United States Patent [19]
Schroeder

[11] **3,909,212**
[45] **Sept. 30, 1975**

[54] REMOVAL OF SULFUR FROM CARBONACEOUS FUELS

[76] Inventor: **Wilburn C. Schroeder**, 7316
Radcliffe Dr., College Park, Md.
20740

[22] Filed: **June 29, 1973**

[21] Appl. No.: **375,013**

[52] **U.S. Cl.** .... **44/1 R;** 201/17
[51] **Int. Cl.**^{2}... **C10L 9/02;** C10L 9/08; C10B 57/00
[58] **Field of Search** .... 44/1 R; 201/17; 208/8

[56] **References Cited**

UNITED STATES PATENTS

2,595,366	5/1952	Odell et al.	201/17
2,608,526	8/1952	Rex	208/8
2,772,265	11/1956	Siddiqui	201/17
3,824,084	7/1974	Dillon et al.	44/1 R

Primary Examiner—Carl F. Dees
Attorney, Agent, or Firm—Bacon & Thomas

[57] **ABSTRACT**

The sulfur content of solid carbonaceous fuels, such as coal or lignite, is reduced by reacting a portion of the fuel with oxygen and steam without complete carbonization of the fuel, so as to generate nascent hydrogen at the surface and within the fuel particles for reaction with the sulfur in the fuel to form hydrogen sulfide. The resulting sulfur containing gases are removed and a low sulfur, solid fuel is recovered which can be burned, without further treatment or use of special devices, in furnaces or other combustion equipment with production of stack gases which meet pollution regulations regarding sulfur emissions. Alternatively, the low sulfur solid fuel may be gasified to produce low sulfur fuel gases or gases for the manufacture of industrial chemicals.

17 Claims, 3 Drawing Figures

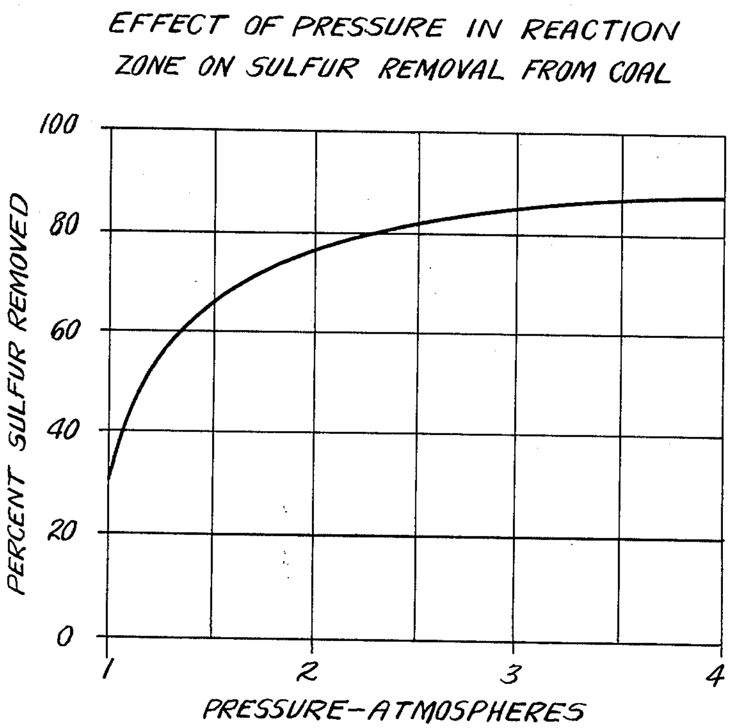
EFFECT OF PRESSURE IN REACTION ZONE ON SULFUR REMOVAL FROM COAL
PERCENT SULFUR REMOVED
100
80
60
40
20
0
1
2
3
4
PRESSURE–ATMOSPHERES

Fig. 1.

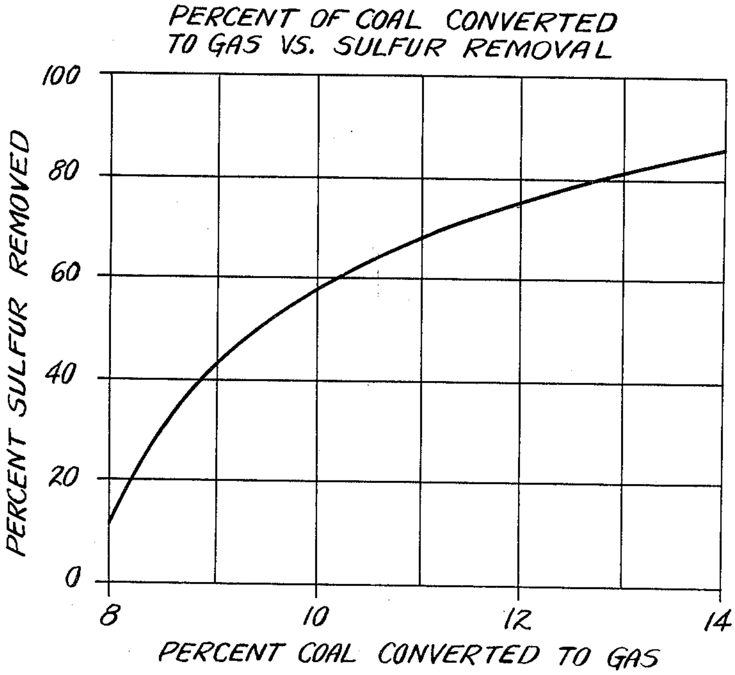
PERCENT OF COAL CONVERTED TO GAS VS. SULFUR REMOVAL
PERCENT SULFUR REMOVED
100
80
60
40
20
0
8
10
12
14
PERCENT COAL CONVERTED TO GAS

Fig. 2.

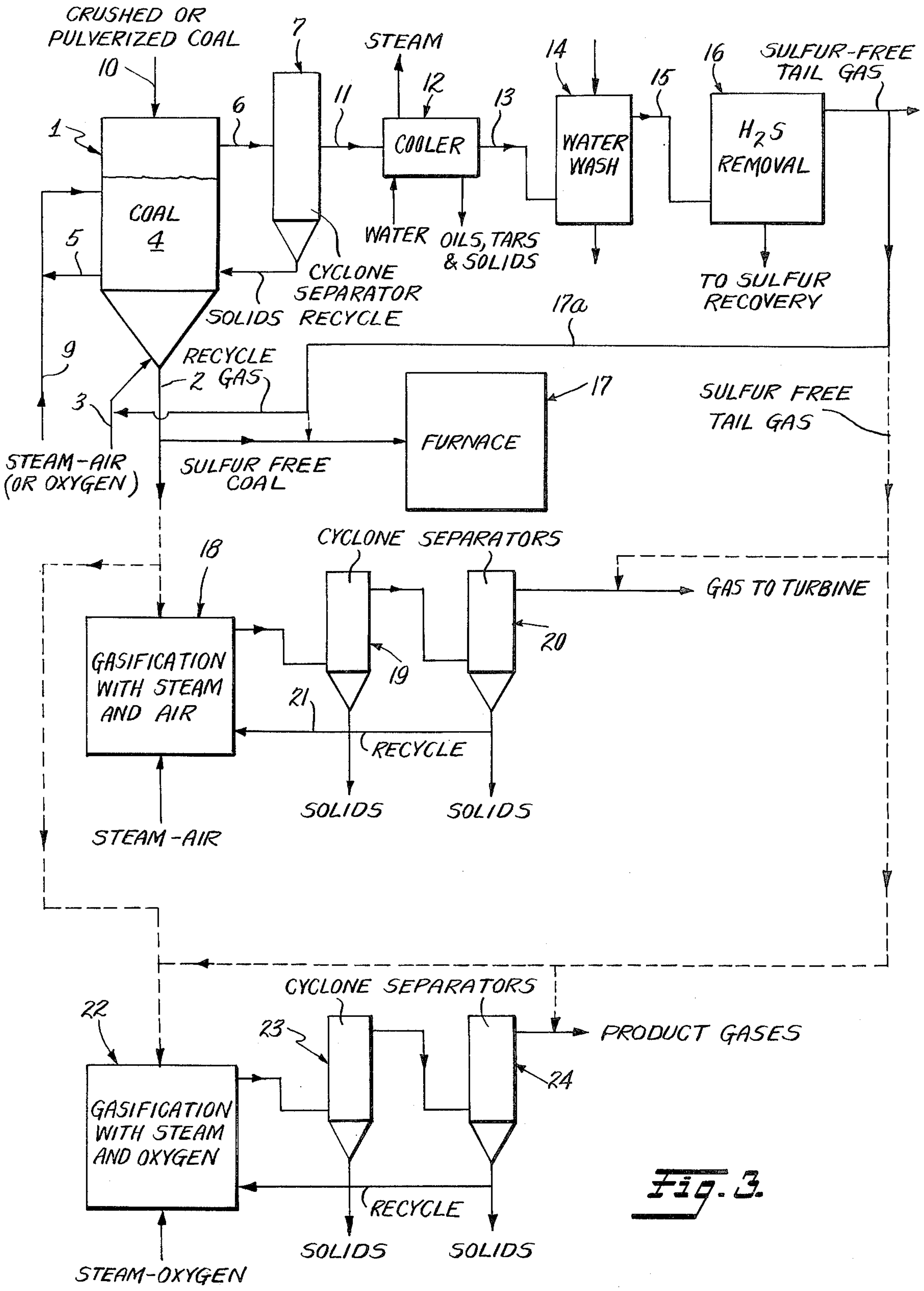
CRUSHED OR PULVERIZED COAL
10
1
COAL
4
5
6
7
11
STEAM
12
COOLER
13
WATER
OILS, TARS & SOLIDS
14
WATER WASH
15
16
H2S REMOVAL
SULFUR-FREE TAIL GAS
TO SULFUR RECOVERY
CYCLONE SEPARATOR
SOLIDS RECYCLE
17a
9
RECYCLE GAS
2
3
STEAM-AIR (OR OXYGEN)
SULFUR FREE COAL
FURNACE
17
SULFUR FREE TAIL GAS
18
CYCLONE SEPARATORS
GAS TO TURBINE
20
19
21
GASIFICATION WITH STEAM AND AIR
RECYCLE
SOLIDS
SOLIDS
STEAM-AIR
CYCLONE SEPARATORS
22
23
24
PRODUCT GASES
GASIFICATION WITH STEAM AND OXYGEN
RECYCLE
SOLIDS
SOLIDS
STEAM-OXYGEN

Fig. 3.

REMOVAL OF SULFUR FROM CARBONACEOUS FUELS

This invention relates to a process for reducing the sulfur content of solid carbonaceous fuels, such as coal and lignite, to provide a solid fuel product which can be burned, without further treatment or use of special devices, in furnances or other combustion equipment and which will produce stack gases which meet pollution regulations regarding sulfur emissions. The solid sulfur-containing fuel is contacted with air or oxygen and with steam under conditions resulting in generation of nascent hydrogen for reaction with the sulfur of the fuel without complete carbonization of the fuel. The sulfur is removed as hydrogen sulfide. In this application of the invention to reduce the sulfur content of fuels the nitrogen content of the fuel is also reduced to some extent, which assists in the control of nitrgoen oxide emissions when the fuel is burned.

The invention further provides a solid fuel which can be gasified with air to produce a gaseouos fuel under pressure, which gaseous fuel is low in sulfur and in particulate matter, and suitable for use in a gas turbine or a combined cycle consisting of a gas turbine followed by a steam cycle.

It is a further purpose of the invention to provide a solid fuel which can be gasified with oxygen and steam under pressure to produce a gas high in CO and H_2 and which can be used to produce liquid fuels, alcohols, and other oxygenated hydrocarbons, ammonia, and pipeline gas.

The manner in which the fuel is used for these purposes will be made evident in the following description of the invention.

A variety of methods have been suggested to reduce the discharge of sulfur compounds into the atmosphere when sulfur containing fuels such as coal are burned for heating purposes or to produce steam for the generation of electric power. Two general methods have been tried. The first attempts to remove the sulfur from the stack gases after the sulfur containing fuel is burned, the second attempts to remove the sulfur from the fuel before it is burned.

One of the simplest methods proposed to remove sulfur from the stack gases is to add limestone to the furnace where it is calcined to CaO, which in turn reacts with the SO_2 in the stack gases to form solid $CaSO_4$ which can be taken out in the precipitators. This was not found to be very effective and under good conditions was unable to remove more than about 30 percent of the SO_2 in the stack gases. Also the precipitators became less effective when the SO_2 concentration in the stack gases was reduced. Some furnaces could not operate well with the additional amount of solid and the disposal of the solid was a further problem.

Another method tested was to pass the stack gas through wet scrubbers before it was discharged into the air. Various types of slurry or solutions for scrubbing the gases were used such as those containing limestone or lime, dolomite, magnesium oxide or other alkaline materials. These were found to be 50–70 percent effective in removing the sulfur compounds from the stack gases.

Many problems were encountered with the scrubbing methods. The scrubbers were unreliable and plugged up, so that either the combustion gas had to be bypassed or the furnace shut down. Corrosion problems were severe and control of conditions in the scrubber was difficult. The combustion gases were cooled by scrubbing and would not rise into the air after leaving the exit stack and it was often necessary to reheat the stack gases. Disposal of solids from the scrubbing tower was a difficult problem. One of the most serious problems was that a multiplicity of scrubbers was needed and the gas cleaning installation required about as much space as the power plant. Installation costs and operating expenses were high.

Numerous other methods have been and are being tried for stack gas cleaning but none appears to be simple or low cost. The inherent difficulties are the enormous volume of stack gas that must be processed and the very low concentration of SO_2 in these gases.

The problem with stack gas cleaning have resulted in attempts to remove the sulfur compounds from coal before it is burned. If this is successful, than fuel can be burned as it has been in the past, without material change in the operation of furnaces, boilers and utility plants.

About 60 percent of the coal used in industrial furnaces is now cleaned in various density separation or washing processes. This helps to reduce the iron sulfide content of some coals but does not eliminate the organic sulfur. On many coals, especially those east of the Mississippi River, the washing processes have not generally reduced the sulfur sufficiently to meet pollution requirements.

Attempts have been made to dissolve or disperse the coal in solvents, such as aromatic compounds produced from the coal, and then filter off the undissolved material which contains most of the sulfur compounds. The solution process is often carried out under hydrogen pressure which probably aids in dissolving the coal. After filtration the solution is recovered for reuse by distillation from the solid fuel. The plant and equipment for carrying out this process are complex and costly, and the filtration step and the recovery of the solvent are especially difficult problems. Also a substantial residue of combustible material is left which is both high in ash and sulfur. This material must either be discarded and waster or burned and then the sulfur removed from the combustion gases.

Complete hydrogenation of the coal to liquid products can be carried out and this will produce an oil very low in sulfur. The process is highly complex and the capital cost of the equipment is high, which leads to a high cost product.

The gasification of coal or coke with steam and air or oxygen to produce combustible gases has been practiced for over 50 years. When steam and air are used a low Btu gas is produced having a heating value of 150 to 180 Btu per cubic foot. With steam and oxygen the heating value is from 300 to 350 Btu per cubic foot. Either of these gases can be purified to remove sulfur, and then burned in a furnace.

The present invention differes from gasification as practiced heretofore by reacting only the minimum amount of coal with steam and air (or oxygen) which is necessary to reduce the sulfur in the coal to the desired level, and all the remaining coal is removed from the reaction zone. The desulfurized coal still contains sufficient volatile matter so that it is a satisfactory fuel for combustion purposes. The product is not a coke or char. It has been carbonized only to the extend necessary to remove a substantial amount of the sulfur.

Complete gasification as practiced heretofore requires the necessary equipment and facilities for converting all the coal (or coke) to gas and the capital cost is high. The purification process to remove H_2S is also large and costly because of the large volume of gas passing through the equipment. The operation of this equipment to produce gas from coal increases fuel costs from 2.5 to 3 times the cost of the coal itself. In other words, with coal costing $0.30 per million Btu, the cost of the desulfurized gas is between $0.75 and $0.90 per million Btu. In addition, the loss in heating value from heat in the coal to heat in the gas is about 25 percent.

Desulfurization of coal as practiced according to this invention reacts only 5 to about 14 percent of the coal. Consequently, the capital cost of the equipment and facilities to carry out this process are approxiamately one-tenth of the cost for gasification. The purification step is also reduced accordingly. Operating costs are greatly reduced and it is estimated that they will increase fuel costs only by 15 to 20 percent over the cost of the coal. With coal at $0.30 per million Btu the cost of the fuel (desulfurized coal and gas) would be from $0.34 to $0.36 per million Btu. The heat loss in the process is 6 to 8 percent.

The desulfurized coal from the process, containing volatile matter as heretofore noted, is a fuel commonly used in utility boilers. On the other hand, the gas from a gasification process is of much lower Btu content per cubic foot than natural gas and has not been used in utility boilers. This is especially true for gas made with steam and air. Such gas cannot be used in existing boilers without considerably loss in capacity.

In addition to the gasification of coal, processes to treat coal with steam and air or oxygen to substantially completely carbonize the coal to produce a coke or char are well known and are described in many patents. Methods for treatment of the coke or char with hydrogen or other reducing gas to lower the sulfur content of the char have also been practiced. Hydrogen or other reducing gas for treatment of the char has been generated externally or internally. Internal generation of hydrogen or reducing gas has been done with air or oxygen and steam.

None of these processes, however, has been performed in one single step which heats the coal, desulfurizes the coal under optimum conditions, provides a maximum amount of coal for subsequent combustion steps, provides coal which is not carbonized but which instead contains a large amount of volatile matter, making it most suitable for subsequent combustion processes, carries out the desulfurization process with minimum use of air or oxygen at the lowest reaction temperatures, and uses a minimum amount of coal in the desulfurization step. Because of the small amount of coal consumed in the process the H_2S is contained in a relatively small amount of gas from which it is easily removed. The product gases are combustible gases which are valuable for subsequent combustion processes.

Furthermore, the invention can be used on strongly caking bituminous coals, non-caking subbituminous coals, or lignite. The coal particle, without previous thermal treatment of any kind, is introduced into a bed of particles at operating temperature, which heats the coal particle rapidly. Combustion with oxygen at the particle surface provides further heat for rapid expansion of the particle and creation of large surface areas. The increased porosity of the particle as well as its large surface area make the hydrogen more effective in sulfur removal.

The coal particle heats and expands in the presence of steam which reacts with the hot carbon to produce nascent hydrogen which is highly effective in reacting with sulfur or sulfur compounds to produce H_2S. The H_2S is carried out with the other gaseous constituents and removed from the gas by well known purification methods.

Temperatures, nascent hydrogen production, and coal throughput are all controllable, and are so controlled that they provide maximum sulfur removal, minimum change in the coal itself, and minimum heat loss. The result is a process which is low in captial investment and operating cost and gives minimum increase in fuel cost over the cost of the coal itself. The coal product can be used in existing boilers or in new boilers without the addition of spacial facilities to the boiler itself and without loss of steam output and without change in the method of operating the boiler.

None of the prior known processes operates in such a manner as to produce a high yield of low sulfur coal containing substantial volatile matter.

This invention achieves these results by converting the sulfur or sulfur compounds in the coal to H_2S. This is done by generating hydrogen through reaction of a small amount of the coal with steam (either added or generated from the moisture in the coal) at elevated temperature, as follows:

$$H_2O + C \rightarrow CO + H_2$$

Part of the coal is burned with air (or oxygen) to create the temperature required for the above reaction. This reaction and attainment of the desired temperature ae favored by preheating both the air (or oxygen) and steam used in the desulfurization process.

The invention as further illustrated in the accompanying drawings, wherein:

FIG. **1** is a graft showing the effect of pressure in the reaction zone on sulfur removal from coal.

FIG. **2** is a graft showing the percent of coal converted to gas vs. sulfur removal.

FIG. **3** is a flow diagram showing representative steps in processes utilizing the invention.

The temperature required depends on the types of coal and the amount of sulfur to be removed. The bituminous coals prevalent in the eastern and midwestern parts of the United States often contains from 2.5 to over 4 percent sulfur. To meet pollution requirements it is generally necessary to reduce the sulfur to below one percent. The temperature required is in the range from 1100° to 1300°F, although it may go as high as 1500°F for the low volatile butuminous coals.

The western coals are lower in sulfur, often close to one percent, and are subbituminous coals with most of the sulfur present or organic sulfur. Temperatures in the range from **900** to **1400**°F will usually reduce the sulfur in these coals to the required levels.

In the process all the coal particles pass through the heated zone and are subjected to the action of the hot hydrogen and CO produced at the coal surface, thereby reducing the sulfur in the particle to H_2S. The coal particle then passes out of the reactor as a low sulfur fuel which can subsequently be burned in a furnace and the resulting combustion gases will be low enough to sulfur to meet pollution control regulations.

The temperature is controlled by the amount of air (or oxygen) and steam admitted for a given coal flow through the reactor. More air increases the temperature. More stem decreases the temperature but generates more hydrogen. The amount of hydrogen produced is very important. At a given operating temperature, sulfur removal can be increases by increasing the hydrogen concentration considerably beyond the stoichiometric hydrogen required.

In addition to this hydrogen formed by the reaction of hot carbon and steam some hydrogen is also released from the coal particle as it is brought to high temperature. In general coals contain 4 to 5 percent by weight of hydrogen and some of this forms hydrogen gas. It is believed that this hydrogen also helps in removal of the sulfur from the coal.

It has been found that the generation of hydrogen (and CO) at the surface of and within the coal particle is much more effective than passage of hydrogen (and CO) from an external source through the hot coal particles. Under atmospheric pressure in the reaction zone, hydrogen or hydrogen and CO from external sources has little effect in removing sulfur from the coal. At increased pressure some sulfur was removed but the amount was very small compared to the amount removed when the CO and hydrogen were generated at the surface of the coal particle. It is believed that the favorable conditions for sulfur removal result from the action of the nascent hydrogen which is produced and exists momentarily at the reacting gas-coal interface.

It is important to keep the temperature as low as possible and still secure satisfactory sulfur removal from the coal, especially if the desulfurized coal is to be used in an industrial or utility furnace for steam raising. Coal containing ten or more percent volatile matter burns much more rapidly than coal which has been almost completely devolatilized or coal which has been almost completely devolatilized or coal which has been converted to coke or char, and most boilers are designed for a coal containing volatile matter. By using sufficient steam to generate hydrogen in excess of that required to convert the S to H_2S the volatile matter in coal can be kept well over 10 to 12 percent.

Pressure has been found to be an important variable in the removal of sulfur from coal and the process is sensitive to the total pressure at which the reactions are carried out, as shown in FIG. **1.** A low volatile bituminous coal desulfurized at 1500°F shows less than 40 percent sulfur removal at atmospheric pressure but this increases to over 80 percent when the reactions are carried out under the same conditions at a total pressure of 3 atmospheres.

Purification of the gas stream from the reaction zone removes particulate matter, oils and tars, ammonia, and H_2S. The gas is passed through a cyclone separator to remove as much particulate matter as possible and this is recycled to the reactor. The gas is then cooled both by heat exchange with incoming gas streams and a waste heat boiler to provide steam for the process. This condenses the oils and tars which also carry with them most of the remaining particulate matter. This liquid and solid material contains sulfur and is recycled back to the reaction zone. The gas is then washed by direct contact with water which removes the ammonia and any remaining liquids or solids. Sulfur can be removed from the cooled gas stream by several well-known processes, such as the hot potassium carbonate, or monoethanol amine.

Sulfur may be produced from the H_2S removed in the purification process by a Claus process plant which converts the H_2S to liquid or solid sulfur. The final purified gas is a combustible gas which can be burned along with the desulfurized coal, or which can be utilized for other purposes which will be described later.

The desulfurized coal recovered from the process will be the amount fed less the coal converted to gas. FIG. 2 shows the relationship between the amount of coal converted to gas and sulfur removal for a bituminous coal desulfurized at 1500°F under 3 atmospheres pressure. About 8 percent of the coal is required to maintain bed temperatures. Reaction of additional coal then provides the hydrogen necessary for desulfurization. The gasification of 12 percent of the coal removes **80** percent of sulfur from the coal particles.

Desulfurized coal leaving the reaction zone is at high temperature. In order to avoid loss of the sensible heat the coal particles will be transformed hot to any subsequent combustion process.

Heat losses in the process arise from the production of a small amount of CO_2 and the cooling of the gas stream during purification. Both are small and it is estimated that the total heat loss (including the heat lost from not burning the sulfur) is approximately 8 percent.

In the desulfurization process described herein the use of catalysts on the coal is unnecessary. It is well-known however, that hydrogenation reactions can be favorably influenced by a large number of catalysts, which are usually metals or metal compounds. Some of the best catalysts are compounds of molybdenum and cobalt or mixtures of the two. These are effective in very low concentrations but they are also expensive. Iron, tin, aluminum, and zinc are useful in somewhat higher concentrations and are less expensive. The catalysts may be applied by converting them to water soluble salts which can be sprayed onto the coal or the finely ground metallic compounds may be mixed with coal as solid materials during the pulyerization of the coal.

For coals which are found difficult to desilfurize the addition of a catalyst may increase the effectiveness of the process.

The gas stream leaving the reactor contains CO, H_2, H_2S, ammonia, volatile matter, some CO_2, and oils and tars. If air was used in the desulfurization process it also contains N_2. It is important that the concentration of H_2S in the gas be kept below one volume percent or the reactions to remove sulfur from the coal may be suppressed. Preferable, the concentration of H_2S is kept between about 0.1 and 0.5 percent. The volume of gases produced during gasification is usually too small to maintain this low concentration of hydrogen sulfide. Additional gas may be provided as necessary by recycling purified tail gas (after removal of hydrogen sulfide and ammonia) back to the reactor.

The major constituents in this recycle gas are H_2, CO, and methane. The methane is produced during the partial devolitization of the coal and from the reaction of the coal and hydrogen. The presence of the methane in the recycle gas is beneficial since it helps to suppress further methane formation from the coal.

The amount of steam fed to the reaction vessel should be sufficient to provide hydrogen in excess of stoichiometric requirement for removal of the sulfur in the form of H_2S. To reduce the sulfur in most coal to about 0.5 weight percent in a short time, such as approximately 10 minutes, has been found to require hydrogen concentrations at least 4 to 5 times stoichiometric. The use of superheated steam helps to reduce the heat requirements in the reactor, but this is not a major factor.

It should also be noted that some moisutre is present in the coal which must be taken into account in determining steam requirements. The presence of this moisture is desirable since it is distributed throughout the coal particle and will release hydrogen by reaction with the carbon as soon as the particle reaches a sufficiently high temperature.

Drying of the coal is not desirable unless the moisture content exceeds the amount required for the production of hydrogen. It is recognized that the moisture present in the coal requires combustion of some of the coal to vaporize the water and to bring it to high temperature, but this is not a heavy burden on the process.

In case the moisture in the coal is much in excess of that required to furnish hydrogen the coal should be dried to the desired level before it is fed to the process.

The specific advantages of the coal desulfurization process which has been described are as follows:

1. Sulfur is reduced or removed from crushed or pulverized coal, either caking or non-caking, without the addition of materials other than steam and air (or oxygen).

2. Operating pressures for sulfur removal are low and generally between 1 and 10 atmospheres.

3. The sulfur as H_2S, (and some nitrogen as NH_3) is evolved in a relatively small volume of gas from which it can readily be removed. The concentration of CO_2 in the gas stream is low which simplifies the removal of H_2S and final conversion of the sulfur compounds to sulfur.

4. The solid fuel produced in the process is low in sulfur and may be transferred hot to utility or industrial furnaces and burned in the same manner coal is burned.

5. Both the solid and gaseous fuel from the process can can be produced under pressure and would therefore be useful for complete conversion to gaseous fuel under pressure for use in a gas turbine. The resulting gaseous fuel would be low in sulfur compounds.

6. The reduction of the sulfur content in the coal necessary for a 1000 MW utility plant may be accomplished by passing the coal through 2 to 4 vessels.

The invention will be further understood from the following examples having reference to FIG. **3** of the drawings.

EXAMPLE 1

Crushed or pulverized coal is fed continuously through line **10** at a controlled rate to vessel **1** by gravity, screw conveyor, or other suitable means, and partly devolatized coal is withdrawn from the bottom through line **2.** Vessel **1** is steel, refractory lined to withstand internal temperatures up to about **1700°F**. It is also well insulated on the inside to reduce heat loss. A portion of the coal in vessel **1** is burned continuously by passage of steam and air (or oxygen), admitted through line **3,** through coal bed **4.** Recycle gas is also fed to coal bed **4** through line **3** as needed.

Air, steam and recycle gas fed to vessel **1** may be blown upwardly through a pulverized coal bed. For a bed of crushed coal the air, steam and recycle gas may be blown upward or downward, since crushed coal may be held on a grate near the bottom of vessel **1.** Steam is fed as necessary to produce hydrogen.

For strongly caking bituminous coals it is necessary to recycle coal from near the bottom of bed **4** to the top, to prevent agglomeration of the bed by the introduction of the fresh coal. For this purpose, the coal is withdrawn through line **5** and is lifted to the top of the bed by a small amount of steam and air entering through line **9.**

The gas generated leaves the reactor through line **6** and passes through cyclone spearator **7.** Solid material from the bottom of the separator **7** is returned to coal bed **4.**

The most suitable temperature to be maintained in vessel **1** depends on the coal, rate of throughput, and degree of desulfurization desired. Bituminous coal requires higher temperatures and longer retention times than subbituminous coals or lignite. In most cases bituminous coals will require retention times from 8 to 10 minutes and temperatures in the range from 1100°–1500°F. Retention times for subbituminous coal and lignite are from about 4 to 8 minutes at temperatures of 900°–1400°F. The pressure in the reaction vessel is in the range of from atmospheric up to about 10 atmospheres. Optimum pressures for desulfurization are in the range of 2 to 6 atmospheres.

To heat one ton of coal to 1200°–1500°F, decompose steam, and react the sulfur and some of the nitrogen compounds with hydrogen requires the combustion of approximately 180 to 250 lbs. of coal. The resulting volume of combustion gas is generally between 20,000 and 40,000 standard cubic feet when air and steam are used desulfurization. Methods for purification of the gas stream remove better than 99.5 percent of H_2S present in the gas.

Taking as an example a coal with a proximate analysis as follows:

	Weight Percent
Carbon	68
Volatile matter	18
Ash	6
Moisture	5
Sulfur	3
TOTAL	100

The amount of air required to desulfurize this coal to about 0.5% sulfur is about 20,000 standard cubic feet and the amount of steam is from about 80 to 140 lbs. per ton of dry coal. The amount of pure oxygen required to desulfurize this same coal to 0.5% sulfur is about 4,000 standard cubic feet per ton of coal.

The percent of sulfur eliminated from the coal will depend on the coal, sulfur in the coal, temperature, pressure and time the coal is at temperature. Rate of coal feed, time, temperature, pressure, and amount of hydrogen released care controlled in accordance with this invention. If the resulting fuel is to be used for combustion purposes the elimination of 80 to 85 percent of sulfur in coals containing not more than 3 or 3.5 to begin with is satisfactory. It has been found that retention times of less than ten minutes in the temperature zone are satisfactory.

During the desulfurization n of the coal 10–40 percent of the nitrogen will be converted to NH_3 and carried out with the gas steam. This is advantageous from the standpoint of helping to eliminate nitrogen oxide formation when the coal is burned. Nitrogen in the fuel contributes substantially to nitrogen oxide formation in the stack gases, and it is believed to be an important contributor even in comparison with the nitrogen in the air used for combustion.

The gas from cyclone separator **7** passes through line **11** to cooler **12** where the temperature is reduced to about 400°F. Cooler **12** may be a heat exchanger, a waste heat boiler or a combination of both. Oils, tars, and some solids will be removed from the gas stream by cooling. The gas then passes through line **13** to a water wash in vessel **14.** This cools the gas to below **200°F** and also removes any NH_3 in the gas. Any remaining particulate matter is also removed. The gas then passes through line **15** to an H_2S removal process which takes place as illustrated at **16.**

Any one of several H_2S removal processes may be used, such as scrubbing with hot potassium carbonate or monoethanol amine. The H_2S released from such a process should not be vented to the air since this would cause pollution. The H_2S may be treated in a Claus plant to produce liquid or solid sulfur. Purification processes also may be used which will remove the H_2S and produce solid sulfur directly, such as the Giammarco-Vetrocoke or Stretford processes. After the gas is free of H_2S it is ready for subsequent use in combustion or gasification equipment.

As shown in the drawing,the desulfurized coal from vessel **1** may be fed directly to furnace **17** or to other types of solid fuel combustion equipment. For furnace equipment that burns coal in the pulverized form, the coal fed to vessel **1** should be pulverized and the desulfurization zone in this vessel is operated as a fluidized solids zone. The resulting product may then be used directly for combustion. A portion of the sulfur-free gases from **16** may be added to the pulverized coal through line **17**(*a*) if desired. The remainder is recycled to the vessel **1**, as shown.

If the fuel is fed directly from vessel **1** to the combustion equipment it will be approximately at the temperature of the desulfurization zone. In this case most of the heat used in bringing the coal to the desulfurization temperature will be recovered, and the net heat loss in the desulfurization process will be very small.

The solid fuel from vessel **1** which is used in this manner is low in sulfur and nitrogen compounds but still contains the major portion of the ash which was in the coal. The combustion equipment in which this fuel is used must therefore be equipped with electrostitic precipitators or cyclone separators to prevent the discharge of particulate matter with the combustion gases.

EXAMPLE 2

A gaseous fuel under pressure and free from particulate matter as well as low in ash, and sulfur, is prepared as follows:

Referring again to FIG. **3** of the drawings, vessel **1** is operated under a pressure of 10 to 30 atmospheres. Coal or solid fuel is fed into vessel **1** by a suitable system (not shown), preferably as disclosed in my pending application Serial No. 268,202, filed June 30, 1972 entitled "Methods and Apparatus for Feeding Finely Divided Solids to a Pressurized Gas or Gas-Liquid-Solids System." In addition, the gas purification cycle represented by vessels **7, 12, 14** and **16** is also operated under pressure and the sulfur free gas product is under pressure.

The solid fuel from vessel **1** flows into vessel **18** without loss of pressure or temperature. In vessel **18** the solid fuel is gasified under pressure with air and steam to produce a gas which is largely CO and H_2 containing some volatile matter as well as the nitrogen from the air. The hot, pressurized gas from vessel **18** is freed of particulate matter in cyclone separators **19** and **20.** The ash and unburned coal from the cyclone separators. may be recycled to vessel **18** through line **21** if desired. This will reduce unburned carbon in the ash.

The gas recovered in the sulfur removal step and released from vessel **16** under pressure can not be joined with the gases from cyclone separators **19** and **20.** The combined gases under pressure are excellent fuel for a gas turbine or a combined cycle, such as a gas turbine followed by a steam cycle.

Alternatively, hydrogen and carbon monoxide gases low in sulfur compounds and nitrogen can be prepared by gasifying the desulfurized coal in vessel **18** with steam and oxygen instead of steam and air. In this case the tail gas from vessel **16** should not be added to this gas stream since it contains nitrogen.

Hydrogen and carbon monoxide gas are used in the production of industrial materials such as ammonia, urea, alcohols, and pipeline gas. In addition, these products may be used to make liquid products such as gasoline, diesel oil and jet fuels.

During the past 30 years most of the H_2 and CO necessary for these industrial chemicals has been made from natural gas and oil. Shortages of these fuels makes it highly desirable to substitute coal for oil and gas and the present invention makes this possible in a relatively simple and thermally efficient process.

Processes using H_2 and CO operate under pressures ranging from 10 to 15 atmospheres up to about 200 atmospheres. In general it is most efficient to generate the gases at the operating pressure of the processes.

EXAMPLE 3

If it is desired to produce a tail gas which is nitrogen free the process is operated as follows: referring again to FIG. **3,** vessel **1** is operated at the desired pressure with coal fed to the system as previously described. Stea and oxygen are used instead of steam and air to desulfurize the coal. The hot solid product from vessel **1** is passed to gasification vessel **22** without cooling.

Gasification of the desulfurized coal is carried out in vessel **22** under pressure with oxygen and steam. High temperature steam may be used to increase the H_2 content of the gas. Depending upon the final products to be made, the tail gas from vessel **16** may be combined with the product gas from gasifier **22** (e.g. if pipeline gas is to be made) or may be fed to gasifier **22** so that the gas will be converted entirely to CO and H_2. Gases from vessel **22** are freed of particulate matter in cyclone separators **23** and **24** and are ready for use. At this point they are hot and still under pressure. If it is necessary to cool the gases to some low temperature for processing, this should be done in a waste heat boiler or other system that will recover as much useful energy as possible.

I claim:

1. A process for reducing the sulfur content of naturally-occurring, sulfur-containing, solid carbonaceous fuel to less than 1.0 percent, comprising reacting said fuel in particulate form under a pressure of at least 2 atmospheres with an oxygen-containing gas and with steam in a reaction zone, the amount of oxygen-containing gas being just sufficient to burn a portion of said fuel to raise the temperature of the fuel in said zone to about 1100° to 1500°F. and the steam being present in an amount sufficient to react with the fuel particles to generate nascent hydrogen at the surface and within said particles and form hydrogen sulfide with the sulfur therein, removing the sulfur containing gases from said zone and recovering the fuel of reduced sulfur content.

2. The process of claim **1** wherein the pressure in the reaction zone is between **2** and **6** atmospheres.

3. The process of claim **1** wherein no more than about 14% of the fuel is consumed by the reaction with oxygen and steam.

4. The process of claim **1** wherein the fuel is a bituminous coal and wherein the recovered desulfurized coal retains at least 10 percent volatile matter.

5. The process of claim **1** wherein the residence time of the fuel in the reactor is less than about 12 minutes.

6. The process of claim **1** wherein the amount of hydrogen in contact with the fuel is about 4 to 5 times the amount theoretically required to react with all of the sulfur in the fuel to form H_2S.

7. The process of claim **1** wherein the fuel is bituminous coal, the temperature in the reaction zone is from about 1100° to 1500°F and the residence time of the coal particles in the reaction zone is from about 8 to 10 minutes.

8. The process of claim **1** wherein the fuel is subbituminous coal, the temperature in the reaction zone is about 900° to 1400°F and the residence time of the coal particles in the reaction zone is from about 4 to 8 minutes.

9. The process of claim **1** wherein the sulfur containing gases are purified to remove sulfur and the purified tail gas which is substantially free of sulfur is recycled to the reaction zone to maintain the sulfur content of the gases in this zone between about 0.1 to 0.5 volume percent.

10. The process of claim **1** wherein the recovered fuel without substantial reduction in temperature is reacted in a separate reaction zone to generate heat or produce fuel gases.

11. The process of claim **1** wherein the recovered fuel is gasified in a separate reaction zone to produce low sulfur fuel gases.

12. The process of claim **11** wherein the sulfur containing gases produced in the initial reaction zone are purified to remove sulfur and are introduced into said separate reaction zone with the recovered sulfur free fuel.

13. The process of claim **11** wherein the sulfur containing gases produced in the initial reaction zone are purified to remove sulfur and are combined with the gases from said separate reaction zone.

14. The process of claim **11** wherein the separate reaction zone is under a pressure of 2 to 300 atmospheres, the pressure in the initial reaction zone is at least as high as that of said separate reaction zone, and the hot desulfurized fuel is transferred from said first reaction zone to the separate reaction zone without substantial loss of temperature or pressure.

15. The process of claim **1** wherein the oxygen containing gas is air.

16. The process of claim **1** wherein the oxygen containing gas is oxygen or oxygen enriched air.

17. A process for desulfurizing sulfur-containing coal comprising reacting said coal in particulate form with oxygen and steam in a reaction zone under a pressure of at least **2** atmospheres, the amount of oxygen being just sufficient to burn a portion of the coal to raise the temperature in said zone to about 900° to 1500°F and the amount of steam being sufficient to react with the coal to generate nascent hydrogen in contact with the coal, the amount of hydrogen including that generated by the steam reaction and that present in the coal being about 4 to 5 times that theoretically required for reaction with all of the sulfur in the coal to produce H_2S, removing the sulfur-containing gases from said zone, purifying said sulfur-containing gases to provide a substantially sulfur-free tail gas, recycling the sulfur free tail gas to said reaction zone to maintain the sulfur content of the gases in contact with the coal below about 0.5 volume percent, and removing the desulfurized coal from said zone after a residence time of less than about 12 minutes.

* * * * *