

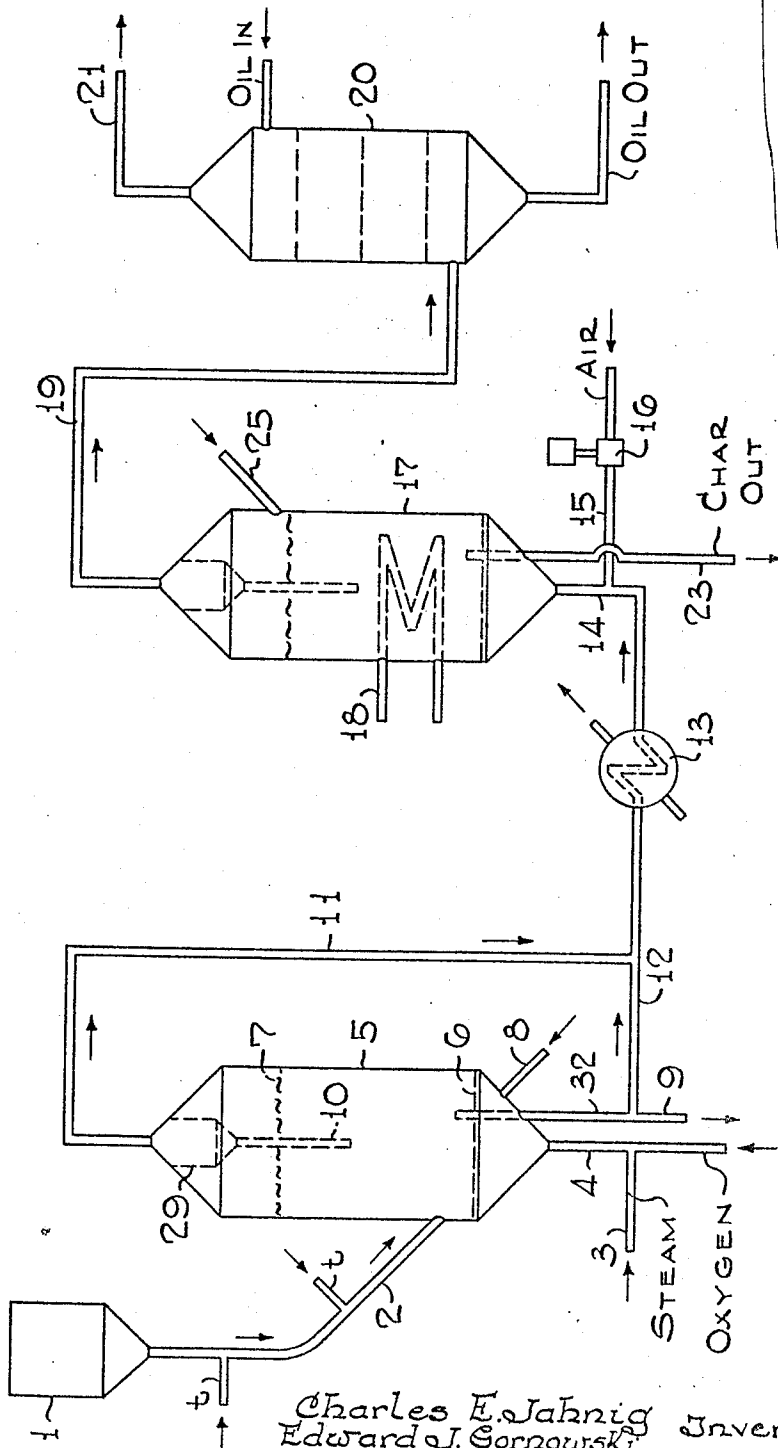
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SYNTHESIS GAS DESULFURIZATION

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SYNTHESIS GAS DESULFURIZATION

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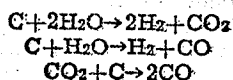
6 Claims. (Cl. 48-206)

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The present invention relates to the production of gases from non-gaseous carbonaceous materials, particularly to the production of gas mixtures containing CO and H₂ from such non-volatile carbonaceous materials as coke, coal, oil shale, heavy oil residues, and the like. More specifically, the present invention relates to an improved process for producing gas containing CO and H₂ from coke or coal by the water gas reaction and making the gas thus produced suitable for utilization in the hydrocarbon synthesis reaction.

In a co-pending application, Serial No. 151,326, filed March 23, 1950, by Sumner B. Sweetser and Robert H. Mueller, there is disclosed a two stage coal gasification process on the production of water gas wherein high surface area char from the first stage is used to desulfurize the water gas produced.

It has long been known that non-volatile fuel materials, such as coke, coal and the like, may be converted into more valuable gases which can be more easily handled and more efficiently used for a greater variety of purposes. One of the most widely practiced gas-generating conversions is the so-called water-gas process in which solid fuels, such as coal or coke of any origin, may be reacted with steam to produce water or producer-gas mixtures of CO and H₂ in varying proportions, depending mainly on the conversion temperatures, which may vary from about 1200° to about 2400° F., and the feed ratio of steam. The flexibility of the process may be illustrated by a series of possible chemical reactions about as follows:



The overall water-gas producing reaction being endothermic, heat must be supplied which is usually accomplished by the combustion of a portion of the carbonaceous feed with an oxidizing gas such as air and/or oxygen at about 1600°-3000° F. The combustion reaction may be carried out either simultaneously with the water-gas reaction or alternately in a make and blow fashion. By the application of suitable combustion conditions, particularly of high temperatures above about 1800° F., the CO content of the combustion gases may be raised to any desired level.

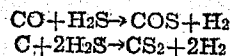
It will be appreciated from the above that the water-gas process permits the production of gas mixtures of widely varying composition and B. t. u. content. The process as such is therefore, well suited not only for the production of

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fuel gases of varying B. t. u. content, but also, for the production of feed gases for hydrogenation processes and particularly for the catalytic synthesis of hydrocarbons and/or oxygenated organic compounds from CO and H₂ which, depending on the products desired, requires H₂:CO ratios varying within the wide limits of 0.5-2 volumes of H₂ per volume of CO.

However, the technical utilization of the water-gas process, particularly for hydrogenation processes and the production of synthesis feed gas, has been appreciably impeded by difficulties encountered in heat supply and continuous operation as well as in the substantial removal of sulfur compounds from the gas, the latter being imperative for the utility of the gas in the hydrocarbon synthesis. The problems of supplying heat of reaction, with continuity of operation have been satisfactorily solved heretofore, by the application of the so-called fluid solids technique wherein the carbonaceous charge is reacted in the form of a dense turbulent mass of finely-divided solids fluidized by the gaseous reactants and products. However, substantial and economic desulfurization of the water gas still constitutes a major problem particularly in practicing the hydrocarbon synthesis based on coal.

The catalysts used in the synthesis of hydrocarbons from CO and H₂ are sensitive to sulfur poisoning and consequently, it is necessary to use a synthesis gas which is low in sulfur, for example, one with a sulfur content of preferably 1 part per million or less. Because of the low sulfur content of some sources of natural gas, it is sometimes unnecessary to desulfurize the synthesis gas prepared from natural gas. Most coals, however, contain appreciable quantities of sulfur and in the preparation of synthesis gas from coal it is always necessary to treat the gas for sulfur removal prior to contacting the synthesis gas with the synthesis catalyst. Difficulties in desulfurizing water gas arise from the fact that the gas leaving conventional water-gas generators contains two different types of sulfur compounds, namely, H₂S formed by the reaction of sulfur with H₂, and organic sulfur compounds such as COS and CS₂ formed by the reaction of CO and C with H₂S, as follows:



These two types of sulfur compounds, due to their different chemical character, are difficult to remove by any single desulfurization treatment. Therefore, it has been the practice here-

tofore first to remove H_2S , for example, by a treatment with alkali, hydrated iron oxides, sodium thioarsenate (Thylox process), sodium phenolate (Koppers process), etc., and then to remove the organic sulfur compounds, for example, either by a conversion into H_2S in the presence of steam and noble metal catalysts followed by a second H_2S removal, or by a single high-temperature catalytic treatment with lead or tin catalysts, etc. The desulfurization procedure requiring two or more separate stages of different design and operating conditions constitutes a heavy load on the economy of any gas utilization depending on sulfur-free fuel gases of which hydrocarbon synthesis is an outstanding example.

A further problem associated with the desulfurizing of water gas to be subsequently employed in the catalytic synthesis of hydrocarbons is that of heat economy. In the prior art practice, as when the sulfur is removed by scrubbing with solutions of amino alcohols, etc., it has been found necessary, in order to have an operative process that the water gas product stream be cooled, say below a temperature of about $110^\circ F.$ before sulfur is removed, as at higher temperatures absorbent requirements increase because of low absorbing capacity and high vapor losses. This cooling represents a considerable detriment, inasmuch as hydrocarbon synthesis is usually carried out at a temperature of about 450° to $650^\circ F.$ and the cooled desulfurized gases may require reheating in order to bring them up to the desired synthesis temperatures. In any event, the required cooling entails additional plant investment and means that more potentially valuable heat content is rejected to cooling water. A further problem encountered in desulfurizing water gas preparatory to its being employed as feed to the hydrocarbon synthesis process is that char fines from the water gas generator are entrained in significant proportions and are carried into the desulfurizing system, the prevention of which requires expensive dust removal systems, further adding to the initial and operating costs of the process.

The present invention overcomes the aforementioned difficulties and affords various additional advantages. These advantages, the nature of the invention and the manner in which it is carried out will be fully understood from the following description thereof read with reference to the drawing which shows a semi-diagrammatic view of apparatus particularly adapted to carry out the invention.

It is, therefore, the principal object of the present invention to provide an improved process for the production of highly valuable combustible gases from solid carbonaceous materials.

Another object is to provide economic means for the substantial desulfurization of combustible gases obtained from solid carbonaceous materials.

A still further object of the invention is to provide an improved process for the production of gases containing CO and H_2 substantially free of sulfur, from solid carbonaceous materials.

A more specific object of the invention is to provide an improved water-gas process for the production of gas mixtures substantially free of sulfur, suitable for the catalytic synthesis of hydrocarbons and/or oxygenated organic compounds from CO and H_2 .

It has now been found that water gas may be substantially desulfurized by employing as the

desulfurizing medium, the spent char produced and obtained from the water gas generation zone, and in accordance with the present invention, this spent char, containing a relatively small amount of carbon, usually in the range of about 10 to 40%, is employed to desulfurize the gases generated in the water gas generator and to prepare a gas suitable for employment in the hydrocarbon synthesis reaction.

In accordance with the present invention, coal is ground to fluidizable particle size and subjected to a fluidized coking process. The char is withdrawn from the coking vessel and passed to a fluidized solids gasification vessel wherein it is contacted with steam at temperatures from about 1700° to $1900^\circ F.$ to produce a mixture of carbon monoxide and hydrogen. Heat may be provided either by addition of oxygen or air or by recycling of heated solids from a subsequent combustion vessel. From the water gas generator, spent solids and product gases flow to a fluidized solids sulfur removal system. This system consists of a vessel containing a fluidized bed of spent char at about 300° to $600^\circ F.$, a small amount of air equivalent to at least $2\frac{1}{2}$ mols air per mol of equivalent H_2S in flue gas is fed to the sulfur removal vessel and as a result of the contacting of the sulfur-containing water gas with the spent char, sulfur is removed mostly in the form of the element deposited on the char and the spent char now fouled with sulfur is passed to a disposal dump while the purified gases flow to a hydrocarbon synthesis plant.

It has in the past been suggested that activated carbon be employed to remove sulfur from gases containing sulfur and its compounds. This removal of sulfur has been accomplished by adsorption of the sulfur on the carbon, usually at low temperatures followed by desorption of the sulfur with steam at elevated temperatures, regeneration of the activated carbon and re-use of the thus regenerated carbon in the process. These carbons are usually prepared from special woods such as beech, coconut, char, etc. and are activated by various physical or chemical means, i. e., by steam, zinc chloride, potassium sulfide, etc. The relative high cost of these activated carbons and the difficulty of regenerating the adsorbent without consuming the latter, has in general, prevented the commercial application of this type of desulfurizing agent for the hydrocarbon synthesis process. In addition, the adsorption process is characterized by several problems. It has been found, for instance, that because of the high surface area, polymerizing of the materials and the gases occurs in activating the carbon so that it can not be regenerated. Activated carbon is an expensive material and losses must be minimized in order to maintain a commercially operable process. Furthermore, the maintenance of an activated carbon plant wherein thousands of tons of carbon must be alternately passed to the adsorption zone or the regeneration zone, is a cumbersome and expensive process. Also, provision must generally be made to remove the sulfur compounds released during regeneration, since it is usually undesirable to vent these to the atmosphere.

In accordance with the present invention, however, which employs spent carbon, the regeneration problem and the sulfur disposal problem are readily solved. The spent char is normally rejected and by its employment as a desulfurizing medium, its usefulness is substantially increased. The use of spent solids to remove sulfur allows

rejecting of the sulfur without regeneration of the contacting material whereby the passing of the sulfur gases to the atmosphere is avoided. Since sulfur in the coal feed amounts to about 100 to 200 tons per day, this is an important consideration for plant locations in highly populated areas. Also, when using spent solids to remove sulfur, removal of dust in the gases leaving the gasification vessel is unnecessary.

Use of spent solids for sulfur removal is only practical under proper conditions. Thus, the process is feasible only at moderate temperatures, e. g. 300°-1000° F. At lower temperatures, excessive reaction volumes are required, while at higher temperatures, the degree of sulfur removal is inadequate, and undesirable side reactions may become excessive.

Having set forth its general nature and objects, the invention will best be understood from the subsequent more detailed description wherein reference will be made to the accompanying drawing which illustrates a system suitable for carrying out a preferred embodiment of the invention.

Referring now to the drawing, fresh coke or coal ground to a finely divided form preferably capable of passing through a 60 mesh screen and even through a 100 mesh screen is fed from supply hopper 1 into standpipe 2 which is provided with a plurality of taps *t* through which slow currents of air or other aeration gas may be injected in order to aerate and suspend the coke or coal therein. The suspension is introduced into generator 5 wherein it is formed into a dense bed fluidized by a mixture of oxygen and superheated steam admitted through lines 3 and 4, which bed is supported by grid 6. Due to the superficial velocity of said steam which is maintained within the limits of about .2 to 3 feet per second, the coke or coal is formed into a dense turbulent mass resembling a boiling liquid and having a well defined upper level 7. Additional oxidizing gases such as air or oxygen may be admitted through line 8 if desired. The steam and carbonaceous material react to form water gas, a gasiform product containing carbon monoxide and hydrogen. The temperature in this zone is of the order of from about 1600° to 2000° F. and the gas pressure may be from atmospheric to about 60 p. s. i. g., although pressures up to 500 p. s. i. g. may, under certain conditions, be employed. The heat required for the reaction is furnished substantially by the combustion of part of the carbonaceous solids in reactor 5 by the oxygen admitted through line 8 and/or line 3. The total supply of oxygen is carefully controlled to generate sufficient heat by combustion to satisfy the heat requirements of the process. It is understood that under the reaction conditions, when fresh coal is employed as the fresh feed, it becomes coked in the fluidized bed in generator 5 so that the solid product subsequently withdrawn, is referred to as char rather than coal.

The gaseous products are withdrawn from generator 5 through a dust separator such as cyclone 29 with dip line 10 extending below the upper level 7 of the fluidized bed for the return of separated dust particles. The water gas is then passed through line 11 for sulfur removal in a manner described below.

The hot carbonaceous solids are allowed to remain within reactor 5 for a sufficient period of time to convert a major portion of the carbon to water gas. As a result of the water gas produc-

ing reaction, the carbon content of the coke is usually reduced from about 75 to about 20%.

Spent hot carbonaceous solids are continuously withdrawn from water gas generator 5 through aerated bottom drawoff pipe 32, which extends above grid 6. The period of residence of the coke or coal within reactor 5, in order to effect maximum utilization of its carbon content consistent with economic operation, depends upon a plurality of operating factors such as type of coal fed, temperature of gas generation, ratio of steam to coke fed in the reactor, solids hold-up time, etc. In general, the residence time and variables above, are so regulated and adjusted that the char withdrawn from reactor 5 has a carbon content in the range of about 10 to 40%.

The spent char (part of which may be removed through line 9) to be used in desulfurizing the water gas is picked up by the latter gas which is removed from the top of water gas generator 5 through line 11. The char is suspended in line 12, passed through a series of coolers and/or heat exchangers, one of which is shown in the drawing as heat exchanger 13, and the resultant suspension of char in water gas is cooled to about 400° to 1000° F. The suspension of char and water gas is admixed with a small amount of air, preferably about 2.5 to 5 volumes of air per volume of equivalent H₂S in the gas to be treated, which air is passed into line 14 through compressor 16 and line 15. The suspension of char, sulfur contaminated water gas and air is passed into desulfurizing vessel 17, wherein a fluid bed of the spent char is maintained by the passage of the gas mixture therethrough. In general, it is desirable to maintain the temperature within desulfurizer 17 at about 400° to 1000° F., hence the preceding coolers and heat exchangers. Furthermore, it is also desirable to maintain cooling means such as cooling coil 18 to maintain the desired desulfurizing temperatures. For most effective desulfurization, the weight ratio of char to sulfur in the gas is of the order of 6 to 50.¹ As a result of the addition of air, the sulfur compounds in the gas, i. e. hydrogen sulfide, are oxidized by air to form free sulfur which is deposited on the carbon, the exothermic heat of reaction being dissipated by means of coil 18. Pressures within desulfurizing tower 17 are of the same order of magnitude as in the gas generator and depend upon the pressure employed in the process for which the water gas is the feed.

Purified water gas from which substantially all of the sulfur compounds have been removed, is withdrawn upwardly from tower 17 through line 19. To remove traces of entrained fines, the purified gas may be passed to an oil scrubber 20 from which overhead through line 21 may be withdrawn substantially solids-free and sulfur-free water gas. This scrubber also serves to remove any tarry materials present in the gas. If desired, last traces of sulfur may be removed by any conventional process (such as "lux masse") and the desulfurized gas is ready for use as a fuel gas, for the synthesis of hydrocarbons and oxygenated organic compounds, etc. The char containing sulfur deposited thereon is withdrawn through bottoms drawoff line 23 and may be employed in any way desired. Thus, where it may be desirable to add heat to the gasification stage as the sensible heat of recycled solids, it may be desirable to subject the spent sulfur contaminated char to a combustion

¹ The desulfurization bed is sized such that about 100 to 1000 CF per hour of gas (measured at 60° F. and atmospheric pressure) are fed, per cubic foot of char.

operation at a temperature above that obtaining in the water gas generator and recycling a portion of the hot ash thus formed to the water gas generator.

The embodiment of the invention illustrated by the drawing permits of numerous modifications. Thus, it may be desirable to contact the spent solids countercurrently with the sulfur contaminated water gas rather than concurrently. In such case, the spent char may be admitted into sulfur removal tower 17 through line 25 and as a result of suitable packing or baffles within the sulfur removal tower, countercurrent flow may be obtained.

The sulfur in the coal feed is of two forms, one as iron sulfide or pyrites in the ash constituents, and the other as organic sulfur compounds. Much of the sulfur is driven out during the coking reaction, so that the sulfur released into the water gas is correspondingly less. Also, the ferrous constituents in the ash are decomposed during coking and gasification, so that it becomes possible to effect sulfur removal of the final product gas by using the "sulfur accepting" properties of the ash constituents. Removal of sulfur by this mechanism is an important part of the present invention in many applications.

In cases where a separate heater vessel blown with air is used to supply heat to the generator, the spent ash used for sulfur removal can be regenerated (i. e. sulfur eliminated) by recycling to the heater vessel, whereby the sulfur is driven off and leaves as SO₂ with the flue gas. Alternatively, a separate regeneration section may be used in order to facilitate collection and recovery of the sulfur.

The invention may be further illustrated by the following specific examples.

The char produced along with the gas above was of the order of 2700 T/D, which if used in the sulfur adsorber would pick up only about 2.1% of its weight in sulfur, while purifying the gas. Data indicate that the char could satisfactorily adsorb sulfur up to 10% of its weight, so that the char production rate is more than ample to give adequate sulfur clean-up.

Besides the investment advantages mentioned above, the process herein disclosed would leave a considerable operating cost advantage over conventional processes. The principal reason for this advantage is that the spent char withdrawn from the water gas generator has little value, whereas the normal process loss of amino alcohols or especially activated chars results in substantial operating costs.

A process producing about 350 million standard cubic feet/day of CO+H₂ generates a raw gas of the following composition:

	Mol percent
CO -----	29.2
H ₂ -----	46.9
CO ₂ -----	8.5
CH ₄ -----	5.2
N ₂ -----	3.0
H ₂ O -----	6.9
S (expressed as H ₂ S) -----	0.3

The sulfur content of gas is equivalent to about 58 T/D of free sulfur. It is estimated that the above gas can be substantially freed of sulfur by the process herein disclosed, operating at 40 p. s. i. g. and 400° F., for an investment outlay of \$1,000,000; it is further estimated that to get the same degree of sulfur removal with the conventional amino alcohol absorbers would require an investment of about \$4,000,000. Use of regular

activated chars which would require regeneration would necessitate an investment on the order of \$2,000,000.

While the description and exemplary operation have served to illustrate specific applications and results of the invention, other modifications obvious to those skilled in the art are within its scope. Thus, the process can be used for removing sulfur from extraneous gases, such as product gas from coking, natural gas, etc. In this case, the gas generator 5 may be a relatively small vessel, the primary purpose of which is to supply the char required for sulfur removal.

What is claimed is:

1. In the process for gasification of solid carbonaceous materials with steam and oxygen in a water gas generation zone at elevated temperatures, wherein a sulfur contaminated gaseous product containing hydrogen sulfide as a contaminant and a spent char of only moderate adsorptive capacity having a carbon content of less than 40% by weight are withdrawn from said zone, the improvement which comprises feeding fresh spent char and the gaseous product from said gasification zone together with about 2.5-5 volumes of air per volume of equivalent hydrogen sulfide to a desulfurizing zone maintained at a temperature of from about 400°-1000° F., maintaining intimate contact therein between said spent char and said gasification product and air, and desulfurizing said gaseous product with said spent char and air.

2. The process of claim 1 in which said solid carbonaceous material is subjected to said gasification reaction in the form of a dense turbulent fluidized bed of finely divided solids.

3. The process according to claim 1 in which hot spent char contaminated with sulfur in said desulfurizing zone is withdrawn therefrom and burned to recover useful heat.

4. The process according to claim 1 in which the hot char introduced into said desulfurizing zone contains not more than about 20 weight per cent carbon, and spent char contaminated with sulfur by said desulfurization is withdrawn therefrom and discarded.

5. An improved process for producing mixtures of CO and H₂ substantially free of sulfur which comprises passing a stream of finely divided carbonaceous solid material into a gasification zone, forming a fluidized mass of solids therein, subjecting said mass to a gasification reaction with steam at temperatures of from about 1600° to 2000° F. to produce a water gas containing sulfur compounds, withdrawing said gas from said zone, withdrawing from said gasification zone a stream of spent carbonaceous solids from which the major portion of the original carbon content has been removed to produce a finely divided iron-containing coke ash having a carbon content of from about 10% to 40% by weight and a correspondingly low free surface area, passing at least a portion of said solids to a gas desulfurization zone, maintaining said gas in intimate contact with freshly introduced spent solids in said last-named zone, withdrawing and discarding from said zone spent solids containing adsorbed and reacted sulfur compounds, and withdrawing a gas from said zone substantially free of sulfur.

6. The process of claim 5 wherein the temperature in said desulfurizing zone is maintained within the range of about 400° to 1000° F.

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