May 9, 1961 J. H. GROVE 2,983,673

DESULFURIZATION OF FLUID COKE

Filed Oct. 9, 1958 3 Sheets-Sheet 1

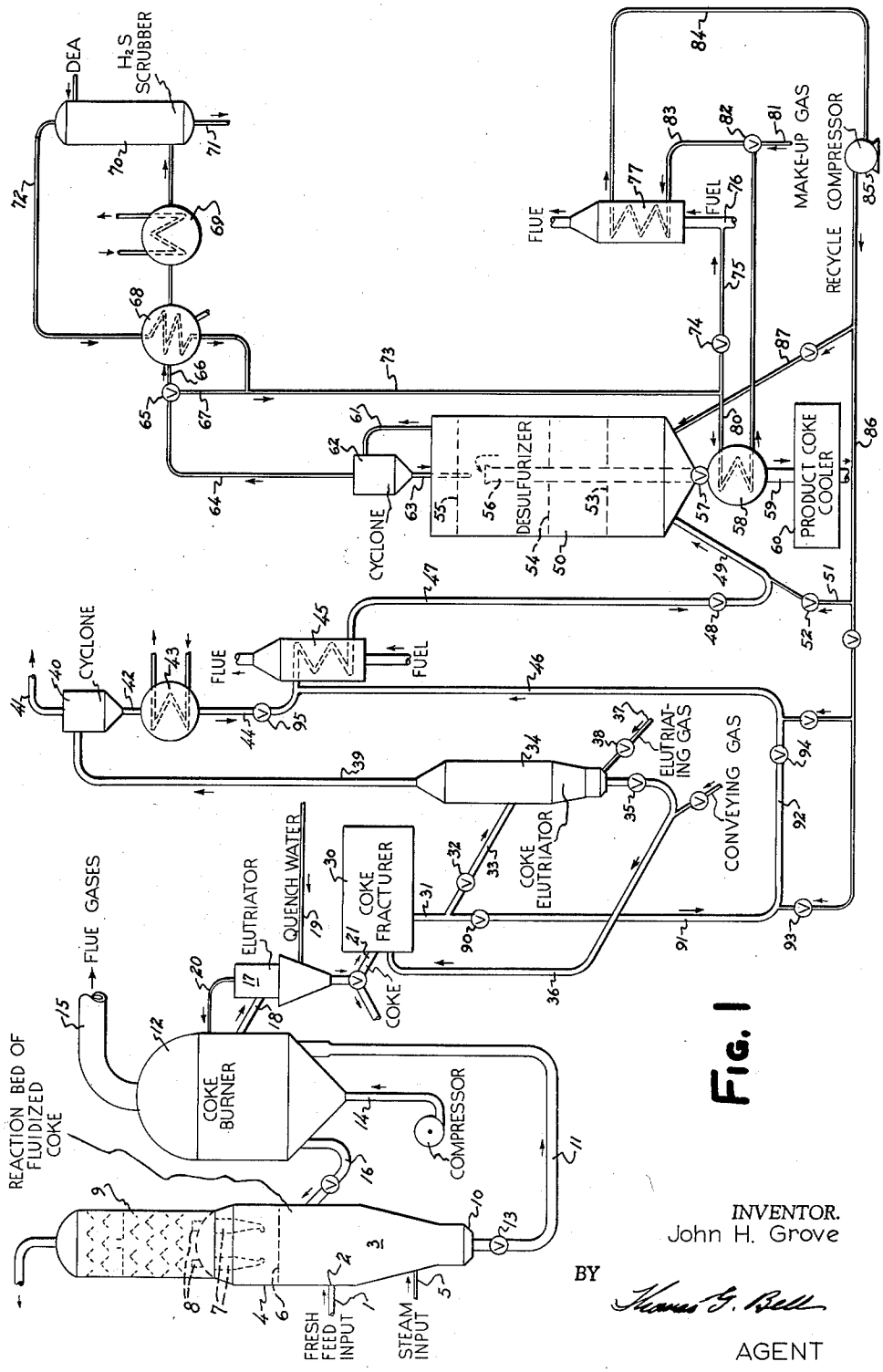


FIG. 1

INVENTOR.
John H. Grove

BY

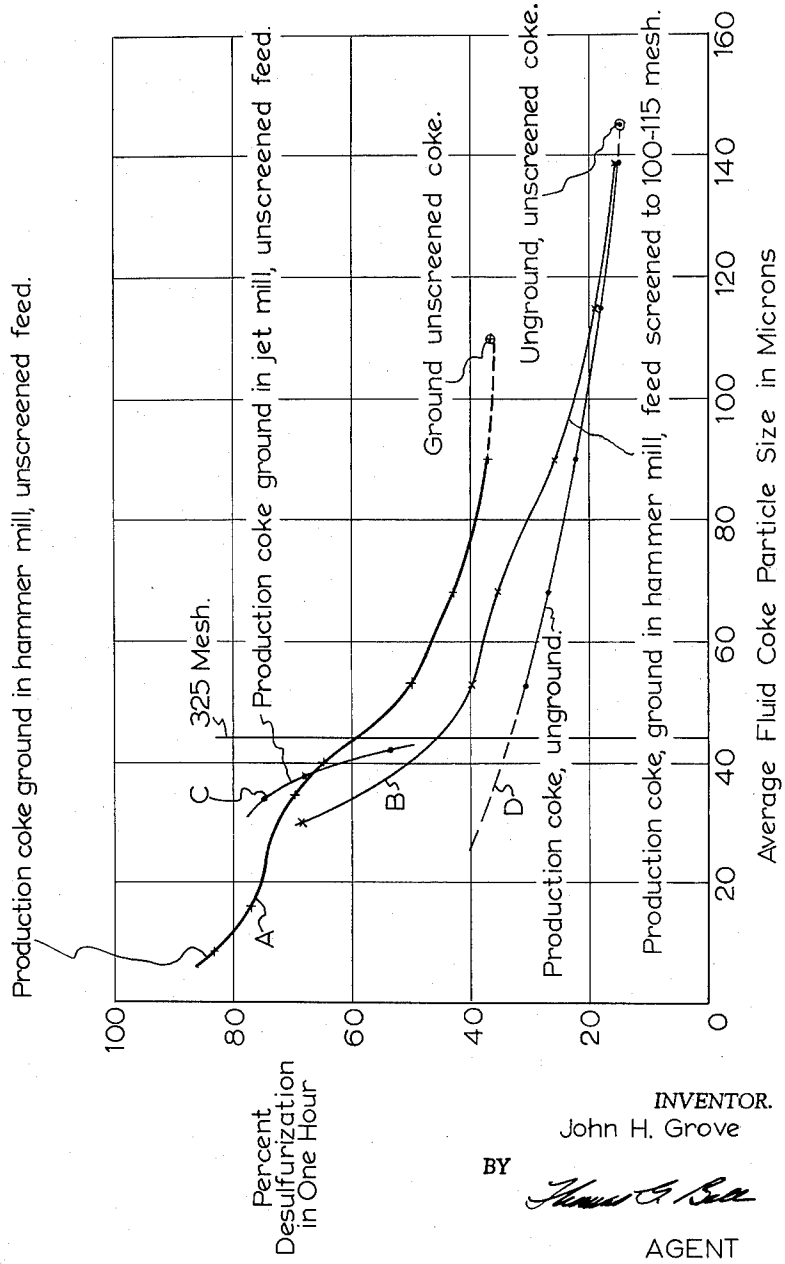
AGENT

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DESULFURIZATION OF FLUID COKE

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FIG. 2



INVENTOR.
John H. Grove

BY

AGENT

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DESULFURIZATION OF FLUID COKE

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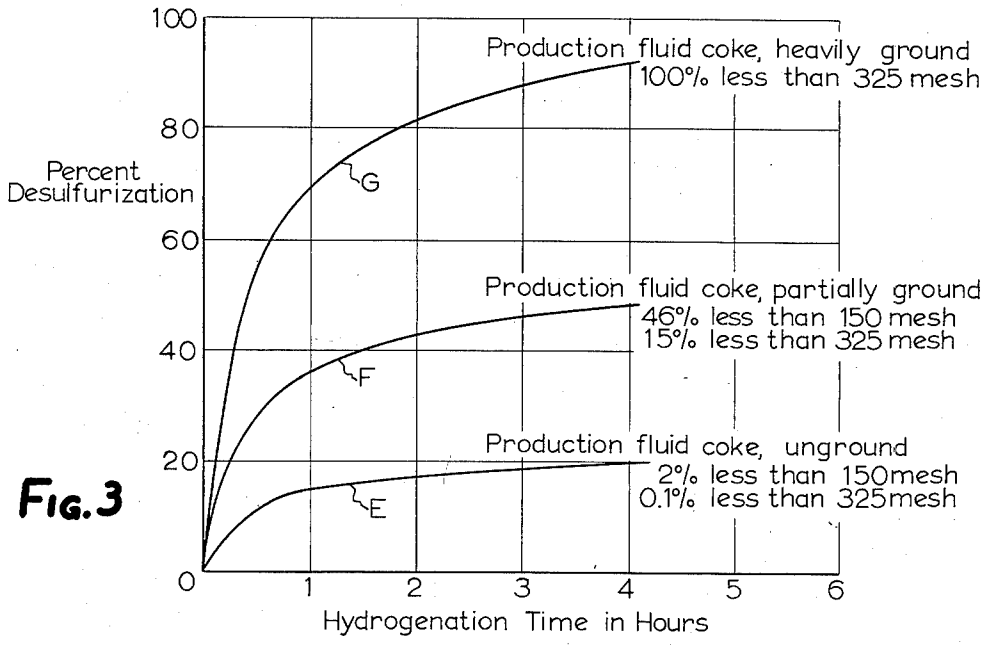


FIG. 3

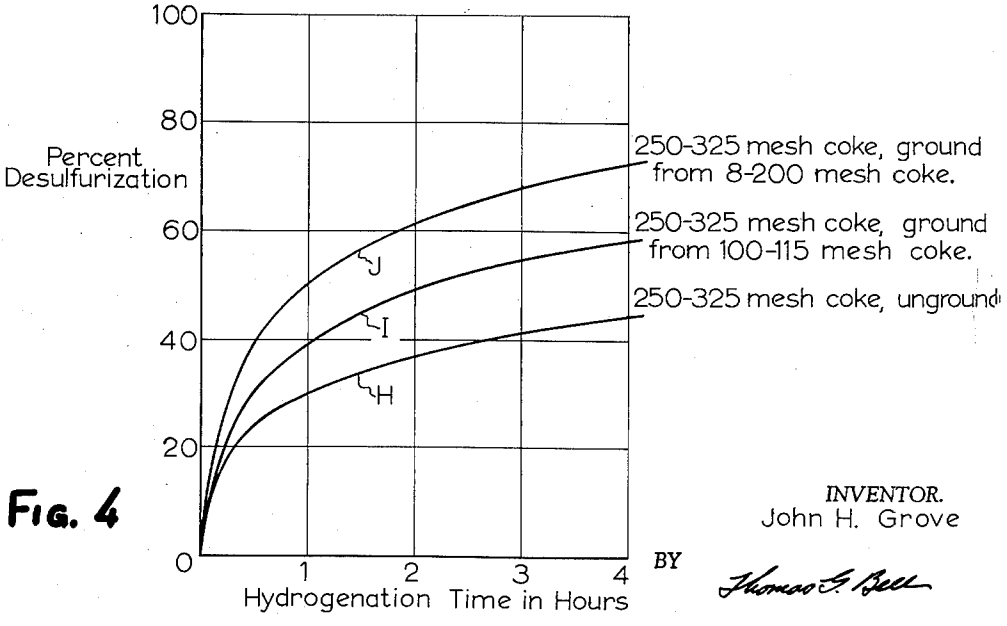


FIG. 4

INVENTOR.
John H. Grove

BY Thomas G. Bell

AGENT

United States Patent Office 2,983,673 Patented May 9, 1961

2,983,673

DESULFURIZATION OF FLUID COKE

John H. Grove, Berkeley, Calif., assignor to Tidewater Oil Company, a corporation of Delaware

Filed Oct. 9, 1958, Ser. No. 766,281

1 Claim. (Cl. 208—152)

This invention relates to improvements in desulfurizing, devolatilizing, and increasing the density of coke containing high percentages of sulfur. More particularly, it relates to an efficient high-yield desulfurization of the petroleum coke particles resulting from the fluid coking process.

The recently-developed fluid coking process (Cf. U.S. Patent No. 2,734,852 to Moser) produces coke while thermally converting heavy hydrocarbon oils to lighter fractions and has led to new problems in the desulfurization of coke. A fluid coking unit basically consists of a reaction vessel or "coker" and another vessel known as the heater or "burner." In a typical operation, heavy oil is injected as feed stock into the coker where it comes into intimate contact with a dense, turbulent, fluidized bed of hot, inert, solid particles of coke. The uniform temperature that generally exists in the coking bed combined with uniform mixing in the bed results in virtually isothermal conditions and effects rapid distribution of the feed stock. In the reaction zone the feed stock is partially vaporized and partially cracked. Product vapors are removed from the coker and sent to a fractionator for the recovery of gas and of light distillates, while the heavy fractionator bottoms are usually recycled to the coking vessel. The recycling continues until the heavy material has all been converted into either usable light distillate, lighter hydrocarbons, or into coke. The coke produced in the process is coated on the original coke particles, so that their size gradually builds up. Stripping steam is injected to remove oil from the coke particles prior to passage of the fluidized coke from the coker to the burner, where the heat for carrying out the endothermic coking reaction is generated.

In the burner the coke is partially burned with enough oxygen-containing gas to raise the temperature to a level sufficient to maintain the system in heat balance. Usually the burner employs a stand-pipe and riser system, and air is supplied to the riser for conveying the coke particles to the burner. The coke in the burner is normally maintained at a temperature higher than that at which the coke bed in the coker is maintained, and about 5% of the coke, based on the oil feed is normally burned in the burner in order to keep this temperature relationship. This may amount to approximately 15% to 30% of the coke made in the process. Most of the unburned coke is recirculated to the coker, while the net coke formed in the process is withdrawn and elutriated to remove the fines (which are returned to the system). This net coke, from which the fines have been removed is commonly referred to as "production coke" and is the type of coke to which the present invention most especially relates, although it is applicable to other fluid coke products.

Heavy hydrocarbon oil suitable as feed stock for coking include heavy or reduced crudes, vacuum bottoms, pitch, asphalt, and other heavy hydrocarbon petroleum residua. Typical feeds have an initial boiling point of

700° F. or higher, an A.P.I. gravity of about 0° to 20°, and a Conradson carbon residue content of about 5% to 40% by weight (ASTM test D–189–52). It is preferable to operate the coker with coke particles ranging in size between 100 and 1,000 microns in diameter, and the preferred average particle size lies in the range between 150 and 400 microns. Preferably, not more than about 5% of the particles should be below 75 microns in diameter, because small particles tend to agglomerate or are swept out of the system with the gases. However, the small particles burn well in the burner. Therefore, the withdrawn production coke usually has a diameter predominantly in the range of about 20 to 100 mesh.

Fluid coking has its greatest utility in upgrading the quality of heavy petroleum oils, that is, low-grade petroleum vacuum residua and pitches from highly asphaltic and sour crudes. Such residua frequently contain high concentrations of sulfur, i.e., 3% by weight or more, and the production coke from these high-sulfur feeds is, of course, high in sulfur content. In general, the percent sulfur content of the production coke from fluid coking processes may be about twice that of the residual feed from which the coke is produced. The sulfur content of the coke from sour residua can range from 4% to 12% by weight or more.

The high sulfur content of production coke poses a major problem in its efficient utilization. For most non-fuel or premium-fuel uses a coke with a low sulfur content, i.e., about 3% sulfur or less, by weight is required. For example, low-sulfur-content coke may be used in the manufacture of phosphorus or calcium carbide, for lime burning in the manufacture of soda ash or other alkalies, for various metallurgic applications, or for the production of electrode carbon for various electro-chemical applications such as the manufacture of aluminum. In electrode-grade coke, the lower the sulfur content the more desirable is the coke, since metallic sulfides are formed when sulfur attacks the metal components of an electrode, and electrodes containing metallic sulfides introduce undesirable metals, such as iron and nickel into the product aluminum.

At one time, a maximum of about 3% sulfur was considered satisfactory but, at the present, even 2% sulfur content is usually not tolerated. In order to produce very-low-sulfur-content electrode coke from fluid coke, calcining has been necessary. However, calcining as normally used with air or steam requires temperatures of 2000° F. to 2800° F., and the reaction time required is quite often inconsistent with good yields of coke, since coke is consumed during the operation. Thus, calcining is an expensive operation. However, there is considerable market for coke of quality comparable to calcined coke, especially if this quality of coke can be produced more cheaply, as by eliminating the calcining step or substantially reducing its duration.

It is also important for many uses that the coke have a low volatiles content. The volatiles content of fluid coke (production coke) is usually in the range of 2% to 10 by weight, which is much too high for use in the manufacture for electrodes for making aluminum. A second function of the expensive high-temperature calcining treatment is the reduction of the volatiles content, and an object of this invention is to obtain comparable reduction at less expense.

Electrode grade coke must also have a relatively high particle density. This high density requirement is based upon the correlation between density and electrical resistance, namely, the higher the density, the lower the electrical resistance and, consequently, the lower the electrode power losses. Uncalcined fluid coke exhibits particle densities of only 1.5 to 1.6. As experience has been

gained with fluid coke, it has become evident that calcining increases the densities up to about 1.8 to 1.9 and thereby achieves the desired electrical properties. Another object of this invention is to increase the density of fluid coke without calcining.

Conventional methods of reducing the sulfur content of petroleum coke from ordinary sources with gaseous reagents have not been too satisfactory in general. The results have been even poorer when the procedures have been applied to fluid coke, for fluid coke is laminar in structure, hard, non-porous, and relatively impenetrable. It may comprise some 30 to 100 superposed hard layers of non-porous coke. Consequently, it is difficult for any reagent to penetrate more than a few outer layers. These difficulties inherent in fluid coke are even further compounded when the sulfur content of the coke is higher than normal due to the use of high-sulfur petroleum feeds.

The present invention utilizes conventional desulfurizing agents such as hydrogen or steam and other known agents such as sulfur dioxide, and other suitable gaseous reagents, but it combines with such prior art treatment the novel step of first fracturing the coke particles. The results are not what one would ordinarily expect. It would be expected that fracturing would produce smaller particles with resultant increase in the total surface area and, therefore, some, but minor, increase in desulfurization. However, the degree of desulfurization resulting from this process has been much greater than would be expected from mere reduction in size. The effective desulfurization of unfractured particles has been compared with that of fractured particles of the same size, and this comparison shows that desulfurization is markedly increased by fracturing. In addition, when large coke particles are fractured to a specified size, desulfurization is markedly greater than when smaller coke particles are fractured to the same specified size.

It appears possible that fracturing the coke cracks open the laminar structure and affords entry of the desulfurizing agent into the fluid coke laminations so that a number of laminations are reached at once.

It is thought that the coke particles are composed basically of graphite crystallites arranged in a hexagon lattice, cemented together into gross particles by condensed aromatic compounds. Imbedded in this aromatic binder are the contaminating elements, such as hydrogen, nitrogen and oxygen, presumably as components. A possible theory of the coke-fracturing procedure of this invention is that fracture of the laminated and cemented particles exposes these contaminating materials so the desulfurizing agents can get into these pores. It follows that the greater the degree of fracturing, the more remarkable will be the desulfurizing effectiveness of a sulfur-removing reagent. In practice, this idea is supported by the very high degree of desulfurization that results when desulfurizing fluid coke that has been fractured to less than 325 mesh (less than 44 microns). The theory is also supported by the aforementioned superior results obtained upon desulfurizing fractured large coke particles, as compared with desulfurizing smaller particles fractured to the same size.

Whatever the actual reason, the fact remains that fracturing the fluid coke before desulfurizing it strikingly increases its desulfurization.

There are many possible ways of fracturing fluid coke. It may be ground in a mechanical grinder, by a hammer mill for example. However, mechanical grinding is not easy as may be found by attempting to hand grind with a mortar and pestle, the fluid coke particles being too hard to grind effectively in this manner. The several methods that are suitable for fracturing coke include, in addition to mechanical grinding by a hammer mill, jet impact grinding and fracturing by impact with other particles. In all these cases, the term "fracturing" is used to indicate a breaking open of the coke particles rather than a wearing off of an outside layer and a mere reduction in size, and fracturing is defined to include all types of so fracturing coke particles, whether done mechanically by grinding or by jets or friction impact or by any other method.

Other objects and advantages of the invention will be better understood from the following detailed description of a preferred embodiment thereof presented in accordance with the statute.

In the drawings:

Fig. 1 is a flow sheet of a fluid coking process incorporating the novel desulfurizing process embodying the principles of this invention.

Fig. 2 is a graph showing the effect of fracturing coke particles upon desulfurization.

Fig. 3 is a graph showing the effect that fracturing the coke particles has in reducing the time of desulfurization.

Fig. 4 is a graph showing the difference in desulfurization of particles of the same size, some samples being ground and others unground.

The purpose of a fluidized coking installation like that shown in Fig. 1 is to treat the residual oils from petroleum refining processes to obtain upgraded, lighter products that can be introduced into thermal or catalytic cracking units. Some naphtha and gas fractions are also produced. As a by-product, coke is obtained in fine sand-like particles. The fluid coking process contrasts with thermal cracking processes which terminate with an asphalt residue and is distinctive in giving both a greater total yield from the crude oil and more salable and more valuable by-products. It is distinguished from "delayed coking" processes by being a continuous process. The system is generally similar to a fluidized catalytic cracking unit but operates with coarser solids.

In Fig. 1, hot oil feed in line **1** at about 400–600° F. is sprayed at inlet **2** through nozzles into a bed **3** of finely divided fluidized coke at a temperature of about 900° to 1050° F. and at a pressure somewhat above atmospheric. The bed **3** is in a conventional coke reactor **4**, throughout which the solid particles are fluidized by steam, which is added at line **5** near the lower end of the reactor **4** and elsewhere through the reactor **4**. Fluidization is enhanced by the cracked products which are generated in the bed **3**. The coke in the reactor **4** acts substantially as a fluid, having what may be called a normal bed level **6**.

The spray of liquid feed at **2** is distributed over the surface of coke particles in the bed **3**. The small, hot coke particles act as heat sources to effect cracking of the feed, forming additional coke and a vaporized effluent which leaves the reactor through a bank of cyclones **7**. The cyclones separate entrained coke particles and return them to the bed **3**, while the hydrocarbon effluent flows up through risers **8** into a scrubber **9**. In the scrubber **9** the effluent is cooled suddenly, by quenching, and is then passed to a fractionator (not shown) and a condenser (not shown), from which it is utilized as desired.

In the reactor **4** the coke, formed by the reaction, deposits as successive layers on the coke particles in the bed **3**. This deposit includes those components of the feed having a high tendency to form coke; also, all but a minor part of the metallic contaminants and ash in the feed are retained in the coke, so that the hydrocarbon effluent is thereby cleaned from the high ash content of the oil feed.

To obtain the hot coke needed in the reactor **4**, part of the coke therein is continuously withdrawn from the lower end **10** and transferred as a steam-borne fluid, via a pipe **11** into a burner **12**, which is also operated as a fluidized bed. Flow through the pipe **11** may be controlled by a valve **13**.

Air is added to the burner bed through line **14**, and some of the coke is burned, forming primarily carbon dioxide and carbon monoxide and heating the bed to a temperature of approximately 1100° to 1200° F. The

combustion products escape through the flue 15. An amount of coke weighing about 5 to 7 percent of the fresh feed oil in line 1 is burned in the burner 12, thereby heating the remaining coke which is recirculated to the reactor 4 through the conduit 16 to maintain the proper reaction temperature. Steam is added where needed to maintain fluidization. As the reaction in reactor 4 cools the coke, the cooler coke is continuously being returned to the burner 12 through the pipe 11, a stripper normally being provided above the reactor bottom wherein the hydrocarbon vapors are displaced by steam to prevent their being carried over to the burner 12.

In the reactor 4, the particle size of the coke continually grows as a result of the coke deposition described above. Since, as is well known, there is a desired maximum particle size, the larger particles are replaced by small "seed-coke," produced by steam jet grinding in the bottom of reactor 4, or by other suitable means.

The present invention is concerned with the by-product coke, which is withdrawn from the burner 12 as net coke formed in the process—over and above the coke that is needed for recirculation and the coke that is burned. This excess coke is sent to an elutriator 17 via a pipe 18. In the elutriator 17 the coke is cooled and washed by water from line 19. The elutriator 17 also serves to return finer particles to the burner-reactor system via the pipe 20, so that only the larger particles of coke are withdrawn from the elutriator 17 through conduit 21. These larger particles are termed herein "production coke." This production coke is thus a sand-like product practically free from the very fine particles. The problem which this invention is concerned with is how to remove sufficient of the impurities—notably sulfur—in this coke to improve its value as a by-product.

In the present invention the key step is fracturing the production coke before desulfurizing it. Thus, as illustrated in Fig. 1, the coke from line 21 passes into a coke fracturer 30 where the coke is broken into smaller particles. The fracturing may be done by mechanical grinding in a hammer mill, or the fracturing can be accomplished by what is known as jet grinding. In the latter process, very high velocity steam (or other gas) impinges the coke against a metal plate and shatters it, or else accelerates some coke particles into impact with other coke particles and fractures them by striking particle against particle at high velocities. The grinding or fracturing may be done as a continuous process, or it may be done on a batch basis. After the coke has been fractured, it may be desulfurized by any desirable means. Fig. 1 shows a preferred example, but not the only possible arrangement. From fracturer 30 the coke passes via line 31, valve 32, and line 33 into a second coke eultriator 34. In the elutriator 34 the larger particles which are not fractured sufficiently fall to the bottom and pass out through a valve 35 into a line 36 and are carried back into the coke fracturer 30 for further treatment. The elutriating gas (such as steam) fed from line 37 through valve 38 at the bottom of the elutriator 34 serves to carry the fine, fractured coke particles up through line 39 into a cyclone 40. In order to insure that substantially all of the coke particles passing through line 39 have been fractured, the elutriating gas from line 37 should be so regulated that the size of the largest particles carried out of elutriator 34 by the elutriating gas are smaller in size than the smallest particles entering fracturer 30 through line 21. In the cyclone 40 the elutriating gas is separated from the solid particles, and the gas is carried away through line 41, while the coke particles fall into line 42.

The fine fractured coke particles are now cooler than the temperature of the desulfurizer. Therefore, preferably they pass through a heat exchanger 43, wherein they are pre-heated to a desired temperature. Then they pass through a line 44 to a main heater 45. At some stage past the cyclone, enough desulfurizing gas from line 46 may be mixed with the coke particles in order to convey them in a fludized condition.

In the heater 45 the fractured coke is raised to above the desulfurization temperature and then passes through line 47, valve 48 and line 49 to the desulfurizer 50. Shortly before it enters the desulfurizer 50, the hot fluidized fractured coke may be mixed with additional desulfurizing gas from line 51 and valve 52. The desulfurizer 50 may include several stages, indicated diagrammatically by partition lines 53 and 54. As many stages are provided as are desired; for example, four stages may be advisable. The level of the fluidized bed is indicated by the numeral 55. The desulfurizer 50, as illustrated, utilizes a fluid bed, but fixed beds or falling beds may be used. The desulfurization may be done on a batch basis, by closing the valves leading into and out from the desulfurizer.

Of the desulfurizing gases that may be used, hydrogen is preferred, though ammonia, steam, carbon dioxide, sulfur dioxide, and other gases may be used, in accordance with known techniques.

Desulfurized coke is exhausted from the desulfurizer 50 by a tube or chute 56 through valve 57, heat exchanger 58, and line 59 into a cooler 60. This is the desulfurized coke which results from practice of said invention, and may be passed to storage.

Additionally, Fig. 1 illustrates preferred treatment of the desulfurizing gas to improve its performance. The gas leaves the desulfurizer 50 by line 61. It first enters a cyclone 62, whence entrained solids drop out and fall via dip leg 63 back into the desulfurizer 50. The gas, freed from solids, then passes from cyclone 62 by line 64. Preferably, at least a portion of it is scrubbed to remove H_2S, in order to maintain the H_2S content of the gas in line 73 at a low level (e.g., below 10% by volume). A valve 65 connects the line 64 to two lines 66 and 67, and adjusts the proportion of gas in each line. Line 66 leads through a first heat exchanger 68 in which the gas is partially cooled and a second heat exchanger 69, where the gas may be cooled by water, and into an H_2S scrubber 70. The spent scrubbing fluid (e.g., diethanolamine) containing H_2S and CO_2 is removed from the scrubber 70 via line 71, whereas, line 72 carries the scrubbed gas back through the heat exchanger 68, where it acts as the cooling fluid for the gas in line 66. From the heat exchanger 68 the gas in line 72 rejoins the gas from line 67, and both streams flow into line 73. The heat exchanger 68 may have a drain for draining out tars, oils, water and other condensation products.

A portion of the gas from line 73 may be withdrawn for purging purposes via valve 74 and line 75, mixed with fuel from line 76 and burned in a gas heater 77. This permits utilizing the fuel valve of that hydrogen which is discarded to maintain a low level of methane, nitrogen, carbon monoxide and other impurities. Most of the gas from line 73 may pass via line 80 through the heat exchanger 59 to cool the desulfurized coke. Then, make-up gas may be added from line 81 and valve 82 and the resultant mixture sent by line 83 through the heater 77. It will be obvious that since the make-up gas may be, for example, pure hydrogen, the removal of the portion through line 75 plus the addition of the make-up portion through line 81 keeps the desulfurizing gas active. From the heater 77 the desulfurizing gas passes via line 84 to a recycle compressor 85 and from there by line 86 to lines 46 and 51 to complete the cycle. Some of the gas in line 86 may be sent through line 87 directly into the desulfurizer 50.

Another embodiment of the invention is also shown in Fig. 1 in which unclassified fractured coke drops through valve 90 and line 91 into a conduit 92 where it is mixed with desulfurizing gas from line 86 and valve 93, and is

carried directly into the heater **45** via lines **92** and **46** and thence to desulfurizer **50**. In order to make this embodiment usable in the same apparatus, a series of valves may be provided as shown. When valves **90, 93,** and **94** are closed and valves **32, 95,** and **48** are open, the coke passes through the elutriator **34** and heater **45**. When the valves **32, 95,** and **48** are closed and valves **90, 93,** and **94** are open, the unclassified coke passes into the desulfurizer **50**. The results from the two forms of operation are somewhat different as will be explained in the examples.

In a typical process of the type illustrated in Fig. 1, the coke flow to the desulfurizer **50** is about 5 tons per hour, or 120 tons per day, and the desulfurized coke coming from the cooler **60** is then about 4.0 to 4.5 tons per hour, 4.5 tons being a typical good yield, or about 80% to 90% recovery after desulfurization. The coke comes from the coke burner **12** at about 1100° F., or between 1000° F. and 1200° F.

The temperature of the coke fines in line **39** from the elutriator **34** varies from about 400° F. to 800° F. or typically about 600° F. The temperature of the coke as fed to the desulfurizer **50** is about 1450° F. Preferably, it lies in the 1350–1550° F. range, or broadly about 1200 to 1800° F. range.

In the desulfurizer the mean temperature is about 1350° F.; preferably it lies in the 1250–1450° F. range, or broadly in about 1100–1600° F. range, when hydrogen is the desulfurizing gas. In such instance, about 400 volumes of hydrogen per hour for each volume of coke in the desulfurizer are used; the preferable range is about 200–800 volumes, and the broad range is about 40–4000 volumes. The average residence time of the coke particles in the desulfurizer is about 6½ hours; the preferred range is 3–10 hours and the broad range about ½ to 50 hours.

As an example, when 25 tons is the total coke charge in the desulfurizer at any one time, the coke may be charged at 5 tons per hour, giving an average reaction time of 5 hours. The desulfurizing gas is hydrogen at 320 s.c.f./min./ton or 8000 s.c.f./min., and, for example, may be at a desulfurizing gas pressure of 2 atmospheres. The temperature of the gas in the cyclone **62** is about 1250° F.

As a particular example of what can be done, production fluid coke was taken from the coke burner, elutriated, cooled with water and a screen analysis was obtained. The analysis was as follows:

TABLE I

Production coke screen analysis

Mesh	Batch A	Batch B
	Weight percent caught by mesh	Weight percent caught by mesh
35	3.0	1.8
48	4.8	5.6
60	10.0	10.8
80	18.4	17.8
100	50.1	40.0
200	99.6	99.6
Through 200	0.4	0.4—

The sulfur content of this production coke was found to be approximately 6.34% by weight.

The material of Batch A was then fractured by being ground four times in a hammer mill. The screen analysis of the ground coke, by volume percent, is shown in Table II.

TABLE II

Screen analysis by volume of ground coke

Mesh:	Volume percent
+100	26.3
100–150	41.0
150–200	6.3
200–250	2.3
250–325	8.9
Through 325	15.2
	100.0

This indicates that coke may be ground satisfactorily by the hammer mill process. However, it also may be ground by impact, as shown in Patent 2,768,938. Similar results are obtained from various methods of grinding.

For purposes of comparison, unground fluid coke was separated, as indicated in Batch B, and various particle sizes were subjected to desulfurization by hydrogen at 1400° F. The time periods included 3 to 4 minutes preheating to 1400° F. with hydrogen and then holding for respective total periods of one-half hour, one hour, and three hours. Coke ground from production fluid coke was similarly treated; that is, it was separated into meshes, was ground, was preheated for 3 to 4 minutes, and was hydrogenated at 1400° F. for total periods of one-half hour, one hour, and three hours. The results are tabulated in Table III.

TABLE III

Comparison of percent desulfurization of unground and ground fluid coke of the same particle size

Coke Size	Percent of Original Sulfur Removed					
	Unground Coke			Coke Ground from Production Coke [2]		
	½ Hr.	1 Hr.	3 Hrs.	½ Hr.	1 Hr.	3 Hrs.
60 to 80 Mesh	9.6	11.1	13.7			
80 to 100 Mesh	12.6	14.6	18.1			
Production Coke [1]	12.5	14.9	18.5			
100 to 115 Mesh	12.8	14.9	18.7			
115 to 150 Mesh	15.6	18.1	22.9			
Ground Production Coke—Average 150 Mesh				29.6	36.4	46.7
150 to 200 Mesh	18.5	22.1	28.2	30.7	37.1	47.9
200 to 250 Mesh	22.2	26.8	35.5	35.2	43.3	57.3
250 to 325 Mesh	24.7	30.1	41.2	39.4	49.9	67.9
−325 Mesh (Average Size about 35 Microns)	Insufficient material to test			55.2	70.0	87.8
40 Microns				51.1	64.7	82.9
16 Microns				62.3	76.7	92.3
8 Microns				70.2	83.4	98.5

[1] This is fluid coke, average 100 mesh. Large, oversized lumps were not present. These are commonly present and sometimes amount to roughly 2–3% of the total production coke.

[2] The 150–200 mesh fraction contains a maximum of about 18% unground coke, the 200–250 mesh fraction contains a maximum of about 4% unground coke, and the 250–325 mesh fraction contains a maximum of about 1% unground coke.

It will be noted from the foregoing that unground production (fluid) coke, after 3 hours of hydrogenation, had still only lost 18.5% of the sulfur content, showing that it is very difficult to remove sulfur from production coke. Compare this with the run of the ground production coke where 29.6% desulfurization was obtained in 30 minutes and 46.7% in 3 hours. Next, compare the ground coke of 150 to 200 mesh with that of the unground coke of the same size; it will be noted that the same size particles were subjected to exactly the same treatment, and that astonishingly different results were obtained. The unground coke, after being hydrogenated for a half hour, had only 18.5% of its sulfur removed, while the ground coke of exactly the same size particles had 30.7% of its sulfur removed in a half hour. In three hours, almost half of the sulfur was removed from the ground coke, while only slightly more

than a quarter of the unground coke sulfur content was removed.

Since grinding also reduces the average particle size, it will be recognized that the total advance due to size reduction and fracture, is very great. For example, compare the unground production coke with all the ground particles. Only a very smal percentage of the unground coke was less than 325 mesh, or in other words, less than 44 microns; there wasn't enough material even to run the test. But as Table II shows, 15.2% of the ground coke was smaller than 44 microns (325 mesh) and the test showed that those particles could be hydrogenated so as to remove 98.5% of the sulfur. Such removals make this finely-ground coke suitable for aluminum reduction anode use.

Table IV illustrates a further point. Substantially, the treatment described above was given to particles of various size ranges, all of which were ground in a hammer mill from the 100 to 115 mesh fraction of the production coke.

TABLE IV

Percent desulfurization of coke ground from 100–115 mesh fraction of production coke

Coke Size	Percent of Sulfur removed from Coke Ground from 100–115 Mesh Fraction		
	½ Hour	1 Hour	3 Hours
100 to 115 Mesh	13.4	16.2	20.5
115 to 150 Mesh	15.2	17.8	22.4
150 to 200 Mesh	19.8	24.8	33.4
200 to 250 Mesh	28.0	35.1	47.7
250 to 325 Mesh	29.9	39.4	54.4
−325 Mesh (Average Size 30 Microns)	53.9	68.0	85.3

A comparison of the figures in Table IV with those in Table III shows that the results were superior to the unground coke but not so good as that ground from production coke. This illustrates an important principle: the fracturing of the material is more effective when large size particles are fractured than when small size particles are fractured.

Table V shows the results obtained from coke fractured in a fluid jet mill to less than 325 mesh:

TABLE V

Percent desulfurization of jet-ground fluid production coke

Coke Size	Percent of Sulfur Removed		
	½ Hour	1 Hour	2 Hours
42 Microns	44.9	53.9	65.2
38 Microns	54.5	67.3	82.9
35 Microns	59.0	73.8	88.1

Figure 2 shows an interesting comparison between the ground and unground coke and between different types of grinding from different fractions of the coke. The percent desulfurization of samples of coke, obtained by desulfurizing for one hour at 1400° F. with hydrogen, is plotted against the average fluid-coke particles size in microns. Curve D is obtained from unground production coke which was sifted into fractions of varying diameters and each fraction separately desulfurized. The smaller the particle size, the greater the percent desulfurization, but the difference between particles about 44 microns in diameter and particles about 144 microns in diameter is an increase of only about 20 to 35% desulfurization.

Curves A, B, and C all relate to ground fluid coke, all the coke used in this test being ground from production coke like that which furnished the basis for curve D. It will be noted that curves A, B, and C all lie well

above curve D, showing that the fracturing of the coke, the breaking open of the hard fluidized coke particles, and exposing of the multiple layers inside, results in considerably increasing the percent desulfurization obtained within the same time. It will be noted that the coke used in obtaining curve A was simply ground in the hammer mill from unscreened production coke. Curve B, on the other hand, was ground from the 100- to 115-mesh fraction of the production coke. Curve C was production coke ground in a jet mill from unscreened feed. The remarkably high figures shown at the upper ends of all three curves contrast considerably with the curve D.

Figure 3 shows an even more interesting comparison. Here are three curves, E, F, and G, obtained by plotting the percent desulfurization against the hydrogenation time in hours. It shows the effect of the size reduction by hammer mill. The bottom curve, curve E, shows the values obtained from unground production fluid coke. Two percent of this coke is less than 150 mesh and only 0.1% is less than 325 mesh. After four hours, only 20% desulfurization was obtained.

Curve F was obtained by partially grinding production fluid coke until 46% of it was smaller than 150 mesh and 15% was smaller than 325 mesh, corresponding in Fig. 1 to sending coke from fracturer **30** to desulfurizer **50** via lines **91** and **92**. The result was a more than doubling of the percent of desulfurization. Thus, at the end of four hours, nearly 50% desulfurization was obtained, as compared with the 20% of the unground coke.

Curve G shows the results of more thorough fracturing of the production fluid coke, so that 100% of the coke was smaller than 325 mesh corresponding in Fig. 1 to routing from fracturer **30** to desulfurizer **50** via elutriator **34**. The improvement over curve F is almost 100%, and the percent desulfurization was between three and four times as high as in curve E. For example, in three hours the curve E particles had been somewhat less than 20% desulfurized, while in curve G the same time gave almost 90% desulfurization.

These very important results indicate the value of fracturing, as by grinding, the production fluid coke, which is already the size of sand and therefore represents about the same size as what the industry has heretofore thought of as "ground coke." The purpose, therefore, is not merely to get smaller particles and greater surface area but to fracture the particles and to expose a number of the concentric layers.

Figure 4 shows another interesting comparison. Here are three curves, H, I, and J, all made from coke of exactly the same particle size, that is, 250 and 325 mesh. The percent desulfurization is compared against the hydrogenation time in hours at 1400° F. and again rather astonishing differences are noted. Curve H represents the values obtained from the 250- to 325-mesh size of unground production fluid coke. A little over 40% desulfurization was obtained after four hours. Curve I represents the values obtained from the same size of coke, but resulting from grinding 100- to 115-mesh production fluid coke. Not only was the total percent desulfurization increased, so that in four hours almost 60% desulfurization was obtained, but the results in one hour were almost as effective as the four-hour process on unground coke particles of the same size.

Finally, curve J shows the same size coke but ground from larger particles, that is, from 8– to 200-mesh coke. Curve J lies substantially above curve I and, in fact, obtains almost within about half an hour the level that required four hours of treatment of unground coke. Within two hours the product of curve J gives better desulfurization than four hours gives on the coke of curve I. Almost three-quarters desulfurization, or over 70%, was obtained after four hours. This indicates that grinding larger particles is more effective than grinding

smaller particles. Whatever the cause may be, the fracturing of the coke does appear to have this effect.

While a primary objective in developing this novel process was the conditioning of fluid coke to obtain rapid and efficient desulfurization, other important objectives are attained by this invention. For example, in order to devolatilize coke to electrode-coke specifications, it has been necessary heretofore to calcine at very high temperatures.

The novel fracturing process permits the common desulfurizing agents, for example hydrogen, to penetrate into and react quite readily with the volatile components. For example, a large sample of production coke ground to minus 325-mesh was desulfurized with hydrogen at 1350° F. for 6 hours to give an 84% product coke yield. The sulfur content was thereby reduced from 6.64% by weight to 0.76%, a reduction of about 88.5% at a low hydrogen gas rate. At the same time, content of volatiles was reduced from 6.0% to 2.1%, a reduction of 65%. In terms of individual volatiles it was found that 20% of the nitrogen content of the coke was removed as ammonia, the 1% of water originally present was removed as well as an additional 0.34% of water obtained by hydrogenation of the oxygen content of the coke. Some oxygen content is also removed as carbon oxides. Additional ammonia is undoubtedly formed, but ammonia partially cracks to nitrogen and hydrogen under the experimental conditions; so ammonia itself is an excellent desulfurizing agent.

A further advantage of this process would be highly unexpected except in the light of the theory of fracturing discussed above. This advantage is in increasing the real density of the coke. For example, the real density of the partially-desulfurized coke discussed in the preceding paragraph increased from 1.54 to 1.71, despite the removal of only 65% of the volatiles.

Thus it can be seen that the process of fracturing fluid coke to very fine sizes, e.g., 30–40 microns, permits subsequent hydrogenation to effectively reduce sulfur content and volatile content, thereby also increasing the real density of the coke as a result of the purification. All this is done at 1300–1400° F. in contrast to conventional 2000–2800° F. calcining procedures used for those purposes.

To those skilled in the art to which this invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the spirit and scope of the invention. The disclosures and the description herein are purely illustrative and are not intended to be in any sense limiting. For example, although the sizing of the coke particles before and after fracturing has been illustrated by the use of elutriators, it will be apparent that other classification means may be substituted for either or both of elutriators **17** and **34**. Screens and classification-tables are two examples of such substitutes.

I claim:

The method of desulfurizing petroleum coke which comprises: elutriating a stream of fluid coke particles from a hydrocarbon oil fluid coking process to obtain a fines stream and a product stream consisting essentially of particles larger than 200 mesh; returning said fines stream to said coking process; subjecting said product stream to a fracturing operation sufficient to break open a substantial number of the coke particles therein; elutriating the resulting fractured product stream to obtain a recycle stream containing substantially all the particles therein larger than 200 mesh and a feed stream consisting essentially of fractured particles smaller than 200 mesh; returning said recycle stream to said fracturing operation; heating said feed stream to a temperature above 1200° F.; contacting the heated feed stream with a gas stream containing at least 20 volumes of hydrogen per volume of said feed stream for a period, at least 30 minutes, sufficient to produce substantial desulfurization of said feed stream; and separating the thus desulfurized stream of coke particles from said gas stream.

References Cited in the file of this patent

UNITED STATES PATENTS

2,814,588	Hutchings	Nov. 26, 1957
2,865,847	Jahnig et al.	Dec. 23, 1958
2,872,387	Nelson et al.	Feb. 3, 1959

FOREIGN PATENTS

770,830	Great Britain	Mar. 27, 1957