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PETROLEUM COKE PRODUCTION

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ABSTRACT OF THE DISCLOSURE

Petroleum sponge coke is produced from hydrocarbon feedstock which forms shot coke in a conventional delayed coking process by blending the feedstock with another feedstock relatively free of asphaltene to form a blended feedstock having an asphaltene content below about 15%.

BACKGROUND OF THE INVENTION

This invention relates to a process for the production of petroleum coke, more particularly sponge-type petroleum coke.

In a conventional petroleum coking operation, the coke which is produced is either a dense, hard particulate product with very low internal porosity coke or a porous low density product called sponge coke. Shot coke is used principally as fuel and in steep production. The latter is used in the manufacture of graphite and carbon electrodes used in the aluminum industry. The former type of coke does not produce satisfactory electrodes because their use results in electrodes with high resistivities. The pitch conventionally used to form the massive carbon bodies used as electrodes in aluminum production has poor binding characteristics for shot coke and results in a product with low compressive and tensile strengths. Oxidation of the electrode during aluminum production causes spalling of major pieces, resulting in shorter electrode life and difficulties in operation because of the portions of the electrode dropping into the cell.

Thus, sponge petroleum coke is ordinarily preferred over shot petroleum coke as a product of a coking operation because of the greater economic value of sponge coke. Therefore, in conventional coking operations, unless a feedstock is employed which from past experience is known to produce only shot coke, coking conditions are usually selected which promote the formation of sponge coke. However, it is well known that certain feedstocks will produce only shot coke, irrespective of the process conditions employed in the coking operation.

A third type of coke, i.e., needle coke, is produced by employing special coking procedures. See The Oil and Gas Journal, pp. 73–77, Sept. 14, 1970. This invention is not related to this specialized coking operation nor to the coke produced by that process.

OBJECTS OF THE INVENTION

It is an object of this invention to provide a method whereby the production of sponge coke in a conventional coking operation is assured. Another object is the provision of a process whereby feedstocks which heretofore could not produce sponge coke can be employed in the production thereof. Other objects will be apparent to those skilled in the art to which this invention pertains.

SUMMARY OF THE INVENTION

According to this invention, sponge coke is produced from coking feedstock which normaly produces shot coke in a conventional coking operation by:

(a) measuring the asphaltene content of a coking feedstock which produces shot coke in a conventional coking process;

(b) using a mixture of that feedstock and a hydrocarbon bottoms having an asphaltene content below about 8%, in a proportion such that the total asphaltene content of the mixture is below about 13% as the coking feedstock in a conventional coking operation.

DETAILED DISCUSSION

It has been found that coking feedstocks which usually or always produce shot coke in a conventional coking operation can be used to consistently produce sponge coke if blended with a hydrocarbon bottoms, e.g., having a low asphaltene content, e.g., less than 8%, preferably 0–5%, more preferably 0–2%, in a proportion such that the resulting mixture of feed stocks has an asphaltene content of less than about 13%, preferably less than 10%.

The maximum asphaltene content of the mixture of feed stocks employed in the coking process of this invention which will still result in the production of shot coke depends in part on the coking conditions employed. As is known, in a conventional coking operation conditions can be selected which promote the formation of sponge coke, e.g., higher pressures, lower feed rates, longer residence time and higher recycle ratios. Because the desired product of the coking process of this invention is sponge coke, those conventional coking conditions which promote the production of sponge coke should therefore be employed. The higher the asphaltene content of the feedstock mixture employed in this process, the more important it is that conditions promoting sponge coke formation be employed.

Petroleum coking feedstock which normally produce shot coke in a conventional coking operation are those having asphaltene contents above about 13%, e.g.,

(a) atmospheric distilled virgin residual hydrocarbons;
(b) vacuum distilled virgin residual hydrocarbons;
(c) solvent extracted residual hydrocarbons; and
(d) hydrocarbon asphalts.

Of these, those having asphaltene contents of about 13 to 25% are preferred as feedstocks for the coking process of this invention, especially atmospheric and vacuum distilled virgin residual hydrocarbons.

Hydrocarbon bottoms which have low asphaltene contents and which can be used with the above-described feedstocks which normally produce shot coke are petroleum hydrocarbons, e.g.,

(a) pressure tars;
(b) aromatic oils;
(c) deasphalted hydrocarbons;
(d) synthetic hydrocarbon residues; and
(e) the residual aliphatic hydrocarbons of a crude oil which is substantially asphaltene-free;

and coal tar hydrocarbons, e.g., aromatic coal tar hydrocarbon. Pressure tars are those produced in the thermal cracking of catalytically cracked cycle stock. Aromatic oils are the heavy bottom residues from thermally cracked, catalytically cracked cycle stock. These residues are used in the manufacture of filler carbon black because of their high aromatic content. Typical API gravity is —1, initial B.P., 650° F., and asphaltene content, 1.5%. Deasphalted hydrocarbons are prepared by propane deasphalting, sulfur dioxide treatment and related processes. Synthetic hydrocarbon residues are the liquid or solid (at room temperature) by-prdoucts of hydrocarbon syntheses, including polyolefin, e.g., polybutadiene, polyethylene, polypropylene, etc., production, and cracking processes for olefins, dienes, acetylenic and aromatic hydrocarbons.

Preferred low asphaltene-containing residues are those which are substantially asphaltene-free, i.e., containing no more than 3% and preferably 0–2% asphaltene. Especially preferred are petroleum hydrocarbon residues, especially the aromatic oils.

The asphaltene content of the feedstocks is determined in the conventional manner, i.e., measuring the percent of the feedstock which is soluble in an aromatic oil and the percent thereof soluble in pentane, the percent asphaltene content being the difference in the two figures. Thus, a feedstock which is completely soluble in an aromatic oil and 83% soluble in pentane has an asphaltene content of 17%, as determined according to ASTM Test No. D2006.

The proportion of substantially asphaltene-free feedstock which is blended with the shot coke forming feedstock to ensure the production of sponge coke will depend on the asphaltene content of the shot coke forming feedstock and the low-asphaltene content hydrocarbon bottoms used therewith. When using the preferred, substantially asphaltene-free hydrocarbon bottoms, about 5–40% by volume will suffice with all except the shot coke forming feedstock of very high asphaltene content, e.g., above 25%.

The process conditions employed in a conventional coking operation designed to produce sponge coke are employed in the process of this invention. The feedstock is heated to up to about 900° F. and pumped into a coking drum at a rate which fills the drum in about 8 to 15 hours, with a recycle ratio of about 1.2 to about 2.5, preferably about 1.5. When the coking drum is filled with coke, the coke is cooled with steam and the cooled coke removed with high pressure water jets. Total cycle time is about 20–26 hours.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be constructed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

EXAMPLE 1

Shot coke forming feedstock: Vacuum virgin residual oil, 15% asphaltene content; initial B.P., 600° F.; API gravity, 4; Watson Characterization Factor, 10.8.

Low aspheltene-content hydrocarbon bottoms: Aromatic oil, (1.5% asphaltene content; initial B.P., 650° F.; API gravity, —1; Watson Characterization Factor, 9.0.

The shot coke forming feedstock and the aromatic oil blending stock are separately preheated to 915° F. and then separately fed to a coking drum (20′ diameter, 80′ high) at a rate of 350 barrels/hr. and 100 barrels/hr., respectively, with a recycle ratio of 1.5 (total feed/fresh feed). Pressure in the drum is 45 p.s.i.g. Coking time is 12 hours with a total cycle time of 24 hours.

The coke produced is high porosity sponge coke with a bulk density (<1″ crushed coke with about 35%+4 mesh solids) of about 43 lbs./ft.^{3}. Hydrogen content is about 39%, sulfur content, 1.15%; and ash, 0.27%. Total surface area (1″ particle) is about 400–600 ft.^{2}/ft.^{3}. Shot coke of comparable size has a surface area of 75–100 ft.^{2}/ft.^{3}.

Large anodes for alumina electrolytic reduction cells formed from this sponge coke are comparable in every respect to those formed from sponge coke produced from conventional sponge coke forming feedstock.

EXAMPLE 2

Following the procedure of Example 1, sponge coke having substantially the same properties is produced by substituting as the shot coke forming feedstock atmospheric virgin residual hydrocarbons (11% asphaltene content; API gravity, 14.5; Watson Characterization Factor, 11.1).

Similarly, sponge coke is prdouced according to the procedure of Example 1 employing as shot coke forming feedstock the residue of a solvent hydrocarbon extraction (25% asphaltene content) or a hydrocarbon asphalt (35% asphaltene content) in combination with a proportion of aromatic oil which provides a total asphaltene content of about 10%.

Sponge coke is also produced according to the procedure of Example 1 by substituting as low-asphaltene content hydrocarbon bottoms, the same proportion of pressure tar (1.5% asphaltene content); bottoms of refined deasphalted hydrocarbons (0.3% asphaltene content); the residues of polyethylene production (0% asphaltene content) or coal tar bottoms (0.1% asphaltene content).

What is claimed is:

1. A process for the production of porous, low density sponge coke from coking feedstock which produces dense, hard particulate shot coke in a conventional delayed coking operation which comprises the steps of:

(a) measuring the asphaltene content of a coking feedstock having an asphaltene content above about 13% and which normally produces shot coke in a conventional delayed coking process; and

(b) using a mixture of said shot coke forming coking feedstock and a hydrocarbon bottoms having an asphaltene content below about 8%, in a proportion such that the total asphaltene content of the mixture is below about 13%, as the coking feedstock in said conventional delayed coking operation.

2. A process according to claim **1** wherein the shot coke forming feedstock has about 13–25% asphaltene content.

3. A process according to claim **2** wherein the shot coke forming feedstock is selected from the group consisting of

(a) atmospheric distilled virgin residual hydrocarbons;

(b) vacuum distilled virgin residual hydrocarbons;

(c) solvent extracted residual hydrocarbons; and

(d) hydrocarbon asphalts.

4. A process according to claim **1** wherein the mixture of feedstocks has an asphaltene content of less than 10%.

5. A process according to claim **1** wherein the hydrocarbon bottoms has an asphaltene content of 0–2%.

6. A process according to claim **5** wherein the hydrocarbon bottoms is selected from the group consisting of:

(a) pressure tars;

(b) aromatic oils;

(c) deasphalted hydrocarbons;

(d) synthetic hydrocarbon residues;

(e) the residual aliphatic hydrocarbons of a crude oil which is substantially asphaltene-free; and

(f) aromatic coal tar hydrocarbons.

7. A process according to claim **6** wherein the hydrocarbon bottoms is an aromatic oil.

8. A process according to claim **2** wherein the hydrocarbon bottoms has an asphaltene content of 0–2%, and the mixture thereof and said shot coke forming feedstock has an asphaltene content of less than 10%.

9. A process according to claim **8** wherein the shot coke forming feedstock is selected from the group consisting of:

(a) atmospheric distilled virgin residual hydrocarbons;

(b) vacuum distilled virgin residual hydrocarbons;

(c) solvent extracted residual hydrocarbons; and

(d) hydrocarbon asphalts,

and wherein the hydrocarbon bottoms is selected from the group consisting of:

(a) pressure tars;

(b) aromatic oils;

(c) deasphalted hydrocarbons;

(d) synthetic hydrocarbon residues;

(e) the residual aliphatic hydrocarbons of a crude oil which is substantially asphaltene-free; and

(f) aromatic coal tar hydrocarbons.

10. A process according to claim **8** wherein the hydrocarbon bottoms is an aromatic oil.

11. A process for the production of porous, low density sponge coke in a conventional delayed coking operation employing a feedstock which produces dense, hard particulate shot coke, which comprises the steps of:

(a) blending a coking feedstock having an asphaltene content above about 13% and which normally produces shot coke in a conventional delayed coking process with a hydrocarbon bottoms having an asphaltene content below about 8%, in a proportion such that the total asphaltene content of the resulting mixture of feedstocks is less than about 13%, and

(b) using said blend as the feedstock in said conventional delayed coking operation.

12. A process according to claim 11 wherein the hydrocarbon bottoms has an asphaltene content of 0–5% and the blend has an asphaltene content less than 10%.

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U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,684,697 Dated August 15, 1972

Inventor(s) Bernard William Gamson

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 4, after "Calif. 90036" insert ---assignor to Harvey Aluminum (Incorporated), Torrance, Calif. 90509---

Signed and sealed this 17th day of April 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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