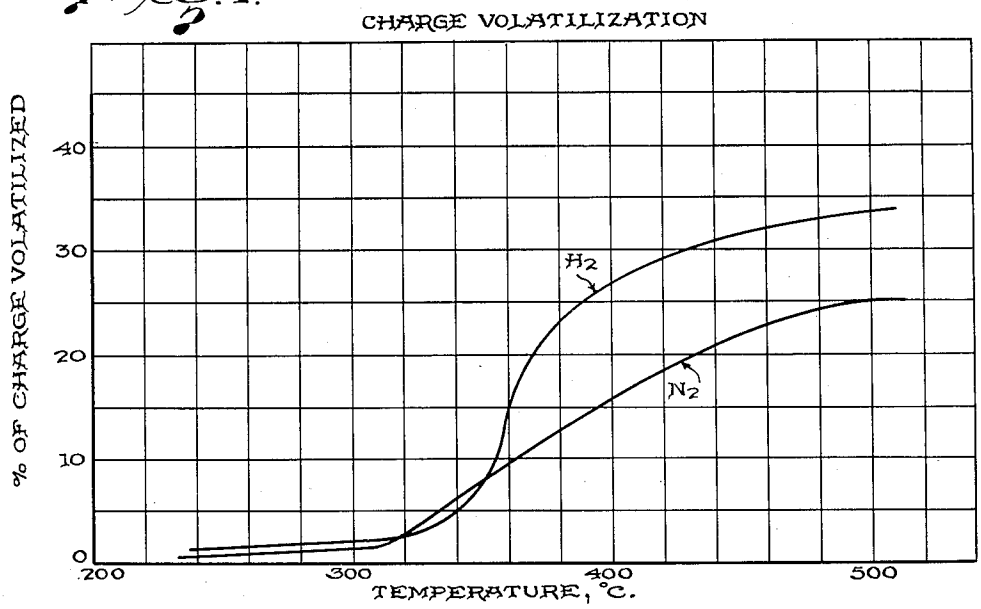
Dec. 6, 1955 J. B. McKINLEY ET AL 2,726,148

PRODUCTION OF LOW SULFUR SOLID CARBONACEOUS FUELS

Filed June 9, 1950 2 Sheets-Sheet 1

Fig. 1.



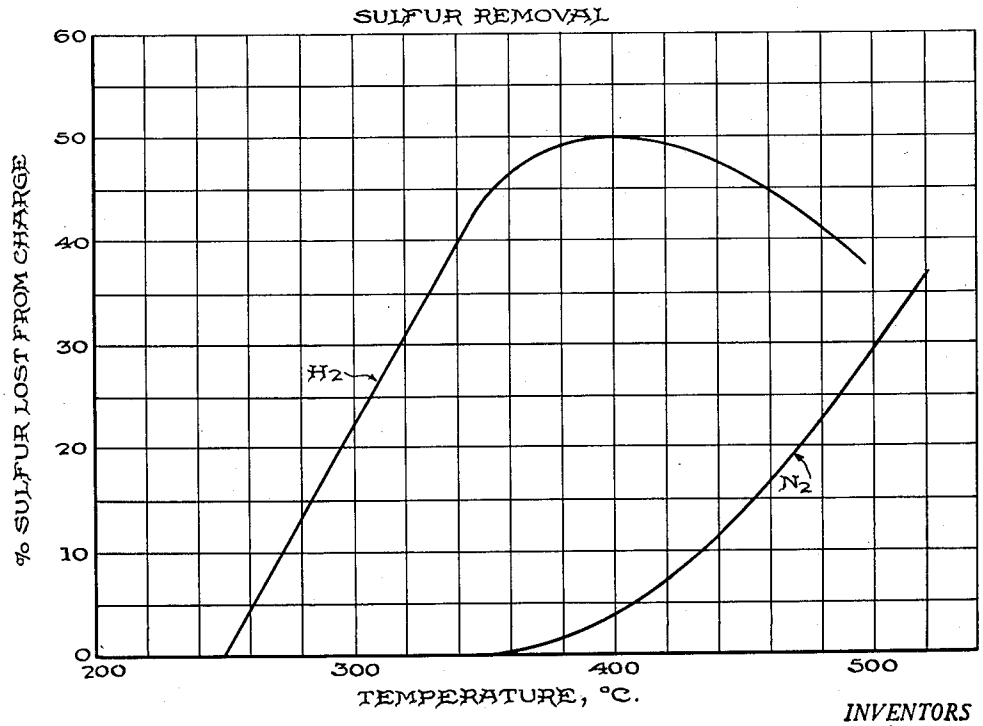


Fig. 2.

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PRODUCTION OF LOW SULFUR SOLID CARBONACEOUS FUELS

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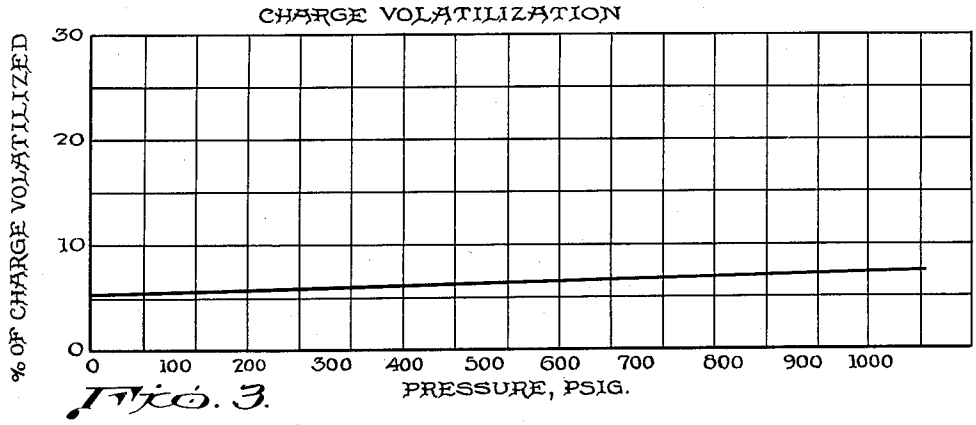


FIG. 3.

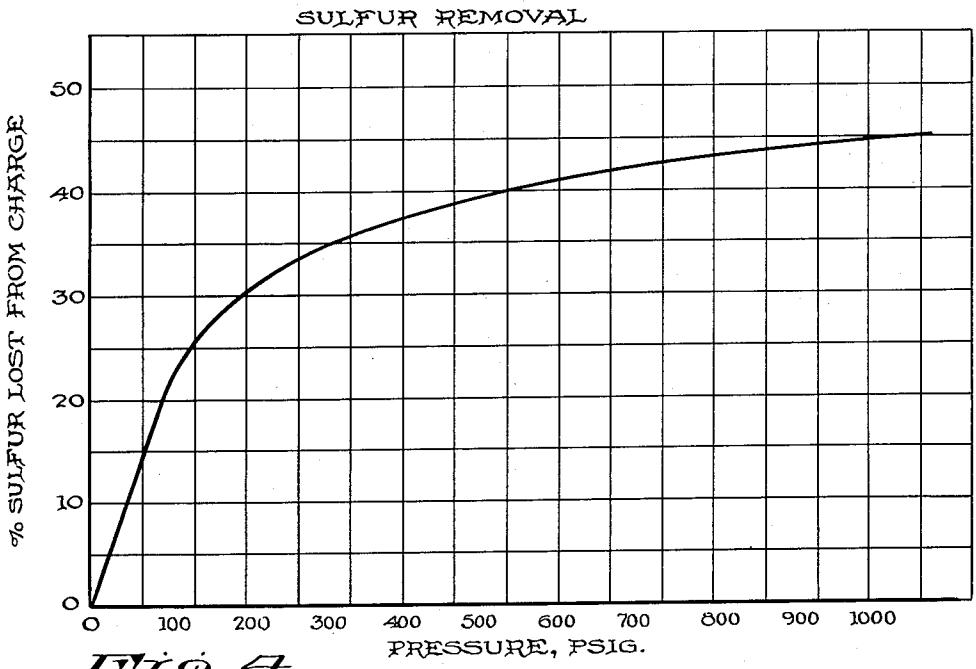


FIG. 4.

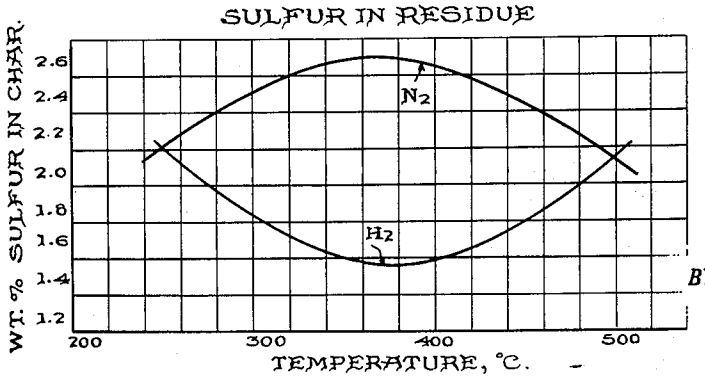


FIG. 5.

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PRODUCTION OF LOW SULFUR SOLID CARBONACEOUS FUELS

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3 Claims. (Cl. 44—1)

This invention relates to a process for removing sulfur from dense, solid carbonaceous materials, such as low temperature coke and the higher ranking coals, by contacting the solid carbonaceous material with hydrogen at elevated temperature and pressure.

Low sulfur solid carbonaceous materials are in demand in a number of industries, for example, where corrosive combustion products are to be avoided. Sulfur in coal may be oxidized to SO_2 and SO_3, during combustion. These gaseous combustion products together with water form corrosive acids injurious to metals.

Sulfur may be present in the coal or other carbonaceous material in various forms, such as pyrites, organic sulfur compounds of unknown composition, sulfates of iron, calcium, magnesium and copper as well as other forms. Normally, the bulk of the sulfur contained in the coal is in the form of pyrites, FeS_2. This invention is most efficacious for reducing pyritic sulfur.

Many schemes for reducing sulfur in coals have been devised. Some of these involve coking and burning off of the sulfur; others involve treatment of the coal 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 coal at elevated temperature and at atmospheric pressure with certain gases. Gases which have been employed to desulfurize coal are nitrogen, carbon monoxide, carbon dioxide, ammonia, water gas and hydrogen. Of these gaseous treatments, that with hydrogen has been the most effective. The work on desulfurization of coal with hydrogen has been carried out at atmospheric pressure and in general at temperatures of from about 500° to 1000° C. These high temperatures are conducive to decomposition of the coal, whereby substantial percentages of the treated stock are volatilized. This is disadvantageous as will be shown in detail hereinafter.

One object of this invention is to provide an efficient economical process by which dense solid carbonaceous materials may be substantially more completely desulfurized than by prior art methods. Another object is to provide a process for producing low sulfur coals for industrial purposes. Still another object is to provide a process for reducing substantially the sulfur content of dense solid carbonaceous materials, wherein substantial coking, decomposition or volatilization do not take place. A further object is to provide a process which requires the use of relatively low temperatures and pressures, whereby

cost of the equipment is made low. Other objects will appear hereinafter.

These and other objects are accomplished by our invention which comprises a process of desulfurizing dense solid carbonaceous materials, which process includes the steps of contacting the dense solid carbonaceous material with hydrogen at a pressure above atmospheric and at a temperature at which substantial desulfurization occurs, but below that at which substantial volatilization of charge occurs, said temperature lying approximately between 300°–425° C. The treatment is continued until a substantial portion of the sulfur contained in said material has been removed.

In the following description we have set forth several of the preferred embodiments of our invention, but it is to be understood that they are given by way of illustration and not in limitation thereof.

The treating of the solid carbonaceous charge stock with hydrogen within our temperature and pressure ranges accomplishes the reduction of pyritic sulfur (and perhaps some sulfur in other forms) to hydrogen sulfide, in which form it may be removed. Within the limits disclosed the rate of desulfurization and yield of low sulfur char are maximum, while caking, coking, decomposition and/or volatilization of the charge are comparatively low.

The process of our invention contemplates the desulfurization of dense solid carbonaceous materials such as low temperature coke, and coals of higher rank than lignite. For the classification of coals see J. F. Barkley and L. R. Burdick, "Curves for the Classification of Coal," U. S. Bureau of Mines Information Circular 6933, 1937. According to these authors essentially all coals may be classified in the following groups which are set forth in the order of decreasing rank: (1) anthracite, (2) bituminous, (3) sub-bituminous and (4) lignite. Each of these main classifications has sub-classifications under which the main type of coal is classified more specifically. In general, sub-bituminous coals and higher are of relatively dense structure while the coals classified as lignite, such as lignite and brown coal, are of substantially more porous structure. It is to these relatively dense coals of higher rank, and materials such as for example low temperature coke which has a similar structure, that this invention relates.

Figures 1–5 are graphical plots of exemplary results obtained, and illustrate the beneficial effects to be attained by the present invention. These figures will be explained in detail hereinafter.

The dense solid carbonaceous material to be desulfurized is preferably comminuted prior to treatment. A particle size of from about 8 to 25 mesh has been found satisfactory. The purpose of the comminution of the charge is merely to increase the reactive surface of the carbonaceous material; consequently, the size of the particles is not critical and has been chosen merely for general reasons of efficiency and economy. It will be apparent that charge stocks having a particle size either smaller or larger may be treated according to the instant invention with some degree of success.

After comminution the carbonaceous material is placed in the reaction chamber and hydrogen is passed over the

charge stock at elevated pressure while the temperature is increased to reaction conditions.

The reaction temperature is one which is sufficiently great to effect substantial desulfurization, but below that temperature at which substantial percentages of charge stock are volatilized. Volatilization of charge is to be avoided, since a portion of the charge stock is lost and since per cent sulfur in char increases therewith. In other words, excessive volatilization reduces residual product; thus, an equal amount of unconverted sulfur remaining in the char would constitute a higher per cent of the solid residue after substantial volatilization occurs. Another reason for avoiding too high temperatures is that caking of the residue occurs, i. e., the charge becomes plastic and impervious to hydrogen, thus reducing the ability of hydrogen to react with sulfur in the charge. A temperature great enough to effect maximum desulfurization with minimum volatilization is most desirable, since the greatest yield of low sulfur char is produced with minimum operating costs. The preferable limits for the particular charge may be easily determined by conventional analysis of the treated char or analysis of the treating gas for sulfur content and by weight loss of the carbonaceous portion of the charge to determine volatilization, or more simply by an inspection of the char to determine what degree of coking or caking has occurred. Coking and/or caking occur simultaneously with volatilization.

The most preferable temperature range varies somewhat with different charging material. A lower limit of about 300° C. and an upper limit of about 425° C. have been found most satisfactory.

As stated previously, the most efficient temperature is chosen to produce maximum desulfurization with minimum volatilization. Increasing the temperature above this limit is to be avoided in view of the undesirable loss of charging material, increased expense of heating, and increase of percent sulfur in the char. For the materials contemplated by this invention, desulfurization is high between the minimum and maximum temperature, and volatilization, coking, and percent sulfur in the residue become undesirably high above the maximum temperature.

The hydrogen pressure may be any pressure above atmospheric, since the amount of desulfurization increases sharply with increased pressure. Generally, the amount of desulfurization levels off at about 500 p. s. i. g. or lower in the case of some coals, and little advantage is gained by increasing the pressure above this point. Furthermore, equipment costs are increased considerably with pressures above about 500 p. s. i. g. Maximum efficiency, that is, maximum desulfurization with minimum equipment cost may usually be attained between the limits of about 50 to 500 p. s. i. g. Increasing the pressure has little or no effect on volatilization of the charge. Space velocity advantageously varies between about 300 and about 500 volumes of hydrogen per volume of charge stock per hour. Lower space velocities are preferred for economical reasons. Since the space velocity has little or no effect on either the amount of desulfurization or volatilization of charge stock, these limits may be varied considerably without materially affecting the results of the process. It will be apparent that the time of treatment will vary according to the conditions employed and principally according to the particle size of the charge and the temperature. Under the conditions indicated above, about 1 to 2 hours is sufficient for substantial sulfur removal. Longer or shorter periods of time may be used depending upon the degree of desulfurization desired. A treating period of ninety minutes has been found to be satisfactory in all experimental work.

It should be noted that prior art treatment of coals with hydrogen at atmospheric pressure have produced only up to about 10 per cent reduction in sulfur content along with substantial coking of the charge, whereas the present invention, involving a limited temperature range and elevated pressure, has produced as high as about 70 per cent desulfurization, and in most cases above about 40 per cent. Since this invention is most efficacious for reducing pyritic sulfur, the per cent of desulfurization depends on the amount of sulfur present in the charge in pyritic form.

As illustrative of the results obtainable by our process exemplary data obtained are presented hereinafter. In carrying out the experiments the following procedure was utilized:

Coals were crushed and sized to 8 to 25 mesh. Large samples were thoroughly mixed and divided into 5 cc. samples which were placed in 12 ml. vials, the stoppers of which were sealed in place with paraffin wax. In a run one of the weighed 5 cc. samples of coal was charged into a ¼" i. d. 40 mesh stainless steel screen cylinder 8" long and held in the cylinder with glass wool plugs at either end of the cylinder. The charged screen cylinder was then inserted into a 7/16" i. d. stainless steel tube. The inlet to this tube communicated with a pressure controlled gas inlet system and the outlet to condensers to trap out liquid product, a pressure reducing valve, and a throttling valve to control the gas flow. The system was thoroughly flushed out with prepurified nitrogen. Nitrogen flow was started over the coal while heating it up to 125–150° C. in forty minutes and maintaining it at this temperature for 4 hours to eliminate moisture. The system was then cooled to room temperature, flushed with hydrogen, and hydrogen flow started over the coal at the desired pressure and S. T. P. space velocity. The coal was heated to the desired reaction temperature, maintained at this reaction temperature for ninety minutes, and cooled to room temperature. Heating up and cooling down times were each kept substantially constant at fifty-five minutes. The cooled coal residue was removed, weighed, and then ground to about 200 mesh and finer. The ground product was analyzed and results calculated. The analytical method employed for sulfur determination is described by E. S. Moore in his work entitled "Coal," 2d ed., pp. 73, John Wiley & Sons, Inc., New York (1940).

The coal upon which the illustrative runs were carried out had the following analysis:

TABLE I

Rank	Illinois No. 6 Coal
	High Volatile—B Bituminous
Typical Sample:	
As Received Basis—	
Percent Moisture	9.33
Percent Ash	7.14
Percent Volatile	34.36
Percent Fixed Carbon	49.17
B. t. u.'s per Pound	12,143
Percent Sulfur	1.31
Dry Basis—	
Percent Ash	7.87
Percent Volatile	37.90
Percent Fixed Carbon	54.23
B. t. u.'s per Pound	13,392
Percent Sulfur	1.44
B. t. u.'s per Pound, Moist m. m. f. Basis	13,190
Particular Sample Employed:	
As Received Basis—	
Percent Moisture	7.0
Percent Sulfur	2.00
Dry Basis—	
Percent Total S	2.15
Percent Pyritic S	1.70
Percent Sulfate S	0.02
Percent Organic S	0.43

The following table sets forth the results of a number of runs carried out on this coal.

TABLE II

Desulfurization of Illinois No. 6 coal (sulfur content: dry basis, 2.15%)

Run No.	Variable Studied	Reaction Conditions				Product		Loss from Charge		Condition of Product
		Gas Stream	Pressure, p. s. i. g.	Gas S. T. P. S. V.	Temp., ° C.	Percent S in—	Percent of Charge	Percent of Total S	Percent of Total Wt.	
1	Temperature	H_2	500	300	243	2.10	98.92	3.3	1.08	Non-coked.
2	do	H_2	500	300	257	2.17	99.13	0.0	0.87	Do.
3	do	H_2	500	300	300	1.73	96.88	21.9	3.12	Do.
4	do	H_2	500	300	350	1.51	93.52	34.4	6.48	Do.
5	do	H_2	500	300	350	1.21	94.09	47.0	5.91	Do.
6	do	H_2	500	300	350	1.21	91.72	48.4	8.28	Slightly Coked.
7	do	H_2	500	300	400	1.51	70.10	50.7	29.90	Coked.
8	do	H_2	500	300	450	1.73	71.97	42.3	28.03	Do.
9	do	H_2	500	300	500	2.01	63.72	40.5	36.28	Do.
10	Pressure	H_2	10	300	350	2.32	93.44	0.0	6.56	Non-Coked.
11	do	H_2	10	300	350	1.85	94.69	18.6	5.31	Do.
12	do	H_2	10	300	350	2.01	95.00	11.2	5.00	Do.
13	do	H_2	10	300	350	2.19	95.49	2.8	4.51	Do.
14	do	H_2	100	300	350	2.21	94.59	2.8	5.41	Do.
15	do	H_2	300	300	350	1.49	94.46	34.4	5.54	Do.
16	do	H_2	500	300	350	1.21	94.09	47.0	5.91	Do.
17	do	H_2	500	300	350	1.21	91.52	48.4	8.48	Slightly Coked.
18	do	H_2	500	300	350	1.51	93.52	34.4	6.48	Do.
19	do	H_2	750	300	350	1.37	92.46	40.9	7.54	Non-Coked.
20	do	H_2	1,000	300	350	1.31	94.12	42.8	5.88	Do.

Figure 1 of the drawings is a plot of the temperature against the volatilization of the charge stock. It will be seen that volatilization of charge increases substantially and quite sharply above about 350° C.

Figure 2 is a plot of the temperature against the percentage of sulfur lost from the charge. It will be seen that the rate of desulfurization increases extremely sharply above about 250° C.

Correlation of the two curves presented in Figures 1 and 2 will illustrate that maximum desulfurization with minimum volatilization of charge can be obtained with temperatures between about 300° to 350° C.

Figure 3 plots pressure against volatilization of the charge. A substantially horizontal linear curve is produced illustrating that increase in pressure has little effect on charge volatilization.

Figure 4 plots pressure against desulfurization. It will be seen that a slight increase in pressure above atmospheric produces a sharp increase in desulfurization. It will be seen that maximum desulfurization with this particular charge stock may be attained at pressures above 50 p. s. i. g. The last-described curve also illustrates that little advantage is to be gained in increasing the pressure above about 500 p. s. i. g.

Figure 5 plots per cent sulfur in the char against temperature. This figure indicates clearly the reason for not exceeding the temperature at which substantial volatilization occurs. At temperatures above about 425° C., where considerable volatilization occurs, the unconverted sulfur remaining in the char constitutes a higher percentage of the residue. Since a principal aim of the invention is to produce maximum yield of low sulfur char, it will be seen that the temperature maximum may not be exceeded substantially without thwarting this aim.

Correlating Figure 5 with Figures 1 and 2, it will be seen that minimum sulfur in char and maximum desulfurization may be attained at temperatures between about 300° C. and 425° C. with comparatively low volatilization of the coal.

In Figures 1, 2, and 5 corresponding runs carried out with nitrogen have been plotted in order to show the unusual effects of hydrogen.

As examples of other results, similar runs were carried out on Thick Freeport Bed coal, a high volatile A bituminous coal, and Pocahontas No. 3 coal, a low volatile bituminous coal. Similar trends were observed. It should be noted, however, that substantial desulfurization began to occur at a temperature of about 300° C. for Thick Freeport Bed coal rather than 250° C. as in the illustrated curve. Sulfur removal for Thick Freeport Bed coal, as in the illustrated runs, increased sharply at pressures above atmospheric with a general leveling off at about 500 p. s. i. g. The effect of pressure on Pocahontas No. 3 coal was likewise very sharp at pressures above atmospheric, but the leveling off occurred at pressures slightly above 100 p. s. i. g. Substantial volatilization of the charge in runs made on Pocahontas No. 3 coal did not begin to occur until a temperature of about 415° C. was reached. In all runs, temperatures between 300°–425° C. produced maximum desulfurization, minimum sulfur in char, with comparatively low volatilization.

Similar runs were also made on coals of the lignite class, specifically North Dakota lignite and Texas lignite. However, in these runs no effect of pressure was noted. While we do not intend to be limited to any theory of operation of our invention, it is our belief that pressure as an important factor in the desulfurization of coal comes into play only in the case of the relatively dense, solid carbonaceous materials, since increased pressure causes increased penetration of the reducing gas, hydrogen, into the physical structure of the coal. Lignite coals are of quite porous structure and are consequently not affected by the use of pressure.

As indicated above the invention is not limited to use of a charge having any particular particle size. As also indicated hereinabove the optimum temperatures for treatment of the coal may vary with the particular charge stock. Thus, in the case of Illinois No. 6 coal the optimum temperature may be slightly different from that of Pocahontas No. 3 coal. In all cases, however, any increase in pressure above atmospheric produced a sharp increase in desulfurization. We also contemplate practicing our invention as either a batch process or as a continuous process. In the latter form any conventional apparatus for treating solid particles continuously may be used.

One advantage of our process is that it provides an efficient, economical method of producing low sulfur coals for use in industry. Another advantage produced by our process is that substantially greater desulfurization is accomplished about substantial volatilization of the coal. A further advantage of the process is that it employs relatively low temperatures and pressure, whereby heating costs and equipment costs are made relatively low.

What we claim is:

1. A process for desulfurizing coal without excessive conversion of the coal into gas or vapor which comprises contacting a comminuted solid mass consisting of coal of high pyritic sulfur content selected from the group consisting of anthracite, bituminous and sub-bituminous coal with a stream of hydrogen under a pressure of about

300 to 500 p. s. i. g., at a temperature of between 300° and 350° C. and maintaining said conditions until a large amount of sulfur contained in the coal has been removed without volatilization of a proportionately large amount of the coal.

2. A process for desulfurizing coal without excessive conversion of the coal into gas or vapor which comprises contacting a comminuted solid mass consisting of coal of high pyritic sulfur content selected from the group consisting of anthracite, bituminous and sub-bituminous coal with a stream of hydrogen under a pressure of between about 300 and 500 p. s. i. g., at a temperature of between 300° and 350° C. and for a period of about 90 minutes, whereby a large amount of sulfur contained in the coal is removed without volatilization of a proportionately large amount of the coal.

3. A process for desulfurizing coal without excessive conversion of the coal into gas or vapor which comprises contacting a comminuted solid mass consisting of coal of high pyritic sulfur content selected from the group consisting of anthracite, bituminous and sub-bituminous coal with a stream of hydrogen under a pressure of about 500 p. s. i. g., at a temperature of between 300° and 350° C. and for a period of about 90 minutes, whereby a large amount of sulfur contained in the coal is removed without volatilization of a proportionately large amount of the coal.

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