

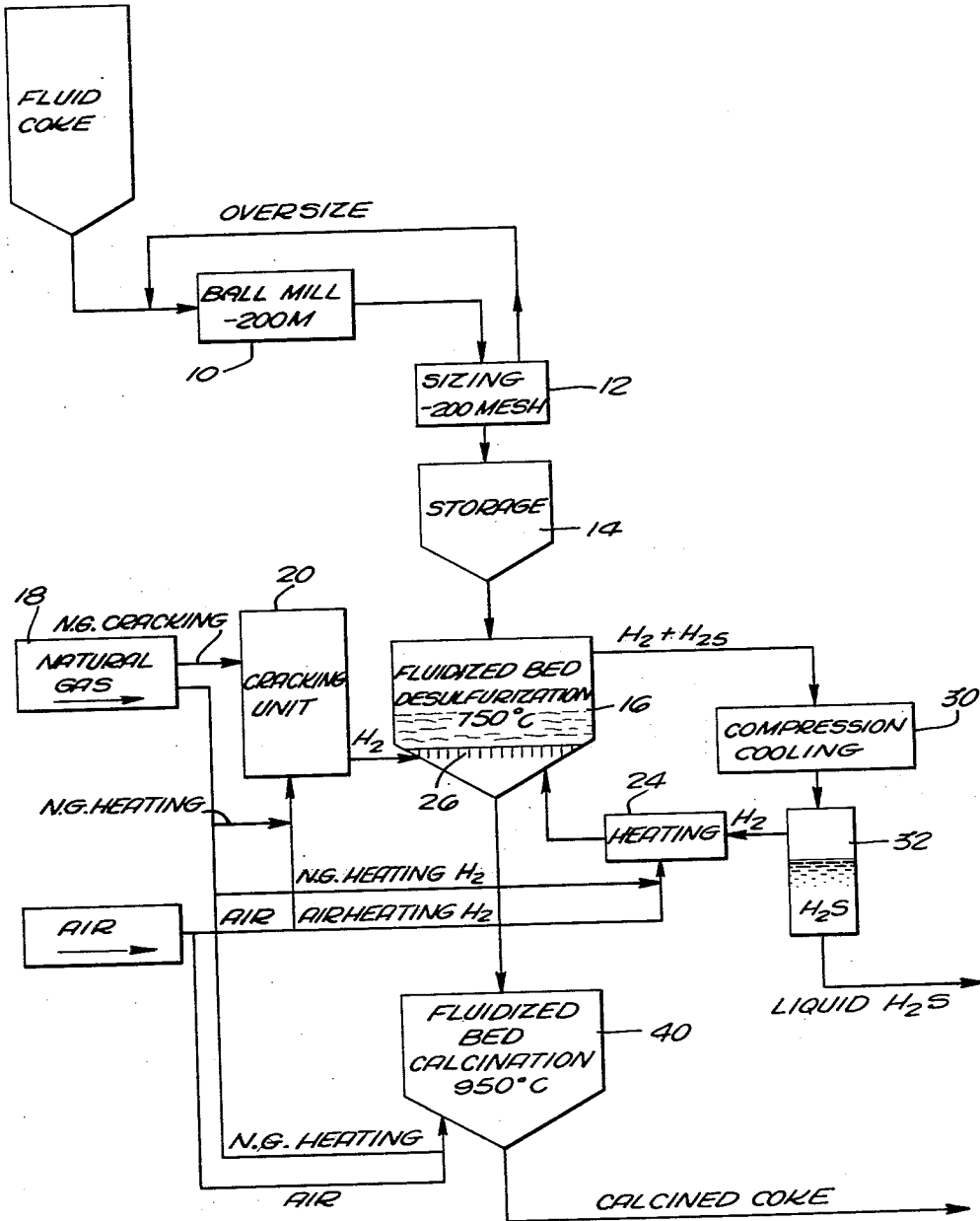
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PROCESS FOR DESULFURIZING PETROLEUM COKE

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**PROCESS FOR DESULFURIZING
PETROLEUM COKE**

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This invention relates to a process for removing sulfur from carbonaceous materials and has particular reference to a process for desulfurizing petroleum coke.

There has recently been developed an improved process known as the fluid coking process for the production of coke and the thermal conversion of heavy hydrocarbon oils to lighter fractions. The fluid coke thus produced is generally quite high in sulfur content and can range from 5% to 8% sulfur or more.

The high sulfur content of the coke product poses a major problem in its efficient utilization. For most non-fuel or premium fuel uses a low sulfur content coke, below about 3 wt. percent sulfur, and in some cases below 1.5% sulfur is required. For example, low sulfur component coke is desired for the manufacture of phosphorus, for the production of calcium carbide, for lime burning, in the manufacture of soda ash or other alkalies, for various metallurgical applications, for the production of electrode carbon for various electrical applications such as the manufacture of aluminum and the like. The presence of high percentages of sulfur in the coke is generally objectionable because at least a part of it contaminates the products being produced by use of the coke. Moreover, when a high sulfur content coke is burned, the sulfur is liberated as sulfur dioxide, resulting not only in corrosion of equipment, but also presenting a health hazard by pollution of the atmosphere.

So-called green or delayed petroleum coke presents a similar problem of sulfur content, although the problem is not so acute as in the case of fluid coke since the sulfur content of green petroleum coke is generally less than that of fluid coke.

Many methods have heretofore been proposed for removal of sulfur from petroleum cokes. Some of these involve burning off the sulfur, others involve treatment of the coke with acid, and in some cases electrolysis is employed in conjunction with the latter. Other methods, more related to the present invention, have involved the treatment of the coke at elevated temperature and at atmospheric or elevated pressure with certain gases. Gases which have been employed are nitrogen, carbon monoxide, carbon dioxide, ammonia, water vapors, oxygen, hydrogen and various combinations thereof. However, all of these processes are subject to certain disadvantages from the standpoint that they are either incapable of reducing the sulfur content to the desired low level, or that they involve excessively expensive operations.

A primary object of the present invention is, therefore, to provide a novel process for the treatment of petroleum coke to reduce the sulfur content thereof to commercially acceptable levels.

Another object of the present invention is to provide a novel process for the desulfurization of petroleum coke which is adapted to be carried out economically on a large-scale basis.

Another object of the present invention is to provide a novel process for the removal of not less than 60% and as much as 90% or more of the sulfur present in petroleum coke.

Other objects and advantages of this invention, it is believed, will be readily apparent from the following detailed description of preferred embodiments thereof when read in connection with the accompanying drawing.

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In the drawing, the single figure is a flow sheet illustrating a preferred embodiment of the process of this invention.

Briefly, this invention comprehends within its scope the discovery that high percentages of sulfur removal from carbonaceous materials containing more than about 3% volatiles, such as petroleum coke, are obtained by subjecting the coke to the action of hydrogen under controlled conditions of temperature, time and particle size of the material being treated. It has been found that under these conditions, when hydrogen is passed through or over the coke, the hydrogen combines with the sulfur in the coke, forming hydrogen sulfide which is removed by the hydrogen flow. It has been further found that the efficiency of sulfur removal is unexpectedly related to the volatiles content of the coke and that for removal of 60-90% or more of sulfur, with which the present process is particularly concerned, the reaction conditions of time and temperature must be such that at least a portion of the volatiles content of the coke is maintained therein until the desired amount of sulfur has been removed. Thus, it has been found that the maximum temperature is critical, in that at temperatures above the calcining temperature of the coke, i.e., about 950° C., the total amount of sulfur which can be removed, even under long periods of heating is substantially less than at lower temperatures. Moreover, the rate of removal of sulfur is at a maximum during the initial heating period at temperatures above about 750° C., but the rate decreases more rapidly during the subsequent heating periods at such higher temperatures than at 750° C. The lowest temperature at which sulfur removals in excess of 60% can be obtained within commercially practicable time periods is about 600° C.

The following Table I illustrates several specific examples of the process of this invention, but it is to be understood that the invention is not to be limited to the details thereof. In carrying out these examples, 1 gm. samples of the coke were placed in a quartz tube and heated to the desired temperature in a tube furnace. In each case, hydrogen was passed over the sample, beginning at room temperature, at a rate of about 20 cc./min.

Table I

Material	Temp., (° C.)	Sulfur Removed in Percent					Total (23 hrs.)
		1st hr.	2d and 3d hr.	4th and 5th hr.	6th and 5th hr.	8th- 23rd hr.	
Fluid Coke, -200 mesh, 5% S	650	20.8	15.8	10.2	6.8	14.6	68.2
	700	29.7	29.0	12.7	4.8	8.2	87.6
	750	39.7	29.0	12.7	4.8	8.2	94.4
	850	50.3	13.4	7.5	3.9	5.5	80.6
	950	60.0	8.9	4.8	2.9	4.7	81.3

The results of the above table show the decreased desulfurization rate, after the initial heating period, with increase in temperature. It is also apparent that under the conditions utilized, the critical temperature for maximum removal of sulfur was 750° C. This holds true for varying conditions as will be illustrated hereinafter. On the other hand, where a desulfurization in the neighborhood of only 60% is desired, a temperature in the neighborhood of 950° C. can be selected inasmuch as the treatment time is at a minimum. Similar results can be obtained by the utilization of lower temperatures in the range at the expense of use of longer times.

The relationships between volatiles content, time and desulfurization rate is illustrated in Table II below, coking coal and metallurgical coke being included for pur-

poses of comparison. The examples were carried out in the same manner as those of Table I, except that in each case the treating temperature was 750° C. The grain size of the materials was -200 mesh in each case, except for the coking coal, which contained particles up to 2 mm.

Table II

Material	Volatiles in percent	Sulfur Removed in percent						Sulfur Content, percent	
		1st hr.	2nd and 3rd hr.	4th and 5th hr.	6th and 7th hr.	8th-23rd hr.	Total	Before	After
Coking Coal.....	39.4	51.6	20.8	4.1	3.9	7.1	87.5	1.2	.15
Green petr. coke.....	10.5	43.3	22.0	8.3	4.0	10.6	88.2	1.1	.13
Fluid Coke Metall. Coke.....	5	39.7	29.0	12.7	4.8	8.2	94.4	5	.28
	2				22.2	.1	22.3	.9	.7

The results shown in this table of the treatment of metallurgical coke, which is the same material as the coking coal, except for the removal of the volatiles, clearly illustrate the importance of maintaining at least a substantial portion of the volatiles in the material before subjecting it to the conditions necessary for removal of the sulfur.

As indicated, it has been found that the particle size of the petroleum coke is critical and must be maintained below about 200 mesh for satisfactory desulfurization. This is illustrated in Table III below. In carrying out the examples for this table, 50 gram samples were utilized in the tube furnace, the hydrogen flow was 120 cc./min., and the time of treatment was 23 hours. Fluid coke initially containing 5% sulfur was utilized in each case.

Table III

Grain Size	Temp. (° C.)	Sulfur Remaining (wt. percent of Sample)
-200 mesh.....	750	0.28
(*).....	750	2.73
-200.....	950	0.94
(*).....	950	4.12

(*) = 37%+80 mesh, 14%+100 mesh, 37%+200 mesh, 12%-200 mesh.

The hydrogen flow rate influences the rate of sulfur removal to some extent, but not proportional to the increase in hydrogen flow. This is evident from the results tabulated in Tables IV and V below, in which the sulfur removal is given in Table IV as percentage of original sulfur present, and in Table V as percent sulfur remaining, based on the original weight of the sample. In carrying out the examples tabulated in these tables, 50 gram samples were utilized in the tube furnace, the mesh size was -200; and the temperature was 750° C.

Table IV

Material	H ₂ Flow, cc./min.	Sulfur Removal in Percent				
		1 hr.	3 hr.	5 hr.	7 hr.	23 hr.
Fluid Coke, 5% S.....	22	12.0	33.9	46.6	53.1	78.6
	60	30.7	53.7	65.6	72.8	87.0
	120	38.7	60.0	71.2	75.5	92.3
Green Petr. coke, 1.1% S.....	120	32.2	50.1	60.6	67.3	80.0
	185	41.2	65.3	73.6	77.6	88.2

Table V

Material	H ₂ Flow, cc./min.	Sulfur remaining in the coke in percent				
		1 hr.	3 hr.	5 hr.	7 hr.	23 hr.
Fluid coke, 5% S.....	22	4.40	3.32	2.67	2.36	1.07
	60	3.47	2.31	1.70	1.38	.65
	120	3.06	2.00	1.46	1.18	.39
Green petr. coke, 1.1% S.....	120	.74	.55	.43	.36	.22
	185	.62	.38	.29	.25	.13

The effects of grain size and temperature on the removal of sulfur from green petroleum coke are illustrated in Tables VI and VII below in which the sulfur removal is given in Table VI as percentage of original sulfur present, and in Table VII as percent sulfur remaining, based on the original weight of the sample. In carrying out the examples tabulated in these tables, 10 gram samples of green petroleum coke containing 1.1% sulfur were utilized in the tube furnace and the hydrogen flow rate was 120 cc./min.

Table VI

Grain Size	t, ° C.	Sulfur Removal in percent				
		1 hr.	3 hr.	5 hr.	7 hr.	23 hr.
-325 Mesh.....	750	43.1	55.5	66.1	71.1	85.5
-60+325 Mesh.....	750	25.5	32.9	35.2	47.4	63.6
-60+325 Mesh.....	850	27.9	31.7	33.9	35.3	38.2

Table VII

Grain Size	t, ° C.	Sulfur remaining in the coke in percent				
		1 hr.	3 hr.	5 hr.	7 hr.	23 hr.
-325 Mesh.....	750	.63	.50	.38	.32	.16
-60+325 Mesh.....	750	.82	.74	.64	.58	.41
-60+325 Mesh.....	850	.79	.75	.73	.71	.69

Desulfurization with hydrogen in accordance with the process of this invention has the advantage that in addition to removal of the detrimental sulfur, the sulfur is removed in the form of hydrogen sulfide which can be used as such, or burned to elemental sulfur or sulfur dioxide which can be oxidized to sulfur trioxide for the production of sulfuric acid.

The hydrogen sulfide can be removed from the unreacted hydrogen by cooling, compression, compression and cooling or by other known means such as chemical absorption. In the latter event, the hydrogen sulfide solution can be processed in the conventional manner for recovery of sulfur. The hydrogen, freed from hydrogen sulfide, is recycled to the desulfurization unit.

The flow sheet illustrates a preferred manner of carrying out the process on a commercial scale. As shown, the fluid coke is fed to a ball mill 10 where it is ground to the necessary -200 mesh particle size. The ground material is sized at 12, the oversize material being recycled to the mill 10. The -200 mesh material is stored at 14 and fed from this storage to the reactor 16.

Natural gas from the supply 18 is fed to a cracking unit 20 wherein it is cracked to produce hydrogen which is fed to the reactor 16. The hydrogen need not be pure and generally will contain approximately 5% natural gas. However, the hydrogen from the cracking unit is preferably purified in the normal manner by washing out at least a portion of the CO₂ and CO and natural gas with an amine solution.

Air and natural gas are fed to the heating unit 24 wherein the mixture is burned, the hot product of combustion being fed to a heat exchanger 26 for heating the hydrogen to the desired temperature, preferably about

750° C. for maximum sulfur removal. The hot hydrogen then passes upwardly through the coke in the reactor 16 under fluidized bed conditions.

The mixture of hydrogen and hydrogen sulfide from the reactor is passed to the compression and cooling unit 30 wherein the hydrogen sulfide is liquified and passed to the storage tank 32. The hydrogen from the unit 30 is recycled to the reactor.

The desulfurized coke is calcined in the unit 40 and then is ready for use such as the preparation of electrodes and the like.

Having fully described my invention, it is to be understood that I do not wish to be limited to the details set forth, but my invention is of the full scope of the appended claims.

I claim:

1. A process for the removal of sulfur from carbonaceous materials having a grain size of -200 mesh and containing at least 3% volatiles, comprising the steps of reacting the material with sufficient hydrogen at atmospheric pressure and under conditions of temperature and time such that at least about 2% of volatiles are maintained in the material until the sulfur has been removed therefrom.

2. A process for the removal of at least 60% of sulfur from petroleum coke having a grain size of -200 mesh, comprising the step of subjecting the coke to the action of hydrogen at atmospheric pressure under conditions of time, temperature, and hydrogen quantity such that at least about 2% of volatiles are maintained in the coke until the said amount of sulfur has been removed therefrom.

3. A process for the removal of from 60-90% of sulfur from petroleum coke having a grain size of -200 mesh, comprising the steps of subjecting the coke to the action of hydrogen at atmospheric pressure and a temperature of 600-950° C., the heating time being such and sufficient hydrogen being present to cause removal of the said amount of sulfur as hydrogen sulfide prior to reduction of the volatiles content to below about 2%.

4. A process for the removal of from 60-90% of sulfur from petroleum coke having a particle size of -200 mesh, comprising the steps of heating the coke in the presence of hydrogen at atmospheric pressure to a temperature in the range of 600-950° C. for from 1 to about 23 hours, the temperature and time being such that at least about 2% volatiles are maintained in the coke until the said amount of sulphur has been removed therefrom.

5. A process for the removal of from 60-90% of sulfur from petroleum coke having a particle size of -200 mesh, comprising the steps of heating the coke in the presence of hydrogen at atmospheric pressure to a temperature in the range of 600-950° C. for from 1 to about 23 hours, a temperature in the upper portion of the stated range being selected for removal of an amount of sulfur falling in the lower portion of the stated range, and a temperature in the lower portion of the stated range and a time in the upper portion of the stated range being selected for removal of an amount of sulfur falling in the upper portion of the stated range, the temperature and time being such that at least about 2% volatiles are maintained in the coke until the said amount of sulphur has been removed therefrom.

6. A process for the removal of at least 60% of the sulfur present in petroleum coke comprising the steps of grinding the coke to -200 mesh, and heating the coke in the presence of hydrogen at atmospheric pressure and a temperature in the range 600-950° C., the temperature and time being such that at least about 2% volatiles are maintained in the coke until the said amount of sulphur has been removed therefrom.

7. A process for the removal of at least 60% of the sulfur present in petroleum coke comprising the steps of grinding the coke to -200 mesh, and heating the coke in the presence of hydrogen at atmospheric pressure and a temperature of about 750° C. for a length of time sufficient to maintain at least about 2% volatiles in the coke until the said amount of sulphur has been removed therefrom.

8. The process of claim 6 wherein the coke is ground to -325 mesh.

9. The process of claim 7 wherein the coke is ground to -325 mesh.

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