarbonaceous materials having a nominal initial boiling point of 538°C or higher, an API gravity of 20° or less, and a Conradson Carbon Residue content of 0 to 40 weight percent.

[0019] The resid feed is subjected to delayed coking. Generally, in delayed coking, a residue fraction, such as a petroleum residuum feedstock is pumped to a

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heater at a pressure of 50 to 550 psig (344.74 to 3792.12 kPa), where it is heated to a temperature from 480°C to 520°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 kPa) 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.

[0020] 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.

[0021] Sponge coke, a lower quality coke, is most often formed in refineries. Low quality refinery coker feedstocks having significant amounts of asphaltenes, heteroatoms and metals produce this lower quality coke. If the sulfur and metals content is low enough, sponge coke can be used for the manufacture of electrodes for the aluminum industry. If the sulfur and metals content is too high, then the coke can be used as fuel. The name "sponge coke" comes from its porous, sponge-like appearance. Conventional delayed coking processes, using the preferred vacuum resid feedstock of the present invention, will typically produce sponge coke, which is produced as an agglomerated mass that needs an extensive removal process including drilling and water-jet technology. As discussed, this considerably complicates the process by increasing the cycle time.

[0022] Shot coke is considered the lowest quality coke. The term "shot coke" comes from its shape that is similar to that of BB-sized [1/16 inch to 3/8 inch (.16 cm to .95 cm) balls. Shot coke, like the other types of coke, has a tendency to agglomerate, especially in admixture with sponge coke, into larger masses, sometimes larger than a foot in diameter. This can cause refinery equipment and processing problems. Shot coke is usually made from the lowest quality high resin-asphaltene feeds and makes a good high sulfur fuel source, particularly for use in cement kilns and steel manufacture. There is also another coke, which is referred to as "transition coke" and refers to a coke having a morphology between that of sponge coke and shot coke or composed of mixture of shot coke bonded to sponge coke. For example, coke that has a mostly sponge-like physical appearance, but with evidence of small shot spheres beginning to form as discrete shapes.

[0023] It has been discovered that substantially free-flowing shot coke can be produced by treating the residuum feedstock with one or more overbased alkaline

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earth metal detergent additives of the present invention. The additives are those that enhance the production of shot coke during delayed coking. A resid feed is subjected to treatment with one or more additives, at effective temperatures, i.e., at temperatures that will encourage the additives' dispersal in the feed stock. Such temperatures will typically be from 70°C to 500°C, preferably from 150°C to 370°C, more preferably from 185°C to 350°C.

[0024] Overbased alkali and alkaline-earth metal-containing detergents are employed as the additive of the present invention. These detergents are exemplified by oil-soluble or oil-dispersible basic salts of alkaline earth metals with one or more of the following acidic substances (or mixtures thereof): (1) sulfonic acids, (2) carboxylic acids, (3) salicylic acids, (4) alkylphenols, (5) sulfurized alkylphenols, (6) organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage. Such organic phosphorus acids include those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of calcium and magnesium. The salts for use in this embodiment are preferably basic salts having a TBN of at least 50, preferably above 100, and most preferably above 200. In this connection, TBN is determined in accordance with ASTM D-2896-88.

[0025] The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing

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agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature of 50°C, and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve alcohol, Carbitol alcohol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-betanaphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60°C to 200°C.

[0026] Examples of suitable alkaline earth metal-containing detergents include, but are not limited to, the basic or overbased salts of such substances as calcium phenates, magnesium phenates, sulfurized calcium phenates, and sulfurized magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility; calcium sulfonates, and magnesium sulfonates wherein each sulfonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility; the calcium and magnesium salts of hydrolyzed phosphosulfurized olefins having 10 to 2,000 carbon atoms or of hydrolyzed phosphosulfurized alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2,000 carbon atoms; calcium and magnesium salts of aliphatic

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carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids; and many other similar alkaline earth metal salts of oil-soluble organic acids. Mixtures of basic or overbased salts of two or more different alkaline earth metals can be used. Likewise, basic or overbased salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more calcium phenates with one or more calcium sulfonates) can also be used.

[0027] As is well known, overbased metal detergents are generally regarded as containing overbasing quantities of inorganic bases, probably in the form of micro dispersions or colloidal suspensions. Thus the terms "oil-soluble" and "oil-dispersible" are applied to these metal-containing detergents so as to include metal detergents wherein inorganic bases are present that are not necessarily completely or truly oil-soluble in the strict sense of the term, inasmuch as such detergents when mixed into base oils behave in much the same way as if they were fully and totally dissolved in the oil.

[0028] Collectively, the various basic or overbased detergents referred to hereinabove, have sometimes been called, quite simply, basic alkali metal or alkaline earth metal-containing organic acid salts.

[0029] The precise conditions at which the resid feedstock is treated with the additive is feed and additive dependent. That is, the conditions at which the feed is treated with the additive are dependent on the composition and properties of the feed to be coked and the additive used. These conditions can be determined conventionally. For example, several runs would be made with a particular feed containing an additive at different times and temperatures followed by coking in a bench-scale reactor such as a Microcarbon Residue Test Unit (MCRTU). The resulting coke is then analyzed by use of an optical and/or polarized light

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microscopy as set forth herein. The preferred coke morphology (i.e., one that will produce substantially free-flowing coke) is a coke microstructure of discrete microdomains having an average size of 0.5 to 10 μm , preferably from 1 to 5 μm , somewhat like the mosaic shown in Figures 1, 2 and 3 hereof. Coke microstructure that represents coke that is not free-flowing shot coke is shown in Figure 1 hereof, showing a coke microstructure that is composed substantially of non-discrete, or substantially large flow domains up to 60 μm or greater in size, typically from 10 to 60 μm .

[0030] Conventional coke processing aids, including an antifoaming agent, can be employed in the process of the present invention. While shot coke has been produced by conventional methods, it is typically agglomerated to such a degree that water-jet technology is still needed for its removal.

[0031] In one embodiment of the present invention, the resid feedstock is first treated with an additive that encourages the formation of substantially free-flowing coke. By keeping the coker drum at relatively low pressures, much of the evolving volatiles can be collected overhead, which prevents mesophase formation and undesirable agglomeration. The recycle ratio ("CFR") is the volumetric ratio of furnace charge (fresh feed plus recycle oil) to fresh feed to the continuous delayed coker operation. Delayed coking operations typically employ recycles of 5 vol.% to 25 vol.% (CFRs of 1.05 to 1.25). In some instances there is 0 recycle and sometimes in special applications recycle up to 200%. CFRs should be low to aid in free flowing shot coke formation, and preferably no recycle should be used.

[0032] While not wishing to be bound to any specific theory or model, the additive or mixture of additives employed are believed to function via one or more of the following pathways: a) as dehydrogenation and cross-linking agents when

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metals present in the feed are converted into metal sulfides that are catalysts for dehydrogenation and shot coke formation; b) agents that add metal-containing species into the feed that influence or direct the formation of shot coke or are converted to species, e.g., metal sulfides, that are catalysts for shot coke formation; c) as particles that influence the formation of shot coke by acting as microscopic seed particles for the shot coke to be formed around, as Lewis acid cracking and cross-linking catalysts, and the like. Additives may also alter or build viscosity of the plastic mass of reacting components so that shear forces in the coker furnace, transfer line and coke drum roll the plastic mass into small spheres. Even though different additives and mixtures of additives may be employed, similar methods can be used for contacting the additive(s) with the feed.

[0033] Typically, additive(s) are conducted to the coking process in a continuous mode. If needed, the additive could be dissolved or slurried into an appropriate transfer fluid, which will typically be solvent that is compatible with the resid and in which the additive is substantially soluble. The fluid mixture or slurry is then pumped into the coking process at a rate to achieve the desired concentration of additives in the feed. The introduction point of the additive can be, for example, at the discharge of the furnace feed charge pumps, or near the exit of the coker transfer line. There can be a pair of mixing vessels operated in a fashion such that there is continuous introduction of the additives into the coking process.

[0034] The rate of additive introduction can be adjusted according to the nature of the resid feed to the coker. Feeds that are on the threshold of producing shot coke may require less additive than those which are farther away from the threshold.

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[0035] For additives that are difficult to dissolve or disperse in resid feeds, the additive(s) are transferred into the mixing/slurry vessel and mixed with a slurry medium that is compatible with the feed. Non-limiting examples of suitable slurry mediums include coker heavy gas oil, water, etc. Energy may be provided into the vessel, e.g., through a mixer for dispersing the additive.

[0036] For additives which can be more readily dissolved or dispersed in resid feeds, the additive(s) are transferred into the mixing vessel and mixed with a fluid transfer medium that is compatible with the feed. Non-limiting examples of suitable fluid transfer mediums include warm resid (temp. between 150°C to 300°C), coker heavy gas oil, light cycle oil, heavy reformat, and mixtures thereof. Cat slurry oil (CSO) may also be used also, though under some conditions it may inhibit the additives' ability to produce loose shot coke. Energy may provided into the vessel, e.g., through a mixer, for dispersing the additive into the fluid transfer medium.

[0037] The present invention will be better understood by reference to the following non-limiting examples that are presented for illustrative purposes.

EXAMPLES

General Procedures for Addition of Additives into Vacuum Resid Feeds

[0038] The resid feed is heated to 70-150°C to decrease its viscosity. The additive (in weight parts per million, wppm) is then added slowly, with mixing, for a time sufficient to disperse and/or solubilize the additive(s) (a "dispersing time"). For laboratory experiments, it is generally preferred to first dissolve and/or disperse the additive in a solvent, e.g., toluene, tetrahydrofuran, or water, and blend it with stirring into the heated resid, or into the resid to which some solvent has been added

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to reduce its viscosity. The solvent can then be removed. In a refinery, the additive contacts the resid when it is added to or combined with the resid feed. As discussed, 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. To assure maximum dispersion of the additive into the vacuum resid feed, the reaction mixture can be heat soaked.

[0039] The following tests were conducted using various additives to a resid feed. Additive concentration, heat soak time, and the resulting coke morphology as determined from optical micrographs are set forth in Tables 1 below. Control samples of resid with no additive was used by way of comparison.

TABLE 1

Resid Feed	Additive (wppm of Metal)	Microstructure of MCR Coke	Type of Coke Indicated
<u>Heavy Canadian</u>	<u>None</u>	Small Domains (10-15 μ m) and Medium/Coarse Mosaic (3-10 μ m)	<u>Transition</u>
<u>Heavy Canadian</u>	<u>Calcium Sulfonate OB Detergent (500)</u>	<u>Medium/Coarse Mosair (1-8 μ m)</u>	<u>Shot</u>
<u>Heavy Canadian</u>	<u>Calcium Salicylate OB Detergent (500)</u>	<u>Medium/Coarse Mosaic (1-9 μ m)</u>	<u>Shot</u>

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CLAIMS:

1. A delayed coking process comprising:
 - (a) heating a petroleum resid in a first heating zone, to a temperature below coking temperatures but to a temperature wherein the resid is a pumpable liquid;
 - (b) conducting said heated resid to a second heating zone wherein the heated resid is heated to coking temperatures;
 - (c) conducting said heated resid from said second heating zone to a coking zone wherein vapor products are collected overhead and a coke product is formed; and
 - (d) introducing into said resid at least one overbased metal detergent additive that is effective for the formation of substantially free-flowing coke, wherein said overbased metal detergent additive is introduced into said resid at a point upstream of the second heating zone, upstream of said coking zone, or both.
2. A delayed coking process comprising:
 - (a) contacting a vacuum resid with an effective amount of at least one overbased alkaline earth metal detergent additive at a temperature from 70°C to 370°C for a time sufficient to disperse the agent uniformly into the feed;
 - (b) heating the treated resid to a temperature effective for coking said feed;

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- (c) charging said heated treated resid to a coking zone at a pressure from 15 to 80 psig (103.42 to 551.58 kPa) for a coking time to form a bed of hot coke; and
 - (d) quenching at least a portion of the bed of hot coke with water.
- 3. The process of claim 1 wherein the residuum feedstock is vacuum resid.
- 4. The process of any preceding claim wherein at least a portion of the additive is soluble in the feedstock.
- 5. The process of any preceding claim wherein the additive is one or more of calcium phenate, magnesium phenate, sulfurized calcium phenate, and magnesium phenate, wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility.
- 6. The process of any preceding claim wherein the additive is one or more of calcium sulfonates, and magnesium sulfonates, wherein each sulfonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility.
- 7. The process of any preceding claim wherein the additive is one or more of calcium salicylates, and magnesium salicylates, wherein the aromatic moiety is substituted by one or more aliphatic substituents to impart hydrocarbon solubility.
- 8. The process of any preceding claim wherein the additive is selected from the calcium and magnesium salts of hydrolyzed phosphosulfurized olefins having 10 to 2,000 carbon atoms or of hydrolyzed phosphosulfurized

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alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2,000 carbon atoms.

9. The process of any preceding claim wherein the additive is one or more of calcium and magnesium salts of aliphatic carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids.
10. The process of any preceding claim wherein the coke produced is substantially a shot coke.
11. The process of claim 1 wherein said overbased metal detergent additive is introduced into said vacuum resid at a point upstream of the first heating zone, upstream of the second heating zone, or both.