United States Patent

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[72] Inventor **Marshall L. Spector**
Bellemead, N.J.

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[73] Assignee **Air Products and Chemicals, Inc.**
Allentown, Pa.

Continuation-in-part of application Ser. No. 60,379, Aug. 3, 1970, now Patent No. 3,599,610, dated Aug. 17, 1971. This application Apr. 21, 1971, Ser. No. 135,981

[54] COMBUSTION OF HIGH-SULFUR COAL IN A FLUIDIZED BED REACTOR

10 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** ..... **110/1 J,** 110/1 K, 110/28 J, 122/4
[51] **Int. Cl.** **F23d 19/00**
[50] **Field of Search** ..... 122/4 D; 110/1 J, 1 K, 28 J

[56] **References Cited**

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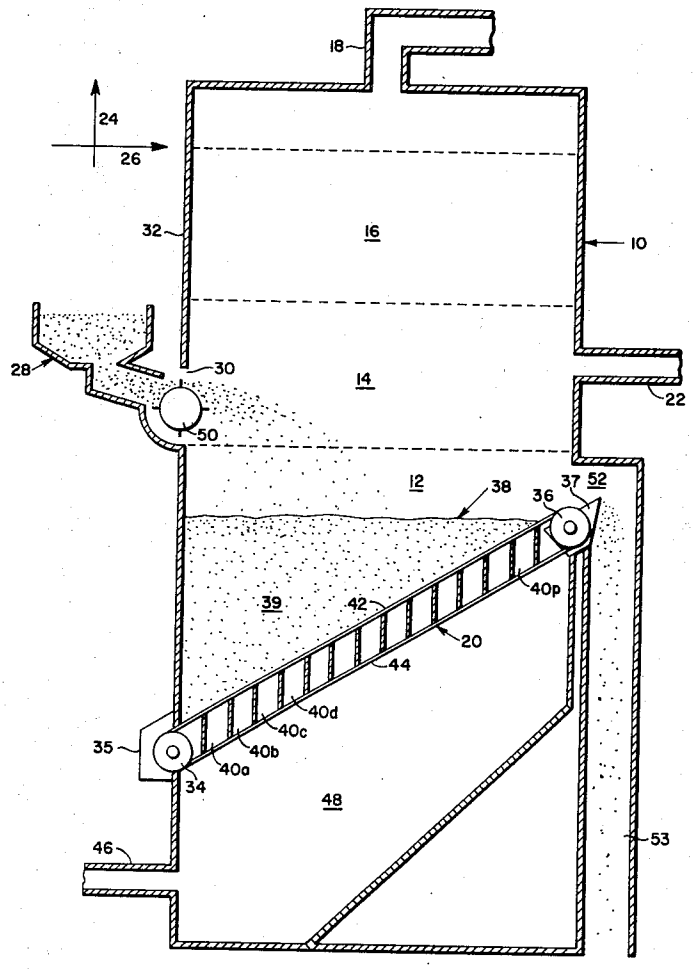
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Primary Examiner—Kenneth W. Sprague
Attorneys—Barry Moyerman and B. Max Klevit

ABSTRACT: Heating values are recovered from sulfur-containing coal in a reactor which includes a gasification zone, a combustion zone and a heat recovery zone. A fluidized bed of coal and limestone is maintained within the gasification zone, which is supported by a moving foraminous grate. Primary air, which is also the fluidizing medium, enters the gasification zone through the grate. The zone is operated adiabatically, under reducing conditions, to yield CaS and an effluent rich in CO. The CaS is discharged from the gasification zone by the moving grate and the gaseous effluent, containing entrained desulfurized coal fines, enters the combustion zone where secondary air is added. The exotherm of combustion is retrieved in the heat recovery zone, using conventional techniques. The flue gas from the reactor contains little sulfur dioxide to pollute the environment. The CaS may be processed in several ways to recover elemental sulfur.



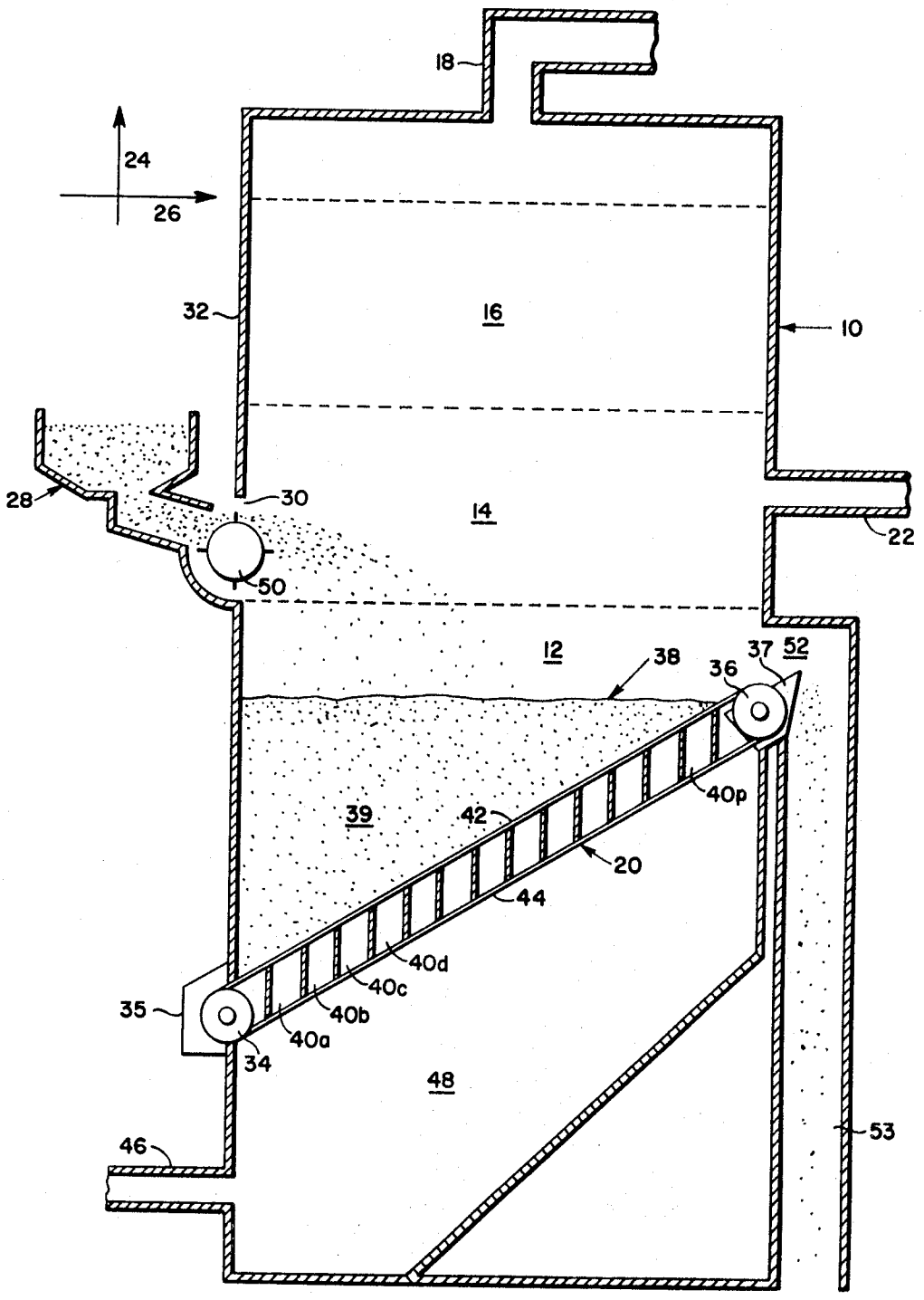
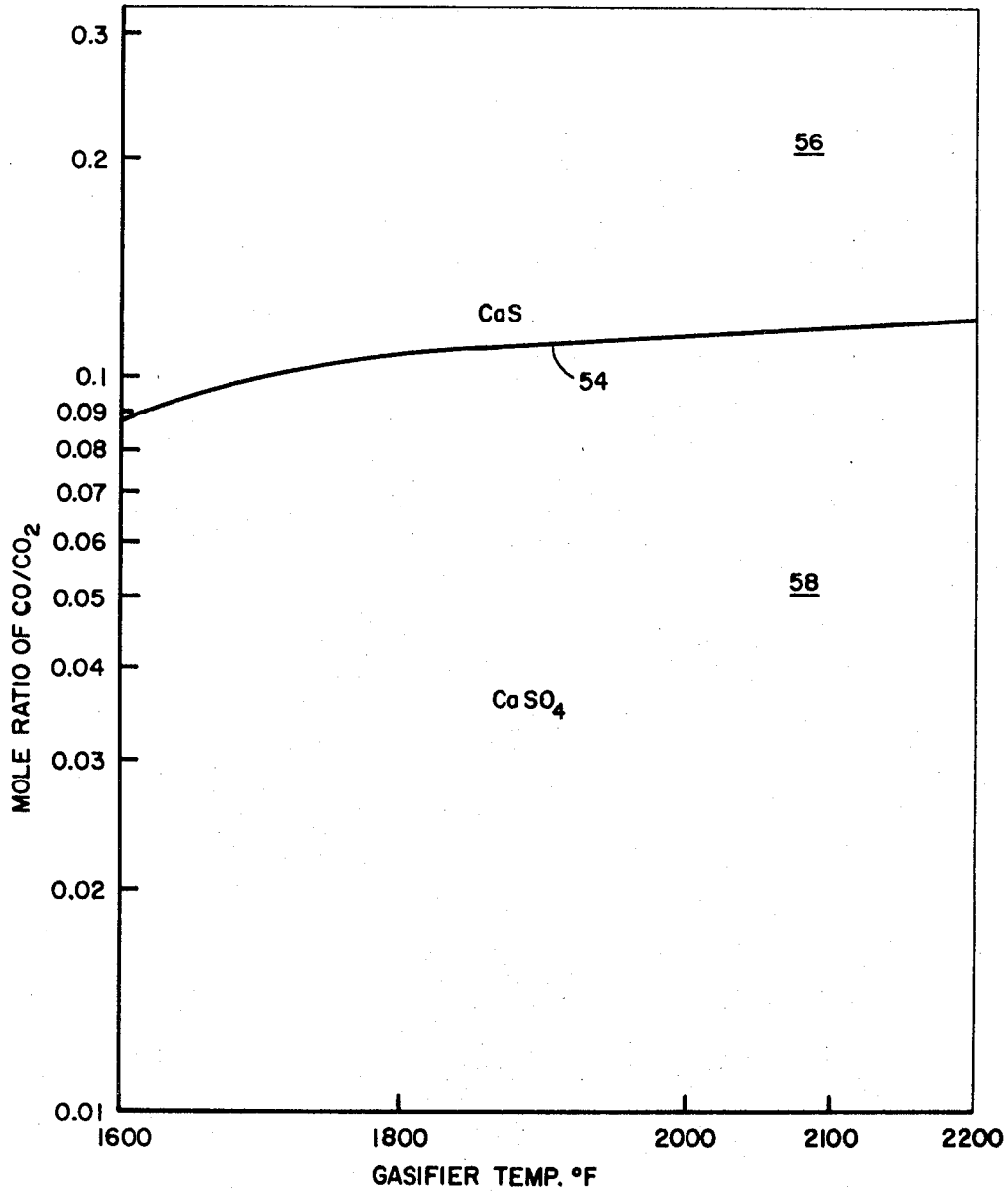


Fig. 1

INVENTOR.
Marshall L. Spector
BY Barry Moyerman.
ATTORNEY

Fig. 2

APPROXIMATE MINIMUM MOLE RATIO OF CO/CO_2 NECESSARY IN GASIFICATION ZONE OFF-GAS TO PREVENT OXIDATION THERE IN OF CaS TO $CaSO_4$



INVENTOR.
Marshall L. Spector
BY Barry Moyerman.
ATTORNEY

COMBUSTION OF HIGH-SULFUR COAL IN A FLUIDIZED BED REACTOR

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 60,379, filed Aug. 3, 1970, now U.S. Pat. No. 3,599,610 issued Aug. 17, 1971.

BACKGROUND OF THE INVENTION

1. Field of the Invention

Generally, this invention relates to the desulfurization of coal. More particularly, it pertains to a process for the combustion of sulfur-containing coal wherein the sulfur is removed as calcium sulfide and the flue gas, consequently, contains minimal SO_2.

2. Prior Art

The prior art is legion and it would indeed be presumptuous to attempt a summary herein which would be both comprehensive and objective.

Combustion of coal in fluidized beds is not new. It is shown, for example, in U.S. Pat. No. 3,437,561. Recent work along these lines, done by the British Coal Utilization Research Association, is described in an article by S. Wright et al. "Jl. of the Institute of Fuel" 42, 235–239, June, 1969. There have also been prior attempts to recapture the sulfur content of coal, as calcium sulfate, in the course of single-stage combustion of coal in fluidized bed reactors. These were described, variously, by E. B. Robison et al. in "Fluidized Combustion of Coal for Boiler Capital Cost Reduction and Air Pollution Control" Preprint 45C, A.I.Ch.E., New York (March, 1969) and by C. W. Zielke et al. in "Sulfur Removal during Combustion of Solid Fuels in a Fluidized Bed of Dolomite" Reprints A.C.S., Division of Fuel Chemistry, Vol. 13, No. 4, New York (Sept., 1969). One of the most interesting of the prior art processes is the Winkler process in which fine fuel is gasified in a fixed fluidized bed. This process is discussed in "Industrial and Engineering Chemistry," Vol. 40, No. 4 (Apr., 1948) page 562 et seq.

The recent emphasis on preservation of our environment has now made it extremely desirable to obtain heat values from carbonaceous fuels without polluting the atmosphere with sulfur dioxide. While one obvious solution is to utilize fuels which contain little or no sulfur, such fuels are scarce and relatively expensive. Prior art technology, even that devoted to removal of sulfur from carbonaceous fuels, was more concerned with upgrading the quality of the carbonaceous material than with minimizing the ecological trauma associated with its combustion. The treatment or pretreatment of such materials with various sulfur "acceptors" or "getters" is discussed inter alia in U.S. Pat. Nos. 2,824,047 and 3,387,941. However, in the former, regeneration of the acceptor yields SO_2 and, in the latter, sulfur-derived impurities are released in gaseous form. The general technology of attempts to desulfurize fuels undergoing gasification is reviewed in an article by A. M. Squires in "*Preprints*"Division of Fuel Chemistry, A.C.S., Vol. 10, No. 4, pages 20–41 (1966), which discloses, inter alia, the use of dolemite for desulfurization. Said article is incorporated herein by reference.

In the parent applications referenced above, sulfur-containing coal is treated in a two-stage process which minimizes evolution of volatile sulfur compounds. In the first stage, sulfur-containing coal is reacted with CaO in a fluid bed gasifier, which operates adiabatically under reducing conditions, to yield CaS and a gas rich in CO. The second stage is a conventional boiler in which the off-gas from the first stage and the coal fines entrained therein are delivered to the boiler as fuel. Flue gas from this boiler contains substantially no sulfur dioxide as a pollutant. CaS is withdrawn from the first stage as a valuable byproduct.

The prior art relative to coal gasification discloses the concept of supporting a fluidized bed on a continuous foraminous moving grate through which the fluidizing gas enters the bed. Preferably, the grate is divided into sections so that air flow can be balanced to compensate for varying bed depth. Such a structure is shown, for example, Godel U.S. Pat. Nos. 2,866,696 and 3,302,597.

The instant application is a logical outgrowth of these two technologies. In it, the two stages of the parent application are combined in a single reactor which contains within it a gasification zone, a combustion zone and a heat recovery zone. Thus there is no need for separate gasifier and boiler structures. Further, use of the prior art moving grate permits ready removal of ash and CaS from the gasification zone, within which reducing conditions are maintained.

SUMMARY OF THE INVENTION

Combustion of sulfur-containing coal is effected in a plurality of zones contained with a single reactor. The first zone is a fluidized bed gasification zone, wherein the bed is preferably supported on a travelling grate. Within this zone, which is operated under reducing conditions, CaO (or limestonelike materials capable of yielding CaO), which is added along with the carbonaceous fuel, reacts with the sulfur in the fuel to yield CaS. Operating conditions are set which maintain the reducing environment and prevent oxidation of the desirable CaS to the undesirable $CaSO_4$. The zone contains a steady state mixture of presized limestone (in stoichiometric excess of that needed to react with the sulfur in the fuel) and solid carbonaceous fuel. Reaction temperatures range from about 1,650° F. to about 2,200° F. The products of the first zone are both solid and gaseous. Ash, CaS and some fuel are withdrawn by the moving grate which, in effect, scrapes the bottom of the bed to remove larger and/or heavier solids. Elemental sulfur can be readily recovered from the CaS. An off-gas, rich in CO and H_2 rises to the next zone in the reactor carrying with it, elutriated fines of reduced sulfur content, fly ash and small amounts of CaO and CaS.

Subsequent zones constitute, in effect, a boiler housed in the same reactor shell. In these stages, the heat content of the gases and solids from the first zone is released and recovered. In a combustion zone, which adjoins the gasification zone, secondary air is admitted for the purpose of fully completing the oxidation of both solid and gaseous gasifier effluent. There is subsequent recovery of heat in a conventional heat recovery zone. The flue gas from the recovery zone consists primarily of water, carbon dioxide and nitrogen. It contains negligible SO_2 compared to that which would have been present had the original sulfur-containing fuel been burned in a conventional manner.

Accordingly, it is an object of the invention to provide a method whereby heat values can be recovered from sulfur-containing fuel with minimal production of environment-contaminating SO_2.

Another object of the invention is to provide a method of burning high-sulfur coal which utilizes a series of transversely extending longitudinally aligned zones which together perform the functions of a gasifier and a boiler.

Other objects of the invention will be apparent to those skilled in the art from a consideration of the description which follows, when read in conjunction with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing, wherein like reference numerals indicate like parts:

FIG. 1 is a schematic flow diagram of a preferred embodiment of the invention; and

FIG. 2 is a graph illustrating the minimum CO/CO_2 mole ratio which must be maintained in the first zone off-gas, as a function of gasifier temperatures, to produce CaS rather than $CaSO_4$.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to FIG. 1, there is shown a reactor 10 in which heating values are recovered from coal containing sul-

fur, in a manner which optimally minimizes efflux of volatile sulfur compounds to the external environment. In general, the process of heat recovery from the coal is accomplished within the single apparatus **10**, having three sequential contiguous and generally horizontal overlying zones through which the combustion and heat recovery process takes place before flue gas is released through the stack or outlet line **18**. The sulfur-containing coal is passed into a gasification zone **12** where initial combustion is carried out in a fluidized bed **39** which is supported by a movable foraminous grate **20**, as will be described in detail in the following paragraphs. The gaseous products of initial combustion then pass upwardly into a second stage combustion or oxidation zone **14** where secondary air is admitted into the reactor **10** through secondary air inlet **22**, as shown. The two-stage combusted coal products then pass through a heat recovery zone **16** and finally exit from reactor **10** through the outlet line **18**.

The reactor **10** generally extends in a substantially vertical direction **24** and includes a coal inlet opening **30** passing through lateral wall **32** to gravity direct or feed a mixture of calcium oxide and sulfur-containing coal from an externally located storage reservoir **28** into gasification zone **12**. The mixture of coal and calcium oxide, preferably in the form of limestone, is maintained within the storage reservoir **28** until needed for reaction purposes within the gasification zone **12** of reactor **10**. The coal stored within the reservoir **28** is ground to predetermined size so as to be easily fluidizable when fed into the gasification zone **12**. The amount of limestone in the mixture is in excess of that needed to produce calcium sulfide from the sulfur contained in the coal.

The gasification zone **12** is geometrically defined in a lower surface thereof by the moveable foraminous grate **20** as shown in FIG. **1**. Zone **12** extends vertically above the fluidized layer free surface **38** and terminates in a generally horizontal plane surface contiguous to the second stage combustion zone **14**.

The mechanical grate **20** extends on a continuous closed contour track around first and second driving rollers **34** and **36** secured to support members **35** and **37** respectively, which are secured to a suitable wall surface of reactor **10**. Rotation of the driving rollers **34** and **36** in a clockwise direction, therefore, provides a substantially inclined transverse or horizontal movement **26** to the bottom of the fluidized bed **39** and transports agglomerates to the chute or conduit **53**. As shown in FIG. **1**, first driving roller **34** is positioned below second opposing driving roller **36** to define the grate **20** in an inclined plane with respect to the horizontal direction **26**. One of the rollers **34** or **36** may be driven by a variable speed motor (not shown), whereas the remaining roller may be freely rotatable. By manipulation of the flow rate of coal and calcium oxide from storage reservoir **28** as well as the linear speed of the grate **20**, the fluidized layer boundary surface plane may be maintained at substantially constant height.

Between the upper and lower tracks **42**, **44** of foraminous grate **20** there are included a plurality of air boxes **40***a* . . . **40***p*. Primary air is introduced under pressure into plenum **48** through primary air inlet **46**, located at a point substantially below foraminous grate **20**. The high-pressure air passes from plenum **48** in a vertical direction **24** through the plurality of air boxes **40***a* . . . **40***p* within grate **20**. These elements permit pressure regulation of the vertically directed primary air which maintains the contents of gasification zone **12** in fluidized suspension. The flow of air is largest through box **40***a* and least through box **40***p*, to compensate for the decreasing depth of the fluidized bed **39** above upper track **42**. In this manner provision is made for approximating a unit distribution of gas flow throughout the horizontal direction **26** of the grate **20** passage. This incorporation of air in the manner described enables the fluidized bed **39** to maintain an approximate uniform degree of fluidization in its transverse dimension with the boundary surface **38** remaining in a substantially horizontal plane.

The movable grate **20** is generally of the standard type, well described in the above-mentioned prior art patents. The upper and lower tracks **42**, **46** are constructed of cast iron, or some like material, and are formed into a chainlike extension having air passage openings to permit the vertical flow of primary air. Projections or other vertically oriented extensions may be formed on the track surfaces in contact with the bottom of fluidized bed **39** when the inclination plane of the foraminous grate **20** is sufficient to overcome the frictional contact force between the contiguous surfaces. The projections prevent sliding of the gathered agglomerates in a direction toward the first driving roller **34** and are found to be of use when the inclined angle is substantially in excess of 30°, although the exact angle is a function of the physical properties of the contiguous materials and, as such, may vary over a considerable range.

As has been briefly described, coal and calcium oxide are transported to the gasification zone **12** from an externally located storage reservoir **28**. The incoming mixture may be gravity distributed on the fluidized layer free surface **38** by star feeder or shovel wheel **50** positioned at inlet opening **30** on the lateral wall **32** as shown in FIG. **1**. Alternatively, the feed may be added directly to the body of the bed. The calcium oxide and coal mixture contained in reservoir **28** is premixed in accordance with the predetermined sulfur content of the coal, e.g., approximately a 50 percent excess of stoichiometric amount necessary to effect the reaction resulting in the formation of calcium sulfide and water from calcium oxide and hydrogen sulfide. In general, the limestone used in combination with the coal must always be in excess of that necessary to supply CaO in sufficient quantity to react with the sulfur in the coal. Molar excesses of 50 to 200 percent have been found to be preferable with an optimized range between 75 and 150 percent.

At or near the second driving roller **36**, the upper track **42** vertically emerges from the fluidized layer free surface **38** thus carrying the agglomerates from the bottom of fluidized bed **39** into the solid drawoff zone **52**. The solids comprising a mixture of ash, CaO and CaS are drawn off through solids conduit **53** to a sulfur recovering zone (not shown). It is essential that the drawoff occur within the reducing atmosphere of zone **12**.

Solid and gaseous products are combusted in the initial combustion or gasification zone **12** and pass vertically into the second stage combustion zone **14**. In order that zone **12** produce CaS rather than $CaSO_4$ the off gas moving intrazone must contain CO/CO_2 in mole ratio shown in FIG. **2**.

As has been described, secondary air inlets **22** incorporate air into zone **14** to aid in an optimized combustion therein. Heat of combustion is recovered within heat recovery zone **16**, through utilization of conventional heat exchange equipment and the flue gas leaves the reactor **10** through stack or outlet line **18**. In some instances where there is still a sizeable quantity of solid combustibles in the exiting gas, such combustibles may be recycled to the first stage gasification zone **12** within reactor **10**.

Discharge to the external environment or atmosphere through the stack **18**, where solids recycle is desired, may be preceded by conventional heat recovery and mechanical and/or electrostatic solids removal systems. In this operation, it has been found that electrostatic precipitators are particularly effective due to the high conductivity found in carbon-containing solids.

Typical operation of the embodiment as shown in FIG. **1** is based on 1 ton, i.e., 2,000 lbs. of coal having a sulfur content of 4.5 weight percent with the gasifier zone **12** operating at a temperature approximating 2,150° F. The influx of the coal and limestone mixture from the storage reservoir **28** to the gasification zone **12** totals about 2,420 lbs. The solid material enters at an ambient temperature of approximately 77° F. and its analysis in lbs. and lb./moles is as follows:

		Lbs.	Lb./moles
Coal	C	1,600	133
	S (as H_2S)	93	2.8
	H_2	65	33
	Ash	242	2.0 (as $CaCO_3$)

Limestone	$CaCO_3$	420	4.2
		2,420	175.0

Primary air enters the gasifier **12** through air inlet **46** to provide 64 lb. moles of oxygen and 221 lb. moles of nitrogen input into the plenum **48**. The fluidized bed **39** contains a steady-state mixture of ash, limestone, CaS and coal wherein the size of the limestone is adjusted to avoid excessive elutriation from the bed **39**. In operation, limestone carryover is maintained at minimal quantities, e.g., below 2 percent of the inventory. The limestone carryover is minimal if the particulate lime or lime-yielding material is charged having its size range from 6–9 mm. in diameter combined with a superficial gas velocity through the bed **39** of less than 25 ft./sec.; preferably about 14 ft./sec.

The coal within the storage reservoir **28** is preground so that 99 percent has a diameter size less than 9–10 mm. As gasification proceeds, a given particle is consumed until it is finally entrained and leaves zone **12** and enters the second stage combustion zone **14**.

The maximum size of coal and other solid particles elutriated is a function of the linear velocity in the bed **39**. Optimized conditions are achieved when the coal has a residence time in the bed **39** just long enough to substantially reduce its particle size to the point where it is elutriated into the second stage combustion zone **14**. A carryover of coal from zone **12** to zone **14** between 5–20 is usually found. Coal solids which are not reacted in the second stage combustion zone **14** may be ultimately collected in electrostatic precipitators, as previously described, and returned to the first gasification zone **12** through conventional means. However, in this milieu, carryover is limited by the desiderata that (a) the temperature of the gasification zone **12** be maintained within the range where the desired ash agglomeration occurs; (b) sulfur content of the coal elutriated into combustion zone **14** is within the generally recognized range for low-sulfur carbon fuels, e.g., less than 1 percent by weight of the carbon content of the coal.

Solids drawoff begins when the upper track **42** of the moveable grate **20** emerges beyond the level of the fluidized layer free surface **38** and enters drawoff zone **52** where the ratio CO/CO_2 is as shown in FIG. **2**. By proper adjustment of primary airflow through air boxes **40***a* . . . **40***p* (including selective orifices) within grate **20**, the material in bed **39** above air box **40***p* achieves substantially complete gasification. However, of critical consequence is that not so much primary air be passed through the air boxes **40***a* . . . **40***p* such as to allow the CO/CO_2 ratio to drop below the line shown in FIG. **2**.

FIG. **2**, to which reference has previously been made, is a graph showing the approximate minimum mole ratio of CO/CO_2, as a function of the gasifier zone temperature, necessary to prevent oxidation of CaS to $CaSO_4$. Graph contour line **54** represents the boundary line region between the upper region **56**, wherein CaS is produced, and the lower region **58**, where $CaSO_4$ is produced. As shown, the critical mole ration of CO/CO_2 ranges between approximately 0.87 and 1.2 within a related range of gasifier temperatures extending from 1,600° to 2,200° F. In addition, the critical mole ratio is seen to monotonically increase in value as a function of higher gasifier temperatures, with contour line **54** approximating a linearly rising function after the gasifier has reached a value of about 1,800° F.

At no time during operation may the partial pressures of carbon monoxide and carbon dioxide, within zones **12** and **52**, be such that the critical mole ratio of CO/CO_2 (as defined by boundary line **54** of FIG. **2**) is less than the indicated value. The value of this ratio is essential and critical to the success of the process of this invention, in order to preserve the sulfur values as sulfide and not permit their conversion to a sulfate. This process permits a relatively easy recovery of elemental sulfur from the sulfide, whereas the recovery of elemental sulfur from sulfates may only be accomplished through an expensive reduction process wherein calcium sulfate is reduced to calcium sulfide. In the process as herein defined, calcium sulfide is the direct product of the process.

In addition to some unreacted CaO, about 2.3 lb. moles of CaS and 1.6 lb. moles of ash, expressed as calcium silicate, are drawn off through solids conduit **53**. Though the material drawn off is primarily calcium sulfide and ash, some unreacted coal may be withdrawn, which may be separated and recycled. The calcium sulfide produced in the process may be utilized as such or as the feed for a process to recover elemental sulfur, using any one of several methods.

One method of recovery is to drop the hot solids into water contained in a closed vessel at atmospheric pressure and sparge into the water an appropriate amount of CO_2, preferably derived from plant flue gas. The reaction converts calcium values to calcium carbonate and evolves H_2S quantitatively. The H_2S is readily recovered and can be converted to elemental sulfur using the Claus process. In this method, the ash and calcium carbonate are removed together.

Another method is to quench the hot solids in a body of water maintained at atmospheric conditions. Under these conditions, H_2S and water vapor are released and calcium hydroxide and inerts are recovered as solids.

Still another method, which offers potential for recovery of calcium, while still permitting recovery of sulfur values is to collect the hot solids in water at atmospheric pressure and, subsequently, heat the system to about 125°–200° C. in a pressure vessel. Under these conditions, the sulfide is largely hydrolyzed to soluble calcium hydrosulfide which can be separated from ash and other solids by filtration. If desired, calcium hydrosulfide can be produced at a lower temperature by the addition of H_2S. Following filtration, water and H_2S are stripped from the liquid phase and calcium hydroxide slurry recovered. The slurry is sufficiently free of ash so that it can be recycled for ultimate addition to hopper **28**.

Alternatively, the filtrate may be treated with CO_2 at lower temperature, to release H_2S and a calcium carbonate slurry recovered. The slurry is sufficiently free of ash so that it can be recycled for ultimate addition to hopper **28**, just as the slurry in the above paragraph.

The gaseous components which enter the second stage combustion zone **14** comprise 136 lb. moles of CO, 35 lb. moles of H_2, 0.2 lb. moles of H_2O, 0.4 lb. moles of CO_2, 221 lb. moles of N_2 and traces of H_2S. Due to the nature of the combustion system, these components cannot be measured directly but are calculated on the basis of the restricted airflow fed to the first stage combustion zone **12**. The second stage combustion zone **14**, includes incorporation of secondary air entering through the inlets **22**, which is preferably preheated to achieve maximum second stage combustion.

Flue gas being emitted from the stack **18** contains approximately 136 lb. moles of CO_2, 35 lb. moles of H_2O, 563 lb. moles of N_2 and 0.5 lb. moles of SO_2. The process as herein detailed, therefore performs as if a fuel having 0.8 percent sulfur were being burned conventionally whereas, in actuality, the fuel contained 4.5 percent sulfur. The essential success of the process is attributable to the operation of the gasifier **12** under those critical reducing conditions indicated in FIG. **2**. Accordingly, the feed of air and coal must be adjusted so that the CO/CO_2 ratio is represented by a point on or above the boundary line **54** shown in FIG. **2**.

While a preferred embodiment of the invention has been described, many modifications and variations will be apparent to those knowledgeable with respect to the design and operation of fluidized bed gasifiers. Accordingly, the scope of the invention is to be limited only by a reasonable interpretation of the appended claims.

What is claimed is:

1. A process for burning sulfur-containing coal with minimal pollution of the environment by SO_2 comprising:

a. establishing a plurality of generally horizontal overlying zones within a vertically extending reactor, said zones including a lower gasification zone, an upper heat recovery zone and an intermediate combustion zone;

b. maintaining a bed of particulate coal and limestone within said gasification zone;

c. fluidizing said bed with a stream of primary air;

d. feeding said bed with fluidizable size sulfur-containing coal and with an amount of particulate limestone in excess of that needed to produce CaS from the sulfur contained in the coal;

e. reacting carbon with oxygen in said bed to yield CO;

f. adjusting the feed of primary air and coal to produce and maintain a reducing environment within said gasification zone, as reflected by the CO/CO_2 ratio in the gaseous effluent therefrom, said ratio having a value above the minimum represented by the curve in FIG. 2, whereby oxidation of CaS to $CaSO_4$ is prevented; and

g. withdrawing CaS from the gasification zone as a solid and evolving from said zone, as a gaseous effluent, a mixture comprising CO and H_2, in which are elutriated coal fines having a sulfur content less than that of the coal originally fed to the gasification zone.

2. The process of claim 1 wherein said fluidized bed is maintained on a moving foraminous grate and the fluidizing air enters the bed through the grate.

3. The process of claim 2 wherein said grate moves transversely and upwardly, discharging ash and CaS at its higher elevation.

4. The process of claim 3 wherein different quantities of primary air are fed through different portions of said grate so that, despite the varying depth of bed across the transverse extent of the grate, the linear velocity of fluidizing air flowing therethrough is maintained substantially uniform.

5. The process of claim 1 which includes the additional steps of:

h. adding secondary air to said combustion zone to oxidize the effluent from said gasification zone with a consequent release of heat;

i. recovering substantially all of the combustion zone exotherm in said heat recovery zone; and

j. venting from the heat recovery zone a flue gas containing minimal quantities of SO_2.

6. The process of claim 5 wherein said fluidized bed is maintained on a moving foraminous grate and the fluidizing air enters the bed through the grate.

7. The process of claim 6 wherein said grate moves transversely and upwardly, discharging ash and CaS at its higher elevation.

8. The process of claim 7 wherein different quantities of primary air are fed through different portions of said grate so that, despite the varying depth of bed across the transverse extent of the grate, the linear velocity of fluidizing air flowing therethrough is maintained substantially uniform.

9. The process of claim 8 wherein the amount of limestone fed in step (d) ranges from 50 to 200 mol percent in excess of the stoichiometric quantity.

10. The process of claim 9 wherein about 99 percent of the coal fed to the gasification zone has a size less than 10 mm.

* * * * *

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,625,164 Dated December 7, 1971

Inventor(s) Marshall L. Spector

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 16 "with" should read "--within--"

Column 5, line 27 after "zone 14" insert "--of--"

Column 5, line 27 after "5-20" insert "--%--"

Signed and sealed this 30th day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents