

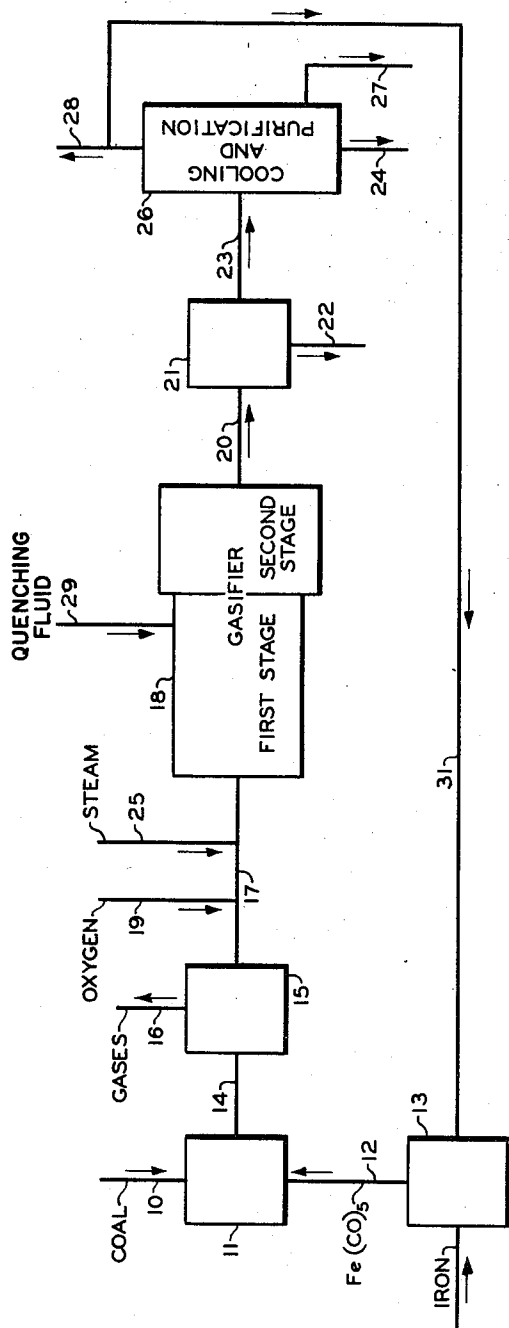
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DESULFURIZATION IN THE GASIFICATION OF COAL

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DESULEURIZATION IN THE GASIFICATION OF COAL

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This invention relates to an improved process for the removal of sulfur simultaneously with the gasification of carbonaceous materials.

The sulfur content of coals may be as high as 10 per cent by weight or more and for this reason fuel gas or synthesis gas made by conventional coal gasification processes is, in many cases, high in sulfur, which is undesirable for various reasons such as corrosion, catalyst poisoning, gum formation, etc. Sulfur compounds may be removed from the gas by many methods including physical absorption and chemical reaction but because of the volume of the gas stream and the presence of high carbon dioxide content, these methods are expensive.

The present invention provides a method for the removal of sulfur simultaneously with the gasification of a carbonaceous material thus eliminating costly purification steps. According to the present invention, iron or another metal carbonyl, formed from finely divided iron and a portion of the carbon monoxide containing gas from the gasification step, is condensed and absorbed on the surface of the coal particles. The carbonyl treated coal particles are then fed to a gasification chamber. At the temperature of gasification the carbonyl is decomposed to elemental iron which is finely dispersed throughout the products of initial gasification and is free to react with sulfur compounds. Iron sulfide is formed and is taken off with the ash, and a gasification product with a lowered sulfur content is produced.

In order to have the iron widely dispersed so that excessive amounts will not be required the following procedure is preferred. Finely divided iron from any source such as, for example, a used fluidized iron synthesis catalyst, is contacted with carbon monoxide containing gas from the gasification step at the most favorable conditions of temperature and pressure for carbonyl formation and volatilization. These conditions are given in the published literature. See, for example, "Researches on the Metallic Carbonyls", R. L. Mond and A. E. Wallis, Journal Chem. Soc., 121, 29-32 (1922). According to this reference, favorable conditions of iron carbonyl formations are:

	Broad	Preferred
Temperature, F.....	300 to 450.....	350 to 400.....
Pressure, Atm.....	1 to 300 or higher.....	5 to 50.....

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in possession of this disclosure that metals other than iron may be used in this process. The gas containing the iron carbonyl vapor is then contacted with powdered coal in the coal feed chamber of a gasification plant. With some cooling the iron carbonyl is both condensed and absorbed on the surface of the coal particles. Upon entering the gasification chamber the carbonyl is decomposed to elemental iron which is then free to react with sulfur compounds.

In the drawing there is diagrammatically represented one form of apparatus which may be used to practice the process of my invention. The process is described with respect to coal but it can be readily modified for any carbonaceous material such as ground oil shale, shale oil refinery residuum, etc. In preparing the coal or other carbonaceous material for gasification, it is desirable to pulverize it to relatively fine state of subdivision, preferably such that it will pass through a standard Tyler screen of about 80 mesh. The powdered coal is treated by conventional mechanical separation methods to remove inorganic sulfur. After being pulverized, the coal is conducted through feed line 10 to chamber 11. In chamber 11, the powdered coal is contacted with iron carbonyl vapor containing gas from line 12. This gas is a recycle gas from the gasification process, contains carbon monoxide and is contacted with a finely divided iron in chamber 13 at suitable conditions to form iron carbonyl. The powdered coal being at room temperature, the iron carbonyl is both condensed and absorbed on the surface of the coal particles in chamber 11. The powdered coal is withdrawn from chamber 11 through line 14 to a separation zone 15. Gases are removed from the separation zone 15 through line 16. The powdered coal is withdrawn from the separation zone 15 through line 17 and blown into the gasification chamber 18 together with oxygen from line 19 and/or steam from line 25. Upon entering the gasification chamber 18, the carbonyl is decomposed to elemental iron which is finely dispersed throughout the product of initial combustion and is free to react with sulfur compounds. Typical operating conditions for the first gasification stage are:

	Broad Range	Preferred Range
Temperature, F.....	1,400 to 3,000.....	1,800 to 2,500.....
Pressure, Atms.....	1.5 to 30.....	2 to 15.....
Contact time, Seconds.....	0.1 to 10.....	1 to 5.....

It will be apparent to one skilled in the art 55

A lower temperature will give a lower hydro-

gen sulfide concentration and would be desirable for fuel gas since methanation would occur and be catalyzed by the iron. Typical operating conditions for the second gasification stage are:

	Broad Range	Preferred Range
Temperature, F.	1,400 to 1,700	1,500 to 1,600.
Pressure, Atms.	1.5 to 30.	2 to 15.
Contact time, Seconds.	1 to 20.	5 to 15.

The lower temperature in the second stage gasification may be obtained by a water or steam quench 29, or by any cooling method known to the art.

The thermodynamic equilibrium for the system $\text{Fe}-\text{FeS}-\text{H}_2-\text{H}_2\text{S}$ is such that at 1600° F., $\text{H}_2\text{S}/\text{H}_2=300^{-1}$. With a concentration of hydrogen at 40 per cent, hydrogen sulfide is 0.13 per cent; thus most of the sulfur leaves as iron sulfide in the ash from the coal. A lower temperature results in an even lower hydrogen sulfide concentration and would be desirable for fuel gas since methanation, which is the formation of methane, would occur and be catalyzed by the iron. For synthesis gas the high temperature is desirable to reduce the residual hydrocarbon, though sulfur removal is less complete and a further sulfur removal step may be desirable.

The gasification products are withdrawn through line 20 to a separation zone 21 where the ash and iron sulfide are taken off through line 22. The gasification products are withdrawn through line 23 and passed to cooling and purification zones 25. Any cooling method and any scrubbing oil known to the art may be used. Tar oil and sludge are removed through line 27 and water removed through line 24. The fuel gas is removed through line 28. A part of the fuel gas containing carbon monoxide is recycled through line 31 to the iron chamber 13, where iron carbonyl is formed from contacting iron with the carbon monoxide containing gas. This gas and iron carbonyl contained therein are then withdrawn through line 12 to contact the coal in zone 11 as previously described.

Herein and in the claims it is to be understood that "coal" has as its full equivalent other gasifiable carbonaceous materials, the essence of the present invention being substantially as set forth in the following paragraph.

Reasonable variation and some modification are possible within the scope of the foregoing disclosure, drawing, and the appended claims to the invention, the essence of which is that in situ formation of an elemental metal, e. g. iron, from a metal carbonyl, is used in a gasification process to simultaneously desulfurize the gases being pro-

duced and that a method for so doing has been set forth.

I claim:

1. A process for the gasification of a solid powdered carbonaceous material containing sulfur which comprises introducing said material and a metal carbonyl into a gasification zone, subjecting said mixture to gasification conditions with the introduction of an oxygen-supplying gas so as to supply the heat of reaction and react the metal of the metal carbonyl with the sulfur component of the carbonaceous material to produce the metal sulfide, removing the metal sulfide from the gases produced and recovering said gases.

2. A process according to claim 1 in which the gasification is carried out in two gasification stages and in which there is effected a cooling of the gases intermediate said stages so as to reduce the temperature of the gases entering into said second stage to a level at which methanation is effected.

3. A process according to claim 1 wherein the solid carbonaceous material is coal and the carbonyl is iron carbonyl.

4. A process according to claim 1 wherein the gasification is effected at a temperature in the range 1400-3000° F. under a pressure of 1.5-30 atmospheres and the time is of the order of 0.1-10 seconds.

5. A process for the gasification of a solid carbonaceous material containing sulfur, which comprises subdividing said material to form a powder thereof; admixing with said powder a metal carbonyl; then introducing said powder admixed with said metal carbonyl into a gasification zone, gasifying said powder at a gasification temperature; then separating gases thus produced from solid residue of the carbonaceous material and metal sulfide formed and recovering said gases.

6. A process according to claim 5 wherein a portion of the gases formed are contacted with a metal to form additional metal carbonyl.

7. A process according to claim 5 in which the gasification is carried out in two gasification stages and in which there is effected a cooling of the gases intermediate said stages so as to reduce the temperature of the gases entering into said second stage to a level at which methanation is effected.

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