# DELAYED COKING PROCESS FOR PRODUCING ANISOTROPIC FREE-FLOWING SHOT COKE

## FIELD OF THE INVENTION

**[0001]** The present invention relates to a delayed coking process wherein substantially all of the coke produced is free-flowing anisotropic shot coke. A coker feedstock, such as a vacuum residuum, is treated with an oxidizing agent, such as air, to increase the level of one or more of asphaltenes, polars, and organically bound oxygen groups. The oxidized feedstock is then heated to coking temperatures and passed to a coker drum for an effective amount of time to allow volatiles to evolve and to produce a substantially free-flowing anisotropic shot coke.

## DESCRIPTION OF RELATED ART

**[0002]** Delayed coking has been practiced for many years. The process broadly 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 gas products. Although the resulting coke is generally thought of as a low value by-product, it does have some value as a fuel (fuel grade), electrodes for aluminum manufacture (anode grade), etc.

**[0003]** In the delayed coking process, the feedstock is rapidly heated in a fired heater or tubular furnace. It is then passed to a coking drum that is maintained at conditions under which coking occurs, generally at temperatures above about 400°C under super-atmospheric pressures. The heated residuum feed further decomposes in the coker drum to form volatile components that are 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 hydrocarbon vapors are purged from the coke drum with steam. The drum is then quenched with water to lower the temperature to about 200-300°F 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.

**[0004]** 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 cut the coke from the drum. The coke removal process adds considerably to the throughput time of the process. That is, since it takes approximately 1 to 6 hours, typically about 3 hours to drill-out and remove the resulting coke mass, the coker drum turn-around time and process costs are increased. Thus, it would be desirable to produce a free-flowing coke in the coker drum that would not require the expense and time associated with conventional agglomerated coke mass removal.

**[0005]** Further, even though the coking drum may appear to be completely cooled, occasionally, a problem arises which is referred to in the art as a "hot drum." This problem occurs when areas of the drum do not completely cool. This may be the result of a combination of morphologies of coke in the drum resulting in a non-uniform drum. The drum may contain a combination of more than one type of solid coke product, i.e., needle coke, sponge coke and shot coke. BB-sized shot coke may cool faster than another coke, such as large shot coke masses or sponge coke. Avoiding "hot drums" is another reason for producing predominantly shot coke in a delayed coker.

[0006] Attempts have been made to produce predominantly, or substantially all of a single type of coke during delayed coking. For example, U.S. Patent No. 5,258,115, which is incorporated herein by reference, teaches a delayed coking process wherein spent caustic is introduced into a delayed coker feed, or into the coker drum itself, to produce shot coke to help alleviate the hot drum problem. It also reduces cooling time.

[0007] Further, U.S. Patent No. 3,960,704, which is also incorporated herein by reference, teaches a delayed coking process wherein isotropic coke is the product. Isotropic coke is coke that has thermal expansion approximately equal along the three crystalline axes. This is achieved by air blowing a petroleum resid feedstock to a certain softening point and running the coking process at relatively high recycle ratios and preferably with a diluent oil.

[0008] Although delayed coking has been in commercial use for many years, there still remains a need in the art for improvements that can shorten the coke removal time.

## SUMMARY OF THE INVENTION

[0009] In accordance with the present invention there is provided a delayed coking process wherein substantially all of the coke produced is substantially free flowing anisotropic shot coke, which process comprises:

a) contacting a vacuum resid feed with an oxidizing agent at a temperature from about 150°C to about 375°C for an effective amount of time to significantly increase the amount of asphaltenes and organically bound oxygen in the resid;

b) heating said oxidized resid feed to a temperature effective for coking said feed;

c) charging said heated oxidized resid to a delayed coker drum at a pressure from about 15 to 50 psig for an effective amount of time to produce volatiles and anisotropic substantially free-flowing shot coke;

d) removing at least a portion of said volatiles overhead; and

e) removing the anisotropic substantially free-flowing shot coke product from the coker drum.

**[0010]** Also in accordance with the present invention there is provided a delayed coking process comprising:

a) contacting a vacuum resid with an oxidizing agent at a temperature from about 150°C to about 375°C for an effective amount of time to significantly increase the amount of asphaltenes and/or polars and other organically bound oxygen groups in the resid;

b) heating said oxidized resid to a temperature effective for coking said feed;

c) charging said heated oxidized resid to a delayed coker drum at a pressure from about 15 to 50 psig for an effective amount of time to produce volatiles and a substantially free-flowing anisotropic shot coke;

d) removing at least a portion of the volatiles overhead;

e) quenching the remaining hot coke bed with water;

f) removing the resulting anisotropic substantially free-flowing shot coke product from the coker drum.

[0011] In one preferred embodiment of the present invention, the oxidizing agent is air.

[0012] In another preferred embodiment of the present invention a caustic can be added to the oxidized resid coker feedstock before, during, or after heating in the coker furnace.

## BRIEF DESCRIPTION OF THE FIGURE

[0013] Figure 1 hereof is a cross polarized light photomicrograph of coke resulting from a San Joaquin Valley vacuum residuum that was not treated with an oxidizing agent prior to coking. The area of view is 170 microns by 136 microns.

[0014] Figure 2 hereof is a photomicrograph of coke resulting from a San Joaquin Valley vacuum residuum that was treated with air for 3 hours at a temperature from 185°C to 225°C prior to coking. The area of view is 170 microns by 136 microns.

## DETAILED DESCRIPTION OF THE INVENTION

[0015] Feedstocks suitable for the delayed coking process of the present invention are petroleum vacuum residua. 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 $SO_2$, $SO_3$, and $NO_x$ upon combustion of the petroleum residuum. Nitrogen compounds also have a tendency to deactivate catalytic cracking catalysts. Typical examples of coker petroleum feedstocks which are contemplated for use in the present invention, include 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 or combinations of these materials. Atmospheric and vacuum topped heavy bitumens can also be employed. Typically, these feedstocks are high-boiling hydrocarbonaceous materials having a nominal initial boiling point of about 538°C or higher, an API gravity of about 20° or less, and a Conradson Carbon Residue content of about 0 to 40 weight percent.

[0016] The coking process of the present invention is delayed coking, which is well known in the art. Generally, in the delayed coking process, a bottoms fraction, such as a petroleum residuum chargestock is pumped to a heater at a pressure of about 50 to 550 psig, where it is heated to a temperature from about 480°C to about 520°C. It is then discharged into 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 about 15 to 50 psig to allow volatiles to be removed overhead. Typical operating temperatures of the drum will be between about 410°C and 475°C. The hot feedstock thermally cracks over a period of time in the coker drum, liberating volatiles composed primarily of hydrocarbon products, that continuously rise through the coke mass and are collected over-head. The volatile products are sent to a coker fractionator for distillation and recovery of coker gases, gasoline, light gas oil, and heavy gas oil. At least a portion of the heavy coker gas oil present in the product stream introduced into

the coker fractionator is captured for recycle and combined with the fresh feed (coker feed component), thereby forming the coker heater or coker furnace charge.

[0017] There are generally three different types of solid delayed coker products that have different values, appearances and properties. These are 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 conductivity and is used in electric arc steel production. It is relatively low in sulfur and metals and is 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 as opposed to the asphaltenes and resins.

[0018] Sponge coke, a lower quality coke, sometimes called "regular 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. This adds considerable time and costs to the process.

[0019] Shot coke has been considered the lowest quality coke because it has the highest sulfur and metals content, the lowest electrical conductivity and is the most difficult to grind. The term “shot coke” comes from its shape which is

similar to that of BB sized (about 1/16 inch to 3/8 inch) 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. The inventors hereof have unexpectedly found that substantially free-flowing anisotropic shot coke can be produced by first treating the residuum feedstock with an oxidizing agent to substantially increase the contents of its asphaltene, and/or polars fractions, such as those containing organically bound oxygen like ketones, carboxylic acids, etc. The residuum feed is subjected to the oxidizing agent, preferably air, at effective temperatures, i.e., at temperatures that will encourage the formation of asphaltenes and organically bound oxygen groups to form. Such temperatures will typically be from about 150°C to about 325°C, preferably from about 185°C to about 280°C, more preferably from about 185°C to about 250°C. The oxidizing agent can be in any suitable form including gas, liquid or solid. Non-limiting examples of oxidizing agents that can be used in the practice of the present invention include air, oxygen, ozone, hydrogen peroxide, organic peroxides, hydroperoxides, inorganic peracids, inorganic oxides and peroxides and salts of oxides, sulfuric acid, and nitric acid. Preferred is air. It is to be understood that after the resid is treated with the oxidizing agent, a caustic, preferably a spent caustic, may optionally be added. The spent caustic can also be added before, during, or after the oxidized resid is passed to the coker furnace and heated to coking temperatures. The caustic will be an alkali-metal material preferably a spent caustic soda and/or potash stream that is typically used in various refinery processes. Such spent caustic streams typically contain one or more of sodium and potassium, sulfur, and other wastes, including organic contaminants that vary depending on the hydrocarbon source but can be organic acids, dissolved hydrocarbons, phenols, naphthenic acids, and

salts of organic acids. The spent caustic stream will usually have a relatively high water content, typically about 50 wt% to 95 wt% water, more typically from about 65 wt% to about 80 wt%.

**[0020]** The precise conditions at which the residuum feedstock is treated with the oxidizing agent is feed dependent. That is, the conditions at which the feed is treated with the oxidizing agent is dependent on the composition and properties of the feed to be coked. These conditions can be determined by one having ordinary skill in the art without undue experimentation. Several runs are made with a particular feed at different oxidizing times and temperatures followed by coking. The resulting coke is then analyzed by use of a micro-carbon test procedure and microscopy as set forth in the examples hereto. The desired coke morphology that will produce substantially free-flowing coke is a coke microstructure of discrete micro-domains having an average size of about 1 to 10 μm, preferably from about 1 to 5 μm, somewhat like a mosaic (Figure 2 hereof). Coke microstructure that represents coke that is not free-flowing anisotropic shot coke is the microstructure represented in Figure 1 hereof that show a coke microstructure that is composed substantially of non-discrete, or substantially large flow domains up to about 60 μm or greater in size, typically from about 10 to 60μm.

**[0021]** U.S. Patent No. 3,960,704 which is incorporated herein by reference, teaches delayed coking wherein a resid feedstock is air blown to a target softening point. The air blown feed is then passed to delayed coking process that is operated at conditions that will favor the formation of isotropic coke. That is, coke particles having substantially equal thermal expansion properties along the three major crystalline axes. This '704 patent requires relatively high recycle ratios and an additional amount of oil as a diluent to produce a pellet-type isotropic coke. For example, the recycle ratio of this '704 patent is from

about 1 to 5. This correlates to 100% to 500% recycle based on fresh feed. Although up to about 15% recycle can be used in the practice of the present invention it is preferred that no recycle be used. The presently claimed delayed coking process does not produce isotropic pellet-type coke - it produces substantially free-flowing anisotropic shot coke. Also, the shot coke that results from the practice of the present invention can be easily removed from the coker drum without drilling or the use of water-jet cutting technology. 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.

**[0022]** It is important to the practice of the present invention that the resid feedstock be first treated with an oxidizing agent to substantially increase its level of asphaltenes, polars, and organically bound oxygen groups that encourages the formation of anisotropic substantially free-flowing shot coke. It is also important to the practice of the present invention that the coker drum be kept at relatively low pressures in order to allow as much of the evolving volatiles to be collected overhead. This helps prevent agglomeration of the resulting shot coke. The recycle ratio, that is the volumetric ratio of furnace charge (vacuum resid plus recycle oil) to fresh feed to the continuous delayed coker operation should also be kept as low as possible. The use of recycle ratio for delayed coking is taught in more detail in U.S. Patent No. 3,116,231 which is incorporated herein by reference.

**[0023]** The present invention will be better understood by reference to the following examples that are presented for illustrative purposes only and are not to be taken as limiting the invention in any way.

Examples

[0024] General Procedure: Approximately 180 g each of five different petroleum residua were added to a 500 cc round bottom flask equipped with a Therm-O-Watch controller, a mechanical blade stirrer, and a condenser attached to a Dean-Stark trap to recover any light ends and water generated during the reaction. The residuum was heated to 180°C at which time air was introduced into the hot residuum feed under its surface by means of a sparger tube. The temperature was raised and controlled to between 220°C to 230°C and the flow rate of air was controlled at 0.675 $ft^3$/hr for three hours or as required depending on the desired degree of oxidation. The sparger tube was removed after the desired time and the flask was allowed to cool to room temperature.

[0025] Deasphalting Procedure: A mixture of fresh or oxidized coker feed and n-heptane were added to a 250 cc round bottom flask in a ratio of 1 part feed to 8 parts n-heptane and allowed to stir for 16 hours at room temperature. The mixture was then filtered through a coarse Buchner funnel to separate the precipitated asphaltenes. The solids were dried in a vacuum oven at 100°C overnight. The heptane was evaporated from the oil/heptane mixture to recover the deasphalted oil. The amount of asphaltenes produced from the oxidized feed was compared to the amount generated from the starting residuum under the same deasphalting procedure. The results are presented in the following table:

TABLE 1. Enhancements of Feed Properties by Air Oxidation Favors Formation of Anisotropic Loose Shot Coke

| | Midwest | | San Joaquin Valley | | LA Sweet | | Maya | | Heavy Canadian | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Raw | Oxidized | Raw | Oxidized | Raw | Oxidized (6 hr) | Raw | Oxidized | Raw | Oxidized |
| Asphaltenes, wt% | 8.9 | 27.0 | 13.6 | 37.8 | 0 | 31.7 | 40.9 | 41.0 | 19.4 | 28.3 |

[0026] Microcarbon residue tests were performed on the above feeds to generate cokes to be evaluated by microscopy. The following is the procedure used for the microcarbon tests:

| Heating Profile | Time (min) | $N_2$ Flow (cc/min) |
|---|---|---|
| Heat from room temperature to 100°C | 10 | 66 |
| Heat from 100°C to 300°C then to 500°C | 30 | 66/19.5 |
| Hold at 500°C | 15 | 19.5 |
| Cool to room temperature | 40 | 19.5 |

[0027] Figures 1 and 2 are cross polarized light photomicrographs showing the microstructure of the resulting coke from a San Joaquin Valley residuum for both the untreated residuum and the residuum treated with air in accordance with the above procedure. The viewing area for both is 170 microns by 136 microns. The untreated residuum resulted in a coke with a microstructure that was not discrete fine domains. The domains were relatively large (10-30 μm) flow domains. This indicates that a mixture of shot coke and sponge coke will be produced in the coker drum of a delayed coker. The microstructure (Figure 2) of the resulting coke from the residuum sample that was first air oxidized shows relatively fine (2-5 μm) discrete fine domains indicating that free-flowing shot coke will be produced in the coker drum of a delayed coker. Following the same procedure, the following changes in flow domain sizes were observed: a Midwest Vacuum Resid (10-50 μm to 2-3 μm), a Louisiana Sweet Vacuum Resid (20-60 μm to 2 to 5 μm) in six hours, a Maya Vacuum Resid (2-10 μm - no change), and a Heavy Canadian Vacuum Resid (10-20 μm to 2-10 μm).

CLAIMS

1. A delayed coking process wherein substantially all of the coke produced is substantially free-flowing anisotropic shot coke, which process comprises:

a) contacting a vacuum residuum feed with an oxidizing agent at a temperature from about 150°C to about 325°C for an effective amount of time to significantly increase the amount of one or more of asphaltenes, polars, and organically bound oxygen groups in the resid;

b) heating said oxidized resid feed to a temperature effective for coking said feed;

c) charging said heated oxidized resid to a delayed coker drum at a pressure from about 103 to about 345 kPag (15 to 50 psig) for an effective amount of time to produce volatiles and anisotropic substantially free-flowing shot coke;

d) removing at least a portion of said volatiles overhead; and

e) removing the product anisotropic substantially free-flowing shot coke from the coker drum.

2. The process of claim 1 further comprising quenching the remaining hot coke bed with water.

3. The process according to claims 1 or 2 wherein the oxidizing agent is selected from air, oxygen, ozone, hydrogen peroxide, organic peroxides, hydroperoxides, inorganic peracids, inorganic oxides and peroxides and salts of oxides, sulfuric acid, and nitric acid.

4. The process of claim 3 wherein the oxidizing agent is selected from air, oxygen, and ozone.

5. The process of claim 3 wherein the oxidizing agent is air.

6. The process according to any of the previous claims wherein the temperature at which the residuum is treated with the oxidizing agent is from about 185°C to about 280°C.

7. The process according to any of the previous claims wherein an aqueous caustic is added to the residuum before, during, or after being heated to coking temperatures.

8. The process of claim 7 wherein an aqueous caustic is added to the residuum after being heated to coking temperatures.

9. The process according to any of the previous claims wherein the particle size of the shot coke is from about 1.58 mm to about 9.52 mm (1/16 inch to 3/8 inch).

10. The process according to any of the previous claims wherein the microstructure of the resulting substantially free-flowing anisotropic coke is characterized as being comprised of substantially discrete domains from about 1 to 10 μm in average size.

11. The process according to any of the previous claims wherein the substantially free-flowing shot coke is removed from the coker drum without drilling or the use of water-jet cutting technology.