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3,214,346 REMOVING ASH COMPONENTS FROM COKE BY LEACHING

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This invention relates to treating coke especially fluid coke particles made by the fluid coking process to render the coke more suitable for use as such or for use in electrodes of the like.

Fluid coking of residuum is known in the art and is being carried out commercially. Pfeiffer et al. Patent 2,881,130, granted April 7, 1959, discloses fluidized coking of residual petroleum oils and the disclosure of this patent is incorporated here by reference thereto.

Coke particles produced in the fluid coking of petroleum residual oils contains ash constituents such as nickel, vanadium and other metals and sulfur which are undesirable constituents in coke and which are difficult to remove because of the compact non-porous nature or structure of the coke particles. While this compact structure is desirable from the standpoint of utilization in electrodes and the like, it prevents removal of contaminants by gaseous treating agents, extractants and the like.

Fluid coke particles from the fluid coking process are a different type of petroleum coke from petroleum cokes from other processes and have different characteristics. In the fluid coking process, coke particles are circulated between the reactor where heavy oil is coked, and the burner where the coke particles are reheated by burning part of the coke particles. The heated coke particles are then recycled to the reactor where the particles have coke deposited on them by the cracking or coking reaction and are then heated to a higher temperature in the burner and this cycle is repeated many times to form spherical coke particles having layers in an onion-like formation or layer-on-layer formation or a shell within a shell structure.

Each fluid coke particle has a new layer of coke added or laid down as it passes through the reactor and at the same time ash constituents and sulfur or sulfur compounds are laid down with the coke. As the coke particles pass through the burner vessel they are heated and have at least some of the volatile matter removed so that the coke particles are stronger and denser than coke obtained in other commercial coking processes. The removal of contaminants or undesirable constituents from the inner dense layers of the fluid coke particles presents a real problem.

According to the present invention in its broad sense ash constituents are removed or at least the amount of such ash constituents is substantially reduced in fluid coke particles. More specifically the present invention includes further treating the coke particles to render them more dense especially where they are to be used in the manufacture of electrodes for the production of aluminum.

The ash constituents, and in particular the vanadium content, are reduced in the fluid coke particles by increasing the porosity of the fluid coke particles by low temperature oxidation and/or steaming, followed by either treatment with gaseous reagents such as chlorine and hydrogen chloride or by extraction with reagents such as aqueous alkaline materials, acids and the like. The high porosity fluid coke particles may be used as such as an adsorbent or they may be further treated to reduce their porosity or surface area. In many instances, such as in the preparation of electrodes, this high porosity of the coke is un-

desirable as a greater quantity of carbonaceous binder is required in making an electrode or other compactions from such coke particles. Because of the favorable grinding characteristics of the highly porous coke particles, the reduction in surface area is preferably not effected until after the highly porous coke particles have been ground and screened to the desired size distribution.

The surface area reduction of the highly porous coke particles comprises treating such coke particles with a hydrocarbon material such as a normally gaseous hydrocarbon; i.e., methane or natural gas and the like in the range between about 1400° F. and 2000° F. The gaseous hydrocarbon is cracked to produce hydrogen and to deposit coke in the pores of the high surface area coke particles to form a finely divided material of low surface area and increased density that will have a minimum adsorption of the carbonaceous binder when used in the preparation of electrodes, compactions, briquettes, pellets and the like. The hydrogen is credited to the process and may be used as a stripping gas to remove sulfur from the highly porous coke particles or for other processes.

The metals purification step is sufficiently flexible to permit satisfactory clean-up when conducted either before or after a sulfur purification step as by hydrogen treatment of the coke. Although low temperature, fluidized solids air oxidation of the coke particles is a preferred method of opening up of the coke and achieving the necessary porosity of the coke particles, high temperature steaming is effective and may be used either in conjunction with or in place of the low temperature oxidation. Such steam treatments are made in a fluidized bed operation at temperatures in the range of 1400 to 2000° F. for periods of two to ten hours. The steam treatment requires the higher temperature and involves consumption of heat; the oxidation is exothermic and liberates heat.

The fluid coking process operates with coke particles having an average particle size ranging between about 35 and 3500 microns in diameter with preferably not more than about 5% having a particle size below 75 microns. Between about 15% and 30% by weight of the coke made in the fluid coking process is burned to supply the heat of coking. The unburned portion of the coke represents the net coke formed in the process and is withdrawn as product and is the product treated by the present invention. The metal content or ash contaminant is influenced by the amount of coke burned as a source of heat. Thus, when only 15% is consumed the metal content from a given residuum is much lower than when 30% is consumed as fuel.

After the low temperature oxidation the high surface area coke particles may be extracted with an ammonium hydroxide solution or with a sodium hydroxide solution. This extraction or successive extractions may be used at ambient temperature or a temperature up to 225° F. Or the high surface area coke particles may either be treated with chlorine or with hydrochloric acid, preferably constant boiling hydrochloric acid, at a temperature between about 50° F. and 250° F. for a time between about 0.5 and 20 hours. Or the high surface area coke particles may be treated or extracted first with an alkali hydroxide solution such as sodium hydroxide and then in a second step with hydrochloric acid, preferably constant boiling hydrochloric acid at its boiling point.

Instead of using only one oxidation and extraction step successive steps at the same or different temperatures may be used to increase the surface area of the coke particles so as to achieve greater degree of metals removal.

EXAMPLE 1

In one example about 400 grams of coke particles obtained by the semi-commercial fluid coking of residuum

and having a vanadium content of about 165 p.p.m. (parts per million) were oxidized in a fluid bed maintained in a fluidized condition by upward passage of air containing 11 weight percent water through the coke particles bed at atmospheric pressure at a temperature of about 750° F. for about 14 hours to increase the surface of the coke particles from about 5 m.²/g. (square meters per gram) to 332 m.²/g. The oxidized coke particles were allowed to cool to ambient temperature and were then extracted five times with fresh ammonium hydroxide (28% NH₃). Each extraction was made with 100 cc. of the ammonium hydroxide solution for 20 grams of oxidized coke particles. The vanadium content of the coke particles following the oxidation step was about 330 p.p.m. and after the extraction steps was about 100 p.p.m. so that an appreciable amount of vanadium was removed from the coke particles.

EXAMPLE 2

High vanadium coke particles (about 400 grams) from a semi-commercial fluid coking plant where residuum from mixed Venezuelan crudes was the feed, were oxidized at about 650° F. in a fluid bed maintained fluidized by the upward passage therethrough of air for about 14 hours to give about a 62% yield of coke. The oxidized coke particles had a vanadium content of about 3000 p.p.m. Extraction with fresh ammonium hydroxide (28% NH₃) in twelve successive contactings at ambient temperature reduced the vanadium content to about 1300 p.p.m. The ammonium hydroxide was used as follows: 100 cc. of ammonium hydroxide solution to 20 grams of oxidized coke particles.

EXAMPLE 3

About 400 grams of coke particles made in a commercial fluid coking process using Elk Basin residuum as feed to the coker and containing about 500 p.p.m. of vanadium were air oxidized (11% water present) at about 700° F. in a fluidized bed for about six hours to give about a 91% yield. The surface area of the oxidized coke particles was about 173 m.²/g. The oxidized coke particles were cooled and extracted with constant boiling hydrochloric acid in Soxhlet equipment for about 7 hours at a temperature of about 200° F. The extraction was with 20 grams of the oxidized coke and a constant boiling acid prepared from 607 grams of concentrated hydrochloric acid and 395 grams of water. Residual acid was removed by water washing. The vanadium content of the extracted coke particles was about 350 p.p.m. A marked improvement resulted upon the activation followed by extraction. For comparison see Example 4 where the oxidation step was omitted. The nickel in the feed coke particles was about 200 p.p.m. and in the extracted coke particles was about 125 p.p.m.

EXAMPLE 4

About 20 grams of the same coke particles used in Example 3 were extracted in Soxhlet equipment for 7 hours with constant boiling hydrochloric acid at a temperature of about 200° F. The treated coke particles were cooled and washed with water to remove the acid. The coke particle feed had a surface area of about 5 m.²/g. and a vanadium content of about 500 p.p.m. The treated coke particles also had a vanadium content of about 500 p.p.m. showing that extraction alone of the untreated coke particles is ineffectual to remove vanadium.

EXAMPLE 5

About 400 grams of the same type of low surface area commercially produced coke particles used in Example 4 were air oxidized in a fluid bed using air containing about 11% water vapor at about 650° F. for about 14 hours to a coke yield of about 91% and a surface area of the coke particles of about 183 m.²/g. The oxidized coke particles were cooled and then extracted in Soxhlet equipment with constant boiling hydrochloric acid for about 7 hours and the vanadium content of the coke particles was reduced

to about 225 p.p.m. The nickel content was reduced from about 200 p.p.m. to about 100 p.p.m.

EXAMPLE 6

In this example the coke particles oxidized as in Example 5 to a surface area of about 183 m.²/g. were given three successive treatments at about 225° F. each with a fresh 20% sodium hydroxide aqueous solution. The time of treatment in each case was about 2 hours. The weight ratio of the oxidized coke particles to the sodium hydroxide solution in each treatment was about 50/1000. The so treated coke particles were freed of excess sodium hydroxide solution by water washing and were found to have a vanadium content of about 375 p.p.m. Thus, low temperature oxidation followed by treatment with a sodium hydroxide solution produces a large removal of vanadium. The coke feed had a nickel content of about 200 p.p.m. and the treated coke particles had a nickel content of about 215 p.p.m. The increased nickel content results from selective carbon removal during the oxidation and ineffectual removal during the subsequent extraction.

EXAMPLE 7

About 20 grams of the product from Example 6 were further extracted with constant boiling hydrochloric acid for about six hours at a temperature of about 200° F. in Soxhlet equipment. The vanadium content of the treated coke particles was reduced by the combined alkaline and acid extraction to about 200 p.p.m. and the nickel was reduced to about 120 p.p.m.

EXAMPLE 8

About 400 grams of the same coke feed used in Example 4, namely coke from an Elk Basin residuum produced in a commercial fluid coking unit, were oxidized with air containing 11% water vapor in a fluid bed at about 700° F. for about 7½ hours and then at about 650° F. for about 7½ hours to a coke yield of about 75% and a surface area of about 194 m.²/g. for the so treated coke particles. This represents a more extensive oxidation than in the foregoing Examples 3, 5, 6 and 7. The oxidized coke particles had a vanadium content of about 620 p.p.m. Upon extraction with constant boiling hydrochloric acid at a temperature of about 200° F. for about 7 hours in Soxhlet equipment the vanadium in the coke particles was reduced to about 200 p.p.m. The nickel in the coke particles was reduced from about 200 p.p.m. to about 110 p.p.m.

EXAMPLE 9

About 400 grams of fluid coke from the commercial fluid coking of Elk Basin residuum were air oxidized as in Example 8. The air contained about 11% water, the oxidation was carried out at 700° F. for about 7½ hours and then at 650° F. for 7½ hours to a coke yield of about 75%. Surface area of the coke particles was about 194 m.²/g. The oxidized coke particles were first contacted with 10% sodium hydroxide solution at ambient temperature, drained and water washed. The so treated coke particles were then extracted with constant boiling hydrochloric acid in Soxhlet equipment for about six hours at a temperature of about 200° F. This extraction was with 30 grams of oxidized coke and 1163 grams of constant boiling hydrochloric acid. The vanadium was reduced to about 185 p.p.m. in the treated coke particles. The nickel was reduced from about 200 for the coke particle feed to about 110 p.p.m. in the treated coke particles.

The above examples demonstrate that relatively low temperature air oxidation conditions or prepares the coke particles for vanadium removal by extraction with either alkaline or acid aqueous solutions and that a combination of steps, namely, successive extractions with alkaline and acid solutions or acid and alkaline solutions gives

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even further improvement in the removal of vanadium from the coke particles.

The coke particles treated according to the above examples have relatively high surface areas and if it is desired to have high density coke particles, it is within the contemplation of the present invention to deposit coke in the pores of the high surface area coke particles. A preferred method of doing this is to treat the coke particles with a hydrocarbon material at a temperature in the range between about 1400° F. and 2000° F. to crack the hydrocarbon material to hydrogen and coke which is deposited in the pores of the coke particles to densify them or increase their density. The hydrogen formed can be recovered and used in hydrogen treating the coke particles or hydrocarbon distillates.

The coke particles which have been treated to remove

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at a temperature of about 650° F. for about 16½ hours. Then the oxidized coke particles were hydrodesulfurized in a fluid bed operation at a temperature of about 1400° F. The surface area of the coke particles was increased in the oxidation step and the hydrodesulfurization step. The so oxidized coke particles were then treated under high temperature conditions with methane to reduce the surface area of the coke particles. At the same time there was an increase in real density which indicates greater compactness. Where the sulfur content of the coke particles is low, the hydrodesulfurization step may be omitted. The hydro-treatment has no effect on the surface area reduction brought about with methane.

Data are given in the following Table 2 obtained from treating coke produced by fluid coking of Hawkins residuum in a semi-commercial unit.

Table 2

Treatment	None	Air Oxidized	Fluidized Hydro Treat After Air Oxid. of Column II	Fluidized CH ₄ Treat After Air Oxid. of Column II	
	(I)	(II)	(III)	(IV)	
Temperature, °F.....		650	1,400	1,500	1,600
Hours.....		16.5	1	1	1
Gas Rate, V/V/Hr. (volume of gas per volume of coke treated per hour).....		150	500	500	500
Inspection Data Surface Area, M ² /g.....	5	136	162	0.0	0.0
Real Density.....	1.55	1.67	1.62	1.72	1.72

vanadium in the above examples can specifically be treated with methane at 1600° F. for about one hour in a fluid bed of coke particles to crack the methane and deposit carbon or coke in the pores of the coke particles to increase the density of the coke particles. The coke particles so treated have substantially zero surface area.

EXAMPLE 10

About 20 grams of the coke particles oxidized in Example 8 and extracted with sodium hydroxide and hydrochloric acid in Example 9 were treated with hydrogen to reduce the sulfur in the coke particles. The so treated coke particles were then treated with natural gas for two hours in a fixed bed at about 1600° F. The combined treatments with improvements and change in properties with each step are as follows:

Table 1

Step (in sequence).....		1	2	3	4
Treatment	None (Feed Coke)	Oxidized at 700° F. and then 650° F. to 75% Yield	Alkaline and Acid Extracted	H ₂ Treated at 1,400° F.	CH ₄ Treated at 1,600° F.
Surface Area, m. ² /g.....	5	194	-----	150	6
Pore Volume, cc./g.....	0	0.09	-----	-----	0
Pore Diameter, A.....	0	19	-----	-----	0
Sulfur, Wt. percent.....	5.0	-----	4.3	1.1	-----
Vanadium, p.p.m.....	500	620	185	200	-----
Nickel, p.p.m.....	200	165	110	115	-----

In Example 10 it will be apparent that the coke particles have been purified and brought back to substantially the same low surface area condition of the original or starting coke feed. If desired, the sulfur removal step with hydrogen may be omitted. Where step 3 is used the coke particles are passed without cooling to step 4 for treatment with methane. The hydrogen produced in the methane cracking can be used as the hydrogen to hydrodesulfurize the coke particles.

EXAMPLE 11

About 29 pounds of coke particles produced by coking a Hawkins residuum were oxidized with air in a fluid bed

Thus following vanadium and/or sulfur removal by extraction, hydrogen treatment or halogen gas treatment, the coke of relatively high surface area can be made suitable for electrode manufacture by treating with methane, natural gas, a hydrocarbon product, etc., at a temperature in the range of about 1400° F.-2000° F. The preferred temperature range is between about 1400° F. and 1800° F. The time of treatment may vary between about 0.25 and 4 hours. Instead of methane, other hydrocarbon gases such as ethane, propane, and in some instances normal butane may be used. Olefinic hydrocarbons, low octane number naphthas and the like may be used.

The hydrocarbon material such as methane is cracked to hydrogen and coke and the coke is deposited in the pores of the coke to densify or increase the density of the coke particles. The hydrogen can be collected and used

to remove sulfur from the coke particles by hydrodesulfurization or it can be used in other processes.

In the oxidation step to open up the coke particle structure set forth as the first step in the examples above set forth, it is not necessary to have the water present and some of the oxidations have been carried out without added water. Some water will be present in the atmospheric air when such air is used, but it is not essential. The air oxidation step may be carried out at a temperature between about 600° F. and 1000° F., preferably between about 650° F. and 850° F. The oxygen-containing gas may be atmospheric air or air enriched with

oxygen. The time of the oxidation step may be between about 1 and 16 hours but is preferably carried out to have a maximum coke yield loss of 20%, preferably 10%. Where higher temperatures are used, short times of heating are used.

In some cases where the vanadium content of the coke is high, more drastic oxidation of the coke particles may be necessary and then the coke yield may go down as low as 60% (see Example 2, above).

The examples have given specific details for the reduction of vanadium content of the coke particles but the invention is not to be limited thereto as most of these conditions may be varied somewhat. For example, in Example 1 the ammonia concentration may be varied between about 5 and 30% by wt. NH_3 . The number of extraction steps may be varied depending on the degree of vanadium removal desired. In Example 1, the number of extractions was five and this reduced the vanadium to about 100 p.p.m. If the vanadium were to be reduced to only 200 p.p.m., say about only one extraction step would be necessary. The ratio of ammonium hydroxide solution to oxidized coke particles may vary between about 30 cc. to 20 g. of coke to about 500 cc. solution to 20 g. of coke. When the vanadium content of the original coke is low as in Example 1, the chief advantage of the ammonium hydroxide extraction is to prevent a vanadium build-up due to preferential oxidation of the carbon when low temperature oxidation is used for other purposes, e.g. for greater ease of sulfur removal.

In Example 3 the time of treating with hydrochloric acid may be varied between about 0.5 and 20 hours. This extraction with hydrochloric acid may be varied over a range of conditions. As a laboratory expedient, extraction in Soxhlet equipment with constant boiling hydrochloric acid was used. This provides for acid of constant composition in the extraction which takes place at a temperature somewhat less than the boiling temperature of the acid. Selection of an acid other than the constant boiling composition would result in concentration variation during the extraction. However, the extraction may be carried out by slurry contacting followed by filtration or by flow of acid through a bed. In either of these alternates the acid concentration may be varied from 5 to 35% hydrogen chloride and the amount of hydrochloric acid solution may be varied so that the ratio of oxidized coke to acid solution is in the range of 20/1200 to 20/50. Likewise, the temperature of the extraction may be varied over the range of 50 to 250° F.

In Example 6, the number of treatments with sodium hydroxide may be less than three, namely one or two. The concentration of the sodium hydroxide solution may be varied between about 3 and 20%. Where a lesser number of treatments are used, than three, the more concentrated sodium hydroxide solutions are preferably used.

The weight ratio of oxidized coke particles to sodium hydroxide solution may be varied between about 50/1000 and 500/1000. The temperature of treatment is not limited to 225° F. and may be varied between about 50° F. and 350° F. The time of treatment may be varied between about 15 minutes and 10 hours, the longer times being selected from the lower temperatures.

In Example 7 the time of treating with the constant boiling hydrochloric acid may be varied between about 1 and 10 hours.

In Example 9 the concentration of the sodium hydroxide solution may be varied between about 3 and 20% and the temperature may be varied from ambient temperature to about 350° F. The time of extraction with the constant boiling hydrochloric acid may be varied between about 1 and 10 hours.

The surface area of the feed coke particles is between about zero and 10 m^2/g . and the surface area of the oxidized coke particles is between about 150 and 350 m^2/g .

What is claimed is:

1. A method of removing ash constituents from coke particles produced in a fluid coking process which comprises oxidizing the coke particles with air at a relatively low temperature between about 650° F. and 850° F. to increase the porosity and surface area of the coke particles, cooling the so treated coke particles and then extracting them with an agent selected from the group consisting of an aqueous alkali metal hydroxide solution and an aqueous hydrogen chloride solution to remove at least part of the ash constituents from the coke particles.

2. A method according to claim 1 wherein the extracted coke particles are treated at a temperature above about 1400° F. in the presence of a hydrocarbon fluid to crack the hydrocarbon fluid to hydrogen and coke and the coke formed by the cracking step is deposited on the extracted coke particles to reduce the surface area of the coke particles to 0-10 m^2/g . and to increase the density of the coke particles.

3. A method according to claim 2 wherein the hydrogen formed in the cracking step is recovered and used to desulfurize the coke particles.

4. A method of removing vanadium and nickle from coke particles produced in a fluid coking process which comprises oxidizing the coke particles with air at a temperature between about 650° F. and 850° F. for a time to obtain a coke yield of not less than about 60% and then treating the oxidized coke particles with a liquid extraction agent a number of times to remove at least a portion of the vanadium and nickel from the coke particles.

5. A method of removing ash constituents from coke particles produced in a fluid coking process which comprises oxidizing the coke particles with air at a low temperature between about 650° and 850° F. to increase the porosity and surface area of the coke particles and extracting the coke particles in at least one step with an alkali hydroxide solution and then an aqueous hydrogen chloride solution to reduce the amount of ash constituents in the coke particles.

6. A method of removing ash constituents from coke particles produced in a fluid coking process which comprises oxidizing the coke particles with air at a low temperature between about 650° F. and 850° F. to increase the porosity and surface area of the coke particles and extracting the coke particles with a hydrochloric acid solution to reduce the amount of ash constituents in the coke particles.

7. A method according to claim 6 wherein at least one oxidizing step is used to increase the surface area of the coke particles into the range between about 150 and 350 m^2/g . and the coke yield is at least about 70%.

8. A method according to claim 7 wherein the coke yield after the oxidation step is about 75%, the surface area of the oxidized coke particles is about 200 m^2/g . and the extracting agent comprises constant boiling hydrochloric acid.

9. A method of removing ash constituents from coke particles having a size mostly above 75 microns produced in a fluid coking process which comprises oxidizing the coke particles with air at a temperature between about 650° F. and 850° F. for a period of time between about 1 and 16 hours to increase the porosity and surface area of the coke particles from about 0-10 m^2/g . to between about 150 and 350 m^2/g . and to have a coke yield of at least about 70%, cooling the so-treated coke particles, and then contacting the cooled coke particles at least once with an aqueous extraction agent to remove at least part of the ash constituents from the coke particles.

10. A method according to claim 9 wherein said extraction agent comprises an aqueous alkali metal hydroxide solution.

11. A method according to claim 9 wherein said extraction agent comprises one selected from the group con-

sisting of an alkali metal hydroxide, chlorine and hydrochloric acid.

12. A method according to claim 11 wherein said extraction agent comprises hydrochloric acid and the temperature during treatment is between about 50° F. and 250° F. and the time of treatment is between about 0.5 and 20 hours.

13. A method according to claim 10 wherein the temperature during treatment with said aqueous alkali metal hydroxide solution is carried out at a temperature between about 50° F. and 350° F. and the time of treatment may vary between about 15 minutes and 10 hours.

14. A method of removing ash constituents from coke particles produced in a fluid coking process which comprises oxidizing the coke particles with air at a temperature between about 650–850° F. for at least an hour to increase the surface area of the coke particles to at least 150 m.²/g., cooling the so-treated coke particles, contacting the cooled coke particles at least once with an aqueous alkali metal hydroxide solution at a temperature of at least 50° F. and a time of at least a half hour, then further treating said coke particles at least once with an aqueous hydrochloride solution for at least a half hour at a temperature of at least 50° F. to remove at least part of the ash constituents from the coke particles.

15. A method according to claim 14 wherein the extracted particles are treated with a hydrocarbon gas at a temperature of at least 1400° F. for a time sufficient to crack said hydrocarbon gas to hydrogen and coke which deposits on the coke particles to reduce the surface area and to increase the density of the coke particles.

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