

[54] **PROCESS AND APPARATUS FOR AUTOMATED REGULATION OF SULPHUR PRODUCTION UNITS**

[75] Inventors: **Guillaume Andral, Pau; Michel Carmassi, Mazerès-Lezons; Bernard Louvel, Buros; Jacques Maurice, Mourenx; Georges Vandesande, Aroagnon, all of France**

[73] Assignee: **Societe Anonyme dite: Societe Nationale des Petroles d'Aquitaine, Courbevoie, France**

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[56] **References Cited**

UNITED STATES PATENTS

3,026,184	3/1962	Karasek	423/573 X
3,219,415	11/1965	Hensley	423/574
3,312,529	4/1967	Evano	423/576 X
3,424,560	1/1969	Carmassi et al.....	23/255 E

OTHER PUBLICATIONS

Opeka PC., "The Oil and Gas Journal," May 2, 1966, pp. 86-89.

Primary Examiner—R. E. Serwin
Attorney, Agent, or Firm—Bacon & Thomas

[57] **ABSTRACT**

A process for automated regulation of a unit producing sulphur by oxidation of hydrogen sulphide, in which the flow of gas carrying oxygen into the unit is regulated so as to keep an operating parameter, based on measurement of the sulphurous compound of the residual gases, level with a reference value.

It is characterized by the fact that the control signal, used to regulate the flow of gas containing oxygen at the unit inlet, is a combination of a signal based on measurements taken at the inlet, and representing the theoretical flow of this gas needed to keep the operating parameter at its reference level and another signal representing the correction needed in this flow to adjust the instantaneous value of the parameter to the reference level.

This process allow better control of the sulphur unit, with increased efficiency and reduced atmospheric pollution.

10 Claims, 1 Drawing Figure

PROCESS AND APPARATUS FOR AUTOMATED REGULATION OF SULPHUR PRODUCTION UNITS

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

PROCESS FOR AUTOMATED REGULATION OF SULPHUR PRODUCTION UNITS

This is a division of application Ser. No. 207,790 filed Dec. 14, 1971 and now abandoned.

This invention concerns an improved process and device for automated regulation of units producing sulphur by oxidation of hydrogen sulphide.

A common way of preparing sulphur is the Claus process, which consists of controlled oxidation of hydrogen sulphide, using oxygen or air, followed by contact with a catalyst. The gas containing the hydrogen sulphide, also called acid gas, is injected into a combustion chamber in which one third of the hydrogen sulphide is converted into sulphur dioxide in the presence of oxygen or air, and some sulphur is formed. The reactive gas mixture leaving the combustion chamber is cooled and sent to a condenser, where the sulphur is separated by condensation. In order to increase output, the gas leaving the condenser is reheated and passes over a catalyst, whereupon the sulphur dioxide reacts with the hydrogen sulphide to form a further quantity of sulphur. Catalytic conversion usually requires two or three converters, each preceded by a heater for the gas, and followed by a condenser in which the sulphur is separated out. The residual gases leaving the last catalytic converter, and containing small amounts of sulphurous compounds such as hydrogen sulphide, sulphur dioxide, sulphur vapour, sulphur vesicles, carbon bisulphide, carbon oxysulphide, may go through a purification installation, which retains a high proportion of these compounds. In the rest of this description, "sulphur unit" refers to a plant functioning on this principle, with or without a purification installation for the residual gas from the final catalytic converter. The effluents from the unit pass through an incinerator, before being discharged into the atmosphere.

The main requirement for sulphur units is to maintain maximum output, with the lowest possible wastage of sulphur and sulphurous compounds, under chosen reaction conditions, and despite variations in these conditions, such as pressure, temperature, reagent concentration. Automated regulation of such a unit consists of taking action in order to keep an operating parameter at a level corresponding to minimum wastage of sulphur and its compounds, under the conditions chosen.

One existing method of providing this regulation involves the principle of negative feedback. The ratio of acid gas to air in the input flow is adjusted, using a control function based on a parameter which represents the overall hydrogen sulphide and sulphur dioxide content of the residual gas from the unit, so as to reduce this parameter to the lowest possible level.

This method is not entirely satisfactory, since it ignores outside factors affecting the sulphur unit, causing rapid fluctuations in the operating parameter, too fast for the measurement process to take account of them.

The result is that information concerning such fluctuations is incomplete so that the unit fails to function at maximum efficiency.

The present invention offers a solution to these drawbacks, by providing a method of regulating sulphur units which helps to reduce rapid fluctuations in the operating parameter, thus allowing regulation of such units to be better adapted to their dynamics. There is a resulting improvement in output, and a correspondingly lower concentration of sulphurous compounds discharged into the atmosphere, thus reducing atmospheric pollution.

The invention concerns a process for automated regulation of a sulphur unit producing sulphur by oxidation of hydrogen sulphide, using a gas containing free oxygen, in which the ratio of the flow of gas containing hydrogen sulphide to the flow of gas containing oxygen is adjusted at the unit inlet, by regulating the flow of gas containing oxygen, in order to keep an operating parameter, based on the sulphurous compound contents of effluents from the unit, at a given level, and in which a signal, representing the theoretical flow of gas containing oxygen needed to keep the operating parameter at its given level is worked out from measurements of the gases containing hydrogen sulphide and oxygen at the unit inlet, another signal, representing the correction needed in the flow of gas containing oxygen, to adjust the instantaneous [valve] value of the parameter to the given level, is worked out from this instantaneous value, obtained by analysing the residual gas from the sulphur unit, the two signals are combined, and the resulting signal is used to regulate the input flow of gas containing oxygen.

According to one feature of the invention, the operating parameter used to regulate the sulphur unit is the molar ratio of hydrogen sulphide to sulphur dioxide in the residual gas from the unit.

According to another feature of the invention, the operating parameter used to regulate the sulphur unit is the sum of the hydrogen sulphide and sulphur dioxide contents of the effluents from the unit.

According to a recommended embodiment of the invention, the flow of gas containing oxygen is regulated by varying a slight additional flow, which is combined with a larger fixed flow.

The signal representing the theoretical flow of gas containing oxygen needed to keep the operating parameter at its given level is obtained from a mathematical model simulating the functioning of the sulphur unit, involving measurements of the input flow, pressure, temperature and composition of the gas containing hydrogen sulphide, and the input flow, temperature, pressure and moisture content of the gas containing oxygen. Depending on the method of regulating the flow of this gas, the signal represents the total theoretical flow or the additional theoretical flow needed to keep the operating parameter at a given level.

According to one embodiment of the invention, the rate of conversion of hydrogen sulphide into sulphur is also worked out continuously, from the input composition of the gas containing hydrogen sulphide, and the composition of the residual gas at the outlet. This measurement can be used to improve regulation of the sulphur unit.

The device embodying the process according to the invention consists of a forecasting calculator which delivers a signal representing the theoretical flow of gas containing oxygen needed to keep the operating pa-

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rameter at a given level, an instrument for sampling the effluents from the unit, a device to analyse these samples, and supply signals representing the amounts of various compounds present in the residual gases, a compensating calculator, which uses the signals from the analysing device to obtain the instantaneous value of the operating parameter and from it a signal representing the correction needed in the flow of gas containing oxygen to adjust the instantaneous value of the parameter to its given level, means of combining the signals from the forecasting and compensating calculators, means of regulating the flow of gas containing oxygen in accordance with the resulting combined signal, and means of measuring the input properties of the gas containing hydrogen sulphide and the gas containing oxygen and supplying the forecasting calculator with signals representing these properties, which allow the signal representing the theoretical flow of gas containing oxygen to be obtained.

The system for regulating the flow of gas containing oxygen includes, in particular, a servomechanism controlling a valve on the inlet pipe for this gas.

In one recommended embodiment, this valve is placed on an additional inlet pipe, with a smaller capacity than the main pipe.

The system for measuring the properties of the gas containing hydrogen sulphide and the gas containing oxygen consists of suitable sensing devices placed on the inlet pipes for these gases, and of an analyser fitted to the pipe for the gas containing hydrogen sulphide. This analyser is preferably a chromatography apparatus, although any other type with equivalent precision and capacity may be used.

The device for sampling the residual gas consists of a sampling tube with an aperture along one generatrix projecting into the residual gas pipe, and leading into a circuit through which the sample flows, and a heating system to keep the tube and circuit at a temperature above the solidifying point of sulphur.

The analysing device accompanying the sampling device may be any analyser with satisfactory precision and capacity. It is preferably a chromatography apparatus equipped with a sample input device separate from the chromatographic column, a storage system for the peaks detected, and a programmer. The sample-input device, which is an adjustable inlet-tap, is placed in a heated, insulated enclosure, the temperature of which is above the solidifying point of sulphur. The compensating calculator consists of a device to obtain the instantaneous value of the operating parameter from signals supplied by the analyser, a filtration device to obtain the average instantaneous value, and a calculating device which works out, from the filtered signal and the signal representing the reference value, the feedback control signal. This device preferably takes proportional, integral and first and second pseudo-differential coefficients into account.

In one embodiment of the invention, the device also includes a system to calculate the rate of conversion of hydrogen sulphide into sulphur, receiving signals from the analyser of the input flow of gas containing hydrogen sulphide, and from the analyser of the residual gas, and supplying a signal representing the rate of conversion.

The invention is explained in the following description, illustrated by the accompanying FIGURE, without being in any way confined to this embodiment.

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The FIGURE shows, diagrammatically, a sulphur unit equipped with a regulating device according to the invention, using as the operating parameter the theoretical molar ratio of hydrogen sulphide to sulphur dioxide in the residual gases, and also including a system to calculate the rate of conversion of hydrogen sulphide into sulphur.

The gas containing hydrogen sulphide, known as the acid gas, and which also contains carbon dioxide and small amounts of other products such as methane, arrives by a pipe 1, on which are fitted a flowmeter 2, pressure-gauge 3, temperature-gauge 4, and sampling device 5. The sample later returns to the pipe 1 by another pipe (not shown here). The acid gas is sampled by the sampling device 5, and analysed in an analyser 6, preferably a chromatography apparatus equipped with a programmer and a storage system allowing the results to be stored between each analysis cycle. This analyser delivers the results of the analysis in the form of electrical signals 7, 8 and 38 representing the hydrogen sulphide, methane and carbon dioxide contents of the gas. The acid gas reached the sulphur unit 23, through the valve 10.

A main air flow arrives by a pipe 11, on which are fitted a flowmeter 12, pressure-gauge 13, temperature-gauge 14 and humidity-gauge 15, and enters the sulphur unit through a valve 17. An additional air pipe 18, equipped with a flowmeter 19, allows the amount of air needed to correct disturbances to enter the unit through another valve 21.

A forecasting calculator 22, receives the information from the sensing devices 2, 3 and 4 on the acid-gas pipe along lines 9, information from the sensing devices on the main air-pipe along lines 16, the signal from the flowmeter 19 on the additional air-pipe along line 20, and the signals from the analyser 6, representing the hydrogen sulphide and methane contents of the acid gas, along lines 7 and 8.

From this data, the forecasting calculator obtains an output signal 35, which represents the theoretical additional amount of air needed to keep the operating parameter (the molar ratio of hydrogen sulphide to sulphur dioxide in the residual gases) at a given level. If the composition of the acid gas is known, from previous experience, the analyser 6 can be left out, and the results of the earlier analysis fed directly into the forecasting calculator 22.

Residual gases, containing nitrogen, carbon dioxide, water vapour and small amounts of sulphurous compounds such as hydrogen sulphide, sulphur dioxide, carbon bisulphide and carbon oxysulphide, escape from the sulphur unit 23 by a pipe 24, and pass into an incinerator 25, the effluent from which passes along a pipe 26 and is discharged into the atmosphere through a chimney 27.

A sampling device 26 in the discharge pipe 24, just before the incinerator inlet, takes a sample of the residual gases. This is done by means of a tubular rod with an aperture among one generatrix, projecting into the middle of the pipe. This sample passes along a pipe 29 to an analyser 30, and back to the pipe 26. The flow ensures short response time. To avoid clogging, the circuit along which the sample flows to the analyser 30 and the pipe 26 are kept above the solidifying point of sulphur, by means of a double casing inside which a heating fluid, such as steam, circulates at a suitable temperature.

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The analyser 30 is a chromatography apparatus equipped with a programmer and a peak-storage system, updated at each cycle. The apparatus also includes a sample-input system designed to operate at high temperatures, and which is separate from the chromatographic column, making it accessible in the event of an accident. This input system is an adjustable tap, and it is placed in a heated, insulated enclosure. This system allows the sample, which is at low pressure, to mix with the vector gas circulating at high pressure. The filling of the column enables all the components of the residual gas samples to be analysed, despite their high moisture content. Peaks corresponding to hydrogen sulphide, sulphur dioxide, carbon bisulphide and carbon oxysulphide are measured every four minutes or so.

The signals representing the hydrogen sulphide and sulphur dioxide contents delivered by the chromatograph storage system are fed by lines 31 into a compensating calculator 32, which gives a signal representing the molar ratio of hydrogen sulphide to sulphur dioxide, filters it to obtain an average, compares this average with the reference value of the operating parameter, posted on the calculator, and finally obtains an output signal 33 from the difference, using a specific regulation algorithm adapted to the dynamics of the unit, and taking the proportional, integral and first and second pseudo-differential coefficients in particular into account.

The signal 33, which represents the flow of air needed to bring the instantaneous level of the ratio of hydrogen sulphide to sulphur dioxide back to its given level, forms the negative feedback control algorithm.

The signal 33 from compensating calculator 32, and the signal 35 from the forecasting calculator 22 are combined in an adaptation device 34, and the resulting signal 36 operates a servomechanism 37, which adjusts the setting of the additional air-inlet valve 21.

The information supplied by the analysers 6 and 30 can also be used to obtain the rate of conversion of hydrogen sulphide into sulphur. To do this, a calculating system 41 receives the signals 7, 8 and 38 from 6, representing the hydrogen sulphide, methane and carbon dioxide contents of the input acid gas and, along lines 40, the signals 39 from the chromatography apparatus 30, representing the hydrogen sulphide, sulphur dioxide, carbon bisulphide, carbon oxysulphide and carbon dioxide contents of the residual gases. From those signals the calculating system 41 works out a signal representing the molar ratio of hydrogen sulphide to carbon dioxide and methane in the acid gas, and a second signal representing the molar ratio of sulphurous compounds to carbon dioxide in the residual gases, then divides the second signal by the first, and subtracts the signal obtained from a unitary signal, to obtain a result signal 42, which shows the rate of conversion of hydrogen sulphide into sulphur. This signal may be used in an additional feedback loop, to improve regulation of the sulphur unit.

Display and recording systems (not shown here) allow the different measurements and calculated signals to be displayed, so that the state of operation of the unit may be checked at any time.

What is claimed is:

1. A device for the automatic regulation of a sulphur unit that produces sulphur by the oxidation of a hydrogen sulphide-containing gas by means of a free oxygen-containing gas, said gases being fed to the inlet of the

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sulphur unit through suitable inlet pipes and said sulphur unit liberating residual gases containing H_2S and SO_2 through a residual gas pipe, said device comprising:

5 a first analyzer for automatically analyzing the H_2S -containing gas fed to the inlet of the sulphur unit for providing a signal representative of the H_2S content of said gas,

10 a first calculator connected to receive the signal provided by said first analyzer for computing the theoretical flow of free oxygen-containing gas to be fed to the inlet of the sulphur unit to keep the $H_2S:SO_2$ molar ratio in the residual gases to a set value and for providing an output signal representative of said theoretical flow,

15 sampling means for continuously taking samples of the residual gases,

a second analyzer for automatically analyzing said samples for providing signals representative of the H_2S and SO_2 contents of the residual gases,

20 a second calculator connected to receive the signals from the second analyzer for computing the instantaneous $H_2S:SO_2$ molar ratio in the residual gases and for computing a correction value representing the correction needed in the flow of free oxygen-containing gases to the inlet of the sulfur unit to adjust said instantaneous ratio to the set value, said second calculator providing a signal representative of said correction value,

25 means for electronically combining the signals provided by said first and second calculators to produce a resulting signal representing their sum, and means responsive to said resulting signal for automatically controlling the flow of free oxygen-containing gas to the inlet of the sulphur unit.

2. A device as recited in claim 1 wherein said controlling means comprises:

a valve connected to the inlet pipe carrying said free oxygen-containing gas, and

35 a servomechanism responsive to said resulting signal for controlling said valve.

3. A device as recited in claim 2 wherein said free oxygen-containing gas is fed to said sulphur unit by a first main pipe and a second, smaller capacity pipe and wherein said valve is connected to said second pipe for controlling the flow of free oxygen-containing gas into said sulphur unit.

4. A device as recited in claim 1 further comprising sensing means connected to the inlet pipes of the H_2S -containing gas and the free oxygen-containing gas to measure flow-rate, pressure, and temperature of the H_2S -containing gas and flow-rate, pressure, temperature, and humidity of the free oxygen-containing gas, said sensing means providing signals representative of said measurements to said first calculator.

5. A device as recited in claim 1 in which said first analyzer comprises a chromatography apparatus.

6. A device as recited in claim 1 wherein said sampling means comprises a sampling tube having an aperture along one generatrix projecting into the residual gas pipe and leading into a circuit through which the sample flows, said device further comprising heating means for maintaining the temperature of said sampling tube and circuit above the solidifying temperature of sulphur.

7. A device as recited in claim 1 wherein the second analyzer comprises a chromatography apparatus having a chromatographic column and equipped with a

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sample input device separate from the chromatographic column, a storage system for storing the peaks detected, and a programmer.

8. A device as recited in claim 7 wherein the sample-input device comprises an adjustable inlet-tap placed in a heated, insulated enclosure, the temperature of said enclosure being maintained above the solidifying temperature of sulphur.

9. A device as recited in claim 1 in which said second calculator comprises:

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a device for calculating the instantaneous value of the $H_2S : SO_2$ molar ratio in the residual gases from the signals supplied by said second analyzer,

filtering means for providing signals representative of the average value of said molar ratio, and means for computing said correction signal from the average value signal and a signal representing the set value of said $H_2S : SO_2$ molar ratio.

10. A device as recited in claim 1 further including a system to calculate the rate of conversion of the hydrogen sulphide into sulphur from the signals provided by said first and second analyzers and to provide a signal representing said rate of conversion.

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