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LOW SULFUR COKE FROM VIRGIN RESIDUA

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ABSTRACT OF THE DISCLOSURE

The sulfur content of coke obtained from high sulfur residua is reduced by oxidation with or without subsequent hydrodesulferization followed by coking and then treating the coke at 1200–1600° F. under high pressures of 50–1000 p.s.i.g. for 30–60 minutes.

BACKGROUND OF THE INVENTION

This invention relates to the preparation of low sulfur coke and more particularly relates to the preparation of such coke from virgin residua.

It is known to produce coke from heavy crude oil fractions by either "delayed" coking or fluid coking. In delayed coking the heavy fractions are delivered into a coking drum in which they remain until carbonized to form a green coke. The green coke is calcined to produce a valuable calcined coke having excellent characteristics from the preparation of electrodes.

Fluid coke is produced by injecting the heavy oil into a dense turbulent bed of hot inert solid particles, preferably coke particles where the feed is partially cracked and partially vaporized. The coke produced is deposited on the solid particles. After stripping, the coke is passed to a burner where a part is oxidized to CO_2 and the remainder is heated to a high temperature by the oxidation and recycled to the coking vessel to impart heat thereto.

It is also known to increase the yield of coke by preoxidizing the feed to the coking process as described in U.S. Pat. to Arey 2,905,615, issued Sept. 22, 1959. Although the sulfur and metals content of the coke thus produced are somewhat reduced the resulting coke is still high in sulfur and metals when very high sulfur-high metals content residua are used as feed to coking.

In copending application, S.N. 44,718, filed June 9, 1970 for Hamner and Moritz and now abandoned there is described a method for preparing low-sulfur coke by hydrodesulfurizing virgin residua prior to coking. In S.N. 884,370, filed Dec. 10, 1969, for Arey and Hammer and now abandoned, there is described a method for reducing the sulfur level in coke from virgin residua by first hydrodesulfurizing the residua and then subjecting the hydrodesulfurized residua to the oxidation and coking process of the Arey Pat. 2,905,615.

SUMMARY OF THE INVENTION

It has now been found that the sulfur content of coke from virgin residua can be further reduced by subjecting the high sulfur (>2%) residua first to hydrodesulfurization to reduce the sulfur content of the non-Conradson carbon components, then oxidized to increase the Conradson carbon, coking the oxidized feed and finally heating the coke under its autogenous pressure to 1200–1600° F. to remove additional sulfur and produce a coke having less than 2% sulfur.

This is a surprising result since it is known that gasification of coke in the presence of oxygen inhibits the removal of sulfur. Thus prior oxidation of the coke feed would be expected to interfere with the removal of sulfur from the coke but surprisingly this is not the case.

DETAILED DESCRIPTION OF THE INVENTION

The hydrodesulferization of virgin residua is carried out under otherwise conventional conditions, using any sulfur resistant hydrogenation catalyst known in the art, e.g. cobalt molybdate, nickel tungstate on alumina, silica-alumina, aluminum phosphates or natural or synthetic high surface area bases. The temperature and pressure conditions and feed rate necessary to give greater than 60% desulfurization fall within the range of 600–850° F., 500–5,000 p.s.i.g., and 0.2 to 2 v./v./hr. with 1000 to 10,000 s.c.f. H_2/bbl. gas rate. One suitable set of conditions are 725° F., 2500 p.s.i.g., and 0.5 v./v./hr. with 3000 s.c.f. H_2/bbl. gas rate. In this step the sulfur is converted to H_2S and the metals are deposited on the catalyst. The process itself may be a fixed bed, ebullating or fluid bed, all well known in the art.

The oxidation treatment is carried out with the heavier portion of the hydrodesulfurized residua. Lighter fractions such as 850° F. and lighter may be removed by a distillation step prior to oxidation. The heavier oil fraction is oxidized in the liquid phase at a temperature between 100 and 850° F. and 10–500 p.s.i.g., in a reactor extraneous to the coking reactor after the oil has been preheated in order to obtain the desired temperature. A minimum of 1.0 wt. percent O_2 is combined by this method. Excess gas is vented before the oxidized residua of increased Conradson carbon content is sent to coking. The use of the extraneous reactor with the venting of oxygen-containing gas results in the sending of the oxidized oil to the coker free of extraneous oxygen-containing gas. In this manner produce degradation and dilution are avoided. Although air is the preferred oxidizing gas, any other oxidizing agents, such a pure oxygen, ozone, peroxides and NO_2 may be used.

The oxidized-hydrodesulfurized residua, free of extraneous oxygen-containing gas is then fed to a delayed or fluid coker which is operated in the conventional manner. The low-sulfur-metals gas oil products are taken overhead from the coker and utilized as feed to catalytic cracking, hydrocracking or low sulfur fuel oil. The coke product removed from the process is suitable for electrode and other coke uses.

The conditions usually encountered in the coking zone are as follows:

Fluid coking	Broad range	Preferred range
Temperature, ° F	850–1,200	900–1,000
Pressure, p.s.i.g.	10–200	10–100
Superficial velocity of fluidizing gas, ft./sec.	0.2–10	0.5–4
Coke circulation (solids/oil ratio)	2–30	7–15
Delayed coking:		
Temperature, ° F	775–1,000	875–950
Pressure, p.s.i.g.	10–200	10–100
Average residence time, hours	0.5–24	1–16

In accordance with this invention the coke which has been subjected to the above procedures, can be further decreased in sulfur by heating the coke in a non-oxidizing atmosphere to a temperature between 1200 and 1600° F. (preferably 1300–1400° F.) and 50–1000 p.s.i.g. (preferably 200–500 p.s.i.g.).

The following example illustrates the benefits to be obtained in accordance with this invention.

EXAMPLE

Coke from virgin residua which had been oxidized in accordance with the teachings of the Arey Pat. 2,906,615 and both oxidized and hydrodesulfurized in accordance with the teachings of Ser. No. 884,370 (both of which are incorporated herein by reference) was heated to 1350° F. under 200 p.s.i.g. for 30 minutes with the autogenous pressure of the gases obtained. Ten to fifteen

percent gas was obtained by the process. These gases contained 71% hydrogen and 23% methane. The following data were obtained:

Pretreatment of residua before coking	Run Number 1 None [1]	2 Oxidized [1]	3 HDS [1]	4 HDS plus oxidation [1]		5 HDS plus oxidation
Coke yield	8	20	5.2	9	16	19
Sulfur, weight percent in coke before treatment	3.1	2.57	2.1	1.0	0.5	2.4
Sulfur, weight percent in coke after treatment	1.8	1.2	1.3	0.6	0.3	1.55
Percent desulfurization	40	53	38	40	40	33

[1] Coke source: Alaskan.
[2] Coke source: Hawkins.

The above data show that thermal treatment of residua which has been oxidized or both hydrodesulfurized and oxidized reduces the sulfur content considerably below the specification level of 2%. It is to be noted that this sulfur reduction occurs despite the fact that the coke yield is increased by the oxidation. The combination of oxidation, desulfurization and thermal treatment reduces the sulfur content of the coke to such a low point that the coke is often eminently suitable as metallurgical coke.

The nature and advantages of the present invention having thus been fully set forth and specific examples of the same given, what is claimed as new, useful and unobvious and desired to be secured by Letters Patent is:

1. A process for producing a low sufur-containing coke from a petroleum oil residuum chargestock containing at least 2.0 wt. percent sulfur, which comprises the steps of:

(a) contacting said chargestock with hydrogen in the presence of a sulfur resistant hydrogenation catalyst in a hydrodesulfurization zone operating at temperatures between about 600 and 850° F. and pressures between about 500 and 5000 p.s.i.g. to remove at least 60 wt. percent of the sulfur from the chargestock;

(b) contacting at least a portion of the resulting partially desulfurized chargestock in liquid phase with an oxidizing agent in an oxidizing zone operating at temperatures between about 100 and 850° F. and pressures between about 10 and 500 p.s.i.g. to increase the Conradson level of the partially desulfurized chargestock;

(c) passing the resulting oxidized chargestock free of extraneous oxidizing agent to a coking zone;

(d) coking the resulting oxidized chargestock in said coking zone operating at a temperature between about 775 and 1,200° F. and pressures between about 10 and 200 p.s.i.g. to produce coke;

(e) treating the resulting coke for about 30 to 60 minutes in a desulfurizing zone at a temperature between about 1200 and 1600° F. and under its own autogenous pressure, varying between 50 and 1000 p.s.i.g., to reduce the sulfur content of the coke, and

(f) recovering the resulting low sulfur coke product.

2. The process of claim 1 wherein said desulfurizing zone temperature is between about 1300 and 1400° F.

3. The process of claim 1 wherein said desulfurizing zone pressure is between about 200 and 500 p.s.i.g.

4. The process of claim 1 wherein hydrogen is contacted with said chargestock in said hydrodesulfurizing zone at a rate between about 0.2 and about 2 v./v./hr. and with about 1000 to about 10,000 s.c.f. H_2/bbl.

5. The process of claim 1 wherein the hydrogen treated chargestock is separated into a first fraction having a boiling point below about 850° F. and a second fraction having a boiling point above about 850° F. and wherein only said second portion is contacted with said oxidizing agent.

6. The process of claim 1 wherein said oxidizing agent is air, oxygen, ozone, peroxides or NO_2.

7. The process of claim 6, wherein said oxidizing agent is air.

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