United States Patent

Thompson

[15] **3,645,551**

[45] **Feb. 29, 1972**

[54] **CONVERSION OF UNDERGROUND SULFUR DEPOSITS**

[72] Inventor: **Robert R. Thompson**, Tulsa, Okla.

[73] Assignee: **Amoco Production Company**, Tulsa, Okla.

[22] Filed: **June 8, 1970**

[21] Appl. No.: **44,554**

[52] **U.S. Cl.** **299/5**, 23/181

[51] **Int. Cl.** **E21b 43/28**

[58] **Field of Search** 299/4.5; 23/181

[56] **References Cited**

UNITED STATES PATENTS

461,431	10/1891	Frasch	299/5
3,498,887	3/1970	McClintock et al.	299/5 X
3,079,233	2/1963	Wenzke	23/181
3,415,573	12/1968	Fraser	299/5 X

Primary Examiner—Ernest R. Purser

Attorney—Paul F. Hawley and Arthur McIlroy

[57] **ABSTRACT**

Sulfur in underground deposits can be readily converted to hydrogen sulfide, and the latter produced, by bringing a suitable hydrocarbon into contact with the sulfur at a temperature of at least 200° F. Where necessary, the formation may be heated to the desired temperature either by means of a bottomhole heater or by combustion. Production of the resulting hydrogen sulfide may be accomplished either through a single-well or multiwell system. The resulting gaseous product can then be processed in a known manner to produce free sulfur.

8 Claims, No Drawings

CONVERSION OF UNDERGROUND SULFUR DEPOSITS

The present invention relates to the recovery of sulfur from underground deposits thereof. More particularly it is concerned with a novel method for converting sulfur in its native state while in said underground deposit into hydrogen sulfide and producing the latter.

BACKGROUND OF THE INVENTION

The major portion of the world's sulfur is obtained from deposits thereof by means of the Frasch process. This procedure employs three concentric pipes, the outermost of which carries hot (approximately 350° F.) water, the innermost pipe compressed air, and the intermediate line contains a mixture of molten sulfur, air and steam, all being forced to the surface by the compressed air which enters the system at high pressures, typically 500 p.s.i. In many cases suitable water is not available at the well site and must be transported, usually by pipeline over considerable distances—in some cases 35 to 40 miles. Also, particularly in instances where the sulfur is present in a relatively thin vein, e.g., 3–5 feet in thickness, the Frasch process requires close well spacing owing to high heat losses.

BRIEF DESCRIPTION OF THE INVENTION

I have now discovered that sulfur may be recovered in useful form from underground deposits thereof by bringing it into contact with a suitable hydrocarbon or mixture of hydrocarbons at elevated temperature. Under such conditions hydrogen sulfide and carbon dioxide are formed, the oxygen in the carbon dioxide being derived from either connate water or from water formed during operation of a bottomhole heater, etc., to raise the temperature of the sulfur to a level such that it will react with the hydrocarbon. Normally, however, enough water is present in crude oil—when used as a hydrocarbon source—or in the formation to supply sufficient oxygen to the system so that at least the major part of the carbon involved in the reaction is converted to carbon dioxide. The presence of some water in the reaction zone is desirable since such condition favors carbon dioxide formation whereas when water is absent the carbon generally is converted into carbon disulfide.

The process of my invention may be carried out either as a single-well huff-and-puff-type operation or as an embodiment employing injection and producing wells. While this procedure may be effected in the presence of native hydrocarbons such condition is rather rare since the large sulfur deposits are generally characterized by the absence of oil and/or gas. Usually where free sulfur and oil are found together the zone in which reaction occurs need not be heated in excess of from about 350° to about 500° F. in order for hydrogen sulfide to be formed in large amounts. In a typical sulfur deposit the latter is heated to a level of from about 300° to about 1,000° F. A hydrocarbon stream is then brought into contact with the hot molten sulfur, resulting in the formation of hydrogen sulfide. In a single-well type of operation the sulfur bearing deposit opposite the well bore is first heated, hydrocarbon injected, and thereafter the well may be shut in for several days, depending on the temperature and the type of hydrocarbon employed. Thereafter, the well is placed on production, permitting the hydrogen sulfide thus formed to be produced. After the hydrogen sulfide flow decreases appreciably, the formation is again heated, if necessary, and the above cycle repeated. In the case of either single-well or interwell operation some molten sulfur will flow into the producing well. This can be recovered merely by using steam traced production tubing and placing the system on pump.

Where injection and producing wells penetrate the sulfur deposit, the latter is preferably hydraulically fractured so as to increase the sulfur surface area that can be contacted with hydrocarbon and to facilitate transmission of heat. After at least a substantial part of the fractured area has been heated, hydrocarbon is brought into contact therewith to form hydrogen sulfide, which is then brought to the surface via the producing well.

A number of practical ways exist for heating the sulfur bearing formation, whether a single or multiple well operation is contemplated. For example, a bottomhole heater of the type described and claimed in Hujsak U.S. Pat. No. 3,223,165 may be employed to bring the sulfur-bearing formation up to the required temperature. Burners of this type operate on natural gas and can generate heat up to about 10 million B.t.u. per day without causing local overheating or other adverse effects. Such sulfur deposits may also be brought up to the temperature required for carrying out the process of my invention by conducting forward or reverse combustion therein as described in White et al. U.S. Pat. No. 3,410,604. In this reference it is pointed out that by combustion temperatures of the order of 500° to about 2,800° F., typically 625° to 1,800° F., can be generated in the sulfur deposit. In some areas the formation temperature conditions may be such that no heat need be added to the system in order to convert free sulfur into hydrogen sulfide on contact with an appropriate hydrocarbon. For example, areas in Southwestern Lousiana, East Texas and South Texas have temperature gradients of the order of about 2.2° per 100 feet of depth. Thus, at a mean surface temperature of 74° F., a 6,000-foot well would have a bottomhole temperature of 206° F. In conditions of this kind a suitable hydrocarbon may be displaced into the deposit—by fracturing if necessary—, the well shut in for a period of from several days to a month or more to permit the conversion of sulfur to hydrogen sulfide, and thereafter the resulting hydrogen sulfide produced. In the case of an interwell operation a fracture can be placed in the sulfur deposit between the injection and producing wells, the producing well(s) shut in, hydrocarbon displaced into the fracture and adequate time given to permit hydrogen sulfide formation, after which production thereof can be commenced. The hydrogen sulfide thus produced can then be converted into free sulfur in a known manner.

The temperature required to effect reaction between the sulfur and hydrocarbon depends primarily on the particular hydrocarbon with which the sulfur is brought into contact. For example, many crude oils when mixed with free sulfur at 350° F. react rapidly to produce copious amounts of hydrogen sulfide. Actually, the reaction will proceed at measurable rates at temperatures as low as about 200° F. Temperatures of the order of 500° to about 700° F. can be generated out into the formation by combustion or suitable bottomhole heaters which may be assisted by fracturing. However, at a given temperature the reaction rate varies with the molecular weight of the hydrocarbon. For example, when sulfur and methane were brought together at a temperature of 700° F. for a period of 4 days, I found that reaction occurred between the methane and sulfur to form a gaseous product containing 62 mol percent hydrogen sulfide. When the temperature was reduced to 500° F. only about 6 percent hydrogen sulfide was obtained over a 12-day period. This work was carried out at pressures of from about 4,000 to 7,000 p.s.i. However, pressure did not seem to have any material effect on the outcome of the reaction.

The nature of the hydrocarbon stream employed may vary widely, the particular type of hydrocarbon selected depending primarily on the temperature that will be available in the sulfur containing formation. Although natural gas may be used as a hydrocarbon source, in general aromatic hydrocarbons or crude oils containing aromatics are preferred because for a given temperature they react with sulfur at a much faster rate than does methane or other paraffin series hydrocarbons. However, the higher molecular weight paraffins, e.g., C_7+, at temperatures of the order of 400–500° F. do react readily with sulfur. Waste refinery or chemical plant streams containing unsaturated hydrocarbons constitute a good hydrocarbon source for use in the process of my invention. Waste streams from styrene plants containing so-called "styrene residues" are especially suited and react relatively rapidly with sulfur to produce hydrogen sulfide at temperatures of the order of 300–400°F. The expression "styrene residues" as used in this description is intended to refer to a hydrocarbon stream boiling at about 500° F. at 100 mm. Hg and having a kinematic

viscosity of about 347 centistokes at 100° F. Such residues contain, for example, 17% styrene, 24% indane, 1½% naphthalene, 5% methyl indane, 2% byphenyl, 6% anthracene, 13½% stilbene, 7% phenyl idane and 5% phenyl naphthalene. The balance of such stream has not been identified other than that it is an aromatic residue containing not more than 2 percent sulfur or sulfur compounds. As used in the present description and claims, the term "hydrocarbon" is to be interpreted as a single compound or as a mixture of saturated and/or unsaturated hydrocarbons.

I claim:

1. In a method for treating free sulfur contained in an underground deposit thereof penetrated by at least one well, the improvement which comprises contacting said deposit—which is already at a temperature of above about 200° F.—with a hydrocarbon, permitting said hydrocarbon and sulfur to remain in contact with one another for a period of at least about several days to 1 month while said at least one well is shut in, whereby said hydrocarbon and sulfur react to produce hydrogen sulfide, thereafter opening said at least one well and recovering through said at least one well the hydrogen sulfide thus formed, the reaction of hydrocarbon and sulfur being effected in the presence of sufficient water so that at least a major part of the carbon reacting is converted to carbon dioxide.

2. The method of claim 1 wherein one well is employed, said hydrocarbon displaced into said deposit, shutting in said well for a period of at least from about several days to 1 month and thereafter recovering the produced hydrogen sulfide via said well.

3. The method of claim 2 wherein a temperature of from about 400° to about 900° F. is employed and liquid sulfur is produced via said well.

4. The method of claim 1 wherein the hydrocarbon component employed is unsaturated.

5. The method of claim 4 wherein the hydrocarbon component employed is a styrene residue stream.

6. The method of claim 3 wherein the hydrocarbon employed is a crude oil.

7. The method of claim 1 wherein said deposit is penetrated by an injection well and a production well, heating at least a portion of said sulfur between said wells to a temperature of from about 400° to about 900° F., thereafter displacing hydrocarbon into said portion, permitting said hydrocarbon and sulfur to remain in contact with one another at a temperature of from about 400° to about 900° F. and recovering hydrogen sulfide thus formed via said production well.

8. The method of claim 7 wherein a fracture is placed between said wells prior to conducting said reaction.

* * * * *