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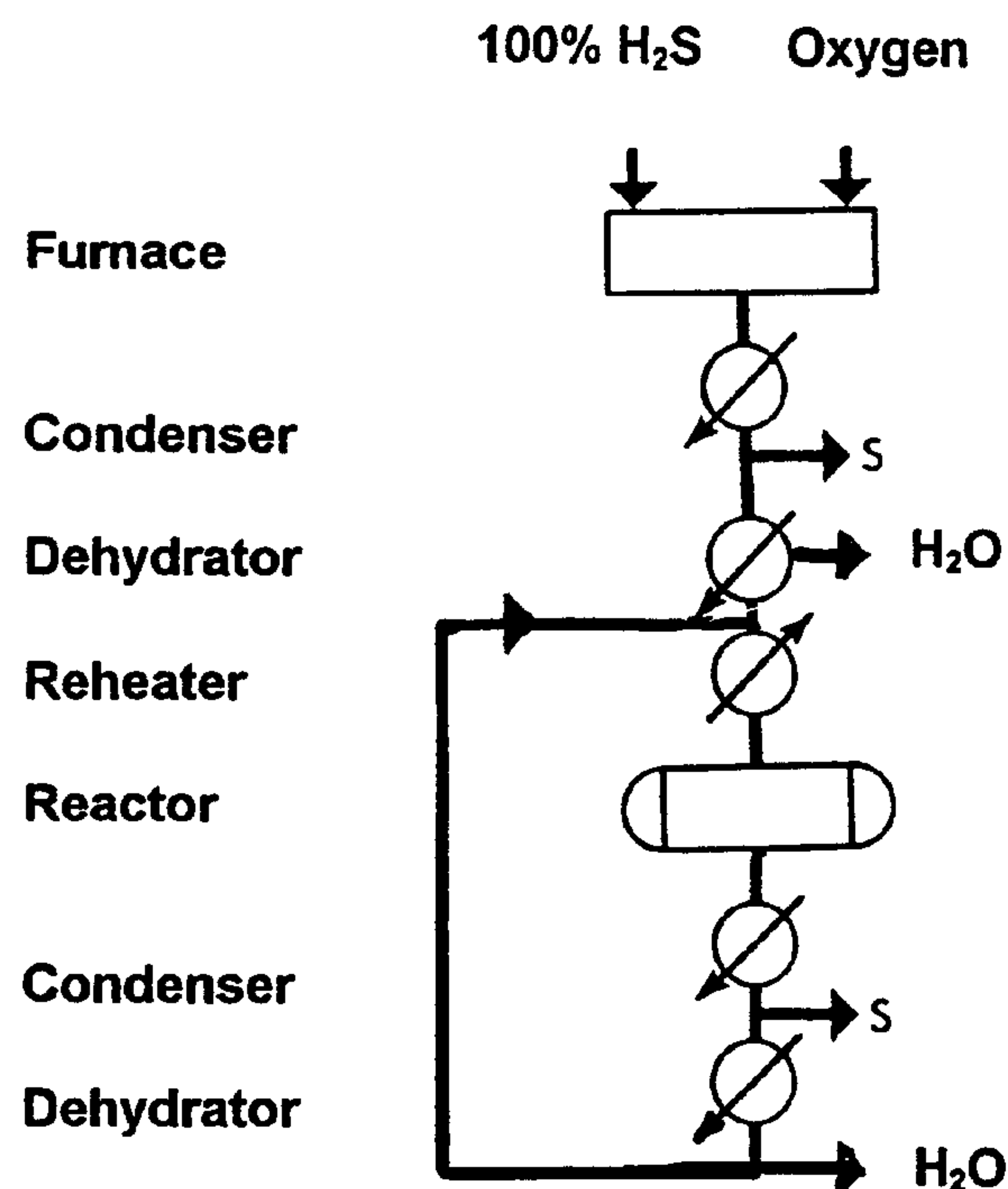
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(54) Titre : PROCEDE D'EXTRACTION DE LA VAPEUR D'EAU

(54) Title: REMOVAL OF WATER VAPOUR FROM ACIDGAS STREAMS



(57) **Abrégé/Abstract:**

The invention disclosed relates to an improved process for the production of elemental sulfur from acidgas streams containing hydrogen sulfide, in which the hydrogen sulfide conversion is improved by removing by product water vapor by dehydration by direct contact of the hydrogen sulfide with concentrate sulfuric acid in a concentration range of about 82 to about 96 wt%.



ABSTRACT

The invention disclosed relates to an improved process for the production of elemental sulfur from acidgas streams containing hydrogen sulfide, in which the hydrogen sulfide conversion is improved by removing by product water vapor by dehydration by direct contact of the hydrogen sulfide with concentrate sulfuric acid in a concentration range of about 82 to about 96 wt%.

REMOVAL OF WATER VAPOR FROM ACIDGAS STREAMS

FIELD OF THE INVENTION

This invention relates to the removal of water vapor from gas streams containing hydrogen sulfide, sulfur dioxide, carbon dioxide and other acidic gases, and in particular to a process for the production of elemental sulfur from such gas streams in which water vapor is removed from the gas to enhance the production of elemental sulfur.

BACKGROUND OF THE INVENTION

Acidic gas streams are often encountered in the processing of natural gas, crude oil, bitumen, heavy oil and coal-derived liquids, for the removal of the sulfur content. Most often, an

acidic component, for example, hydrogen sulfide, is separated or formed in the process and it, in turn, becomes a disposal problem. The sulfur content of such an acidgas is generally converted to elemental sulfur, and the residual acidgas becomes a waste stream. The removal of sulfur prior to emission of the residual gas streams to the atmosphere is regulated by laws to minimize the degree of air pollution.

DESCRIPTION OF THE PRIOR ART

Most commonly, amine absorption is employed in natural gas processing plants to sweeten sour natural gas through hydrogen sulfide removal. After regeneration of the amine solution, a gas stream (acidgas) emerges rich in acidic constituents such as hydrogen sulfide and carbon dioxide. Generally, a version of the modified Claus Process is used to recover elemental sulfur from the acidgas via the following chemical reactions, singly or combined,



Reactions (1) and (2) both proceed in a front-end combustion step, typically in a furnace or burner, resulting in an acid gas containing a 2:1 stoichiometric ratio (reaction 2) of hydrogen sulfide to sulfur dioxide. The additional recovery of sulfur is achieved, based on reaction (2), in staged fixed bed catalytic reactors operating at successively lower temperatures. An additional cleanup unit is usually required to achieve the degree of sulfur removal mandated by emission regulations. The reaction (2) is exothermic and reversible, and an approach to the limiting equilibrium conversion of hydrogen sulfide is desirable. In the

past, this has been achieved by shifting the reaction to the right by removal of the product, sulfur, by condensation after each process reaction stage. Also, by successively lowering the stage temperatures, the equilibrium conversion (and sulfur recovery) is maximized at the outlet of the final stage.

Similarly, the removal of the product water vapor would also theoretically shift the equilibrium conversion additionally to the right. However, the removal of water vapor from modified Claus process streams by pressure-swing absorption has never been utilized in practice because the preliminary economic analyses of such process modification have shown it to be relatively more capital-intensive and uneconomical. Moreover, the condensation of water vapor by cooling a modified Claus process stream apparently has been attempted in the past. Apparently, the attempt using a stainless steel condensor for water removal, failed due to severe corrosion. This failure is not surprising, since it is known that hydrogen sulfide contacting aqueous solutions of sulfur dioxide forms very corrosive polythionic acids called "Wackenroder's solution". See [CHEMISTRY OF THE ELEMENTS, N. N. Greenwood and A. Earnshaw, Pergamon Press Ltd. 1984, page 849].

It is an object of the present invention to provide a process for removing water vapor from acidic gas streams.

It is also an object of the present invention to provide a process for removing water vapor from acidic gas streams in which the water vapor is removed by dehydration with concentrated sulfuric acid.

It is another object of the invention to provide an improved process for the production of elemental sulfur from acidgas streams containing hydrogen sulfide, in which the production of elemental sulfur is enhanced by removing the product water vapor by dehydration with concentrated sulfuric acid.

According to the invention, an improved process for the production of elemental sulfur according to the chemical reactions



including removing elemental sulfur after each reaction stage by condensation above the boiling point of water, the improvement comprising after one or more reaction stages also removing water vapor by dehydration by direct contact of H_2S with concentrated sulfuric acid of a concentration of about 82 to about 96 weight percent, is provided.

The sulfuric acid contact may occur following the removal of elemental sulfur, at one or more stages/locations in the process depending upon the the amounts of water vapor present at those stages/locations, and whether the further improved sulfur recovery in a particular reaction stage is economically justifiable.

Even though the modified Claus process preferably involves a series of stages or reaction steps at successively lower temperatures to achieve higher equilibrium conversions for chemical reaction (3), the temperatures used may be less than the dew-point of sulfur vapor (about 120 °C), but not below the dew-point of water (about 100 °C).

A further improvement in the production of elemental sulfur may be achieved if hydrogen sulfide is permitted to react with the concentrated sulfuric acid, according to the following chemical

reaction,



The extent to which additional elemental sulfur is formed through reaction (4) is determined by the concentration/strength of the sulfuric acid and the reaction temperature used in the dehydration unit. Since SO_2 is a by product of this reaction, further modification of the inlet air : H_2S ratios may be required to accommodate the additional SO_2 .

Reaction temperatures of ambient to about 120°C have been found to be appropriate to both enhance the production of elemental sulfur by both shifting the equilibrium conversion attainable in the reaction stages as described in equations (1) to (3), and in promoting additional sulfur recovery from equation (4).

A still further improvement will be achieved if dehydration by concentrated sulfuric acid contact is combined with the use of oxygen-enriched air or pure oxygen in a continuous process using reactions (2) and (3), as will be apparent hereinafter.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic illustration of a straight-through modified Claus process, as known in the prior art.

Figure 2 is a graph illustrating the conversion of hydrogen sulfide to sulfur, according to the invention.

Figure 3 is a schematic illustration of an apparatus according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

The advantages of removing water vapour are particularly apparent in terms of impact upon process efficiency. Three different examples illustrate gains to be achieved by removal of water vapor from a modified Claus process unit.

Example 1

A simple straight-through modified Claus process without tailgas cleanup is described in figure 1. This process includes a furnace followed by two stages of catalytic reactors. Specifically, the process includes a furnace in which about 1/3 of the H_2S in the feed is oxidized at flame temperatures via chemical reaction (2). The resulting 2:1 ratio of $H_2S : SO_2$ is then chemically reacted over alumina- or titania-based catalysts in two successive reaction stages according to chemical reaction (3). The inlet temperatures to the two stages are, for example, about 280°C and about 260°C, respectively. After the furnace and after each of the two reactor stages, sulfur vapor is condensed at about 120°C to prevent condensation of water vapor. Each of these three stages is adiabatic and attains an H_2S conversion such that the effluent gas composition approaches the equilibrium conversion limit possible for the given operating conditions.

Curves A to C' in figure 2 represent calculated equilibrium conversions {for reactions (4) and (2)} as a function of temperature for four different stream compositions resulting from a 100% H_2S acidgas feed to the furnace. Curve A and the 70% conversion level define the equilibrium conversion attained in a stream leaving the furnace and being cooled from 1100°C to 227°C (500K). The feed composition to the furnace is given by A in table 1.

Table 1

Feed Compositions (wt%)

	H ₂ S	SO ₂	O ₂	H ₂ O	N ₂
A	29.58	0.00	14.79	0.00	55.63
B	6.94	3.47	0.00	24.30	65.29
C	2.74	1.37	0.00	31.49	64.40
C'	4.20	2.00	0.00	0.00	94.00

The sulfur is removed by condensation at about 227°C and curve B shows the equilibrium conversions possible for the resulting stream composition (composition B in table 1). The diagonal broken line represents the adiabatic conversion path in the first catalytic converter. Its intersection with curve B shows that 88% conversion is reached after one catalytic reaction stage. After cooling to about 227°C, followed by a second stage of adiabatic catalytic reaction, a final equilibrium conversion of 94% is attained. The unconverted 6% of sulfur in the feed would necessitate additional processing for tailgas cleanup as required.

If water vapor were removed after the sulfur condensor, by adding concentrated sulfuric acid of concentration of about 82 to about 96 wt% after the first catalytic reactor, the composition of stream C is altered to C'. The equilibrium conversions for the composition of this dry stream are shown by curve C'. The intersection of the second adiabatic reactor path with curve C' shows that the second reactor is now able to achieve a 98.5% conversion.

Removal of water vapor after the furnace, where the bulk of the water is produced (see composition B), would increase the overall

conversion slightly and lower the downstream volumes of total flowing process gas by more than 25% thus requiring smaller processing vessels and lowering the capital costs.

Example 2

If the novelty of dehydration of Claus plant acidgases is combined with the novelty of converting H_2S directly to elemental sulfur (see applicant's co-pending U.S. patent application Serial Number 08/198,790, filed 18 February 1994, the disclosure of which is incorporated herein by reference), their combined application to the modified Claus process becomes even more advantageous. If a combined dehydrator/ H_2S oxidation unit is inserted after the second catalytic converter of figure 1 as well as a dehydrator after the first converter, the feed to the dehydrator/oxidation unit corresponds to that of C' in figure 2. The 4.2% H_2S would be essentially completely converted to elemental sulfur in the dehydrator/oxidation unit at about 120°C and about 96 wt% sulfuric acid. The resulting tail gas would contain the unreacted 0.46% SO_2 and 99.54% N_2 . This would correspond to 99.1% recovery of sulfur. This recovery could eliminate the need for additional tailgas cleanup since the low concentration of SO_2 in the tailgas mixture can, for many locations, be discharged directly to the atmosphere.

Example 3

The use of oxygen-enriched air or pure oxygen in place of an air feed to a modified Claus plant has already been recognized to have some advantages over a conventional Claus plant. The richer feedgas (containing no nitrogen for example) increases the conversions in each reaction stage, and requires a smaller flowing volume, which in turn reduces equipment size requirements, thus lowering capital costs. Figure 3 shows how an oxygen feed could be combined with sulfuric acid dehydration in a continuous, re-

circulating, in which sulfur and water vapor are continuously removed, which theoretically could achieve a zero emission operation. The process operates in the same manner as the aforementioned modified Claus process through reactions (2) and (3), but is designed to re-circulate the substantially dry and sulfur-free unreacted $\text{H}_2\text{S}/\text{SO}_2$ (2:1) ratio to the catalytic reaction stage. Perfect control of the 2:1 stoichiometric feed ratio is essential here, otherwise, the excess gas (H_2S or SO_2) will build up in concentration in successive recycle passes, thereby lowering the conversion and necessitating a purge stream, with its accompanying recovery problems. If SO_2 in excess of the desired 2:1 ratio should buildup, a pure H_2S makeup stream would be required for ratio control. On the other hand, it may be advantageous to operate the re-circulation process with an excess of H_2S to facilitate a more complete conversion of SO_2 during each pass through the catalytic converter. The excess H_2S could then be re-cycled to the plant feed (prior to the furnace) since it is nearly pure H_2S . If minor amounts of other gases, e.g. N_2 or CO_2 are present in the feed, a purge stream will be necessary irrespective of feed ratio control. This purge stream could be incinerated since it cannot be recycled.

The details of the above process conditions essentially follow the established practices employed in the operation of typical modified Claus process plants, and will be well known to those skilled in the art.

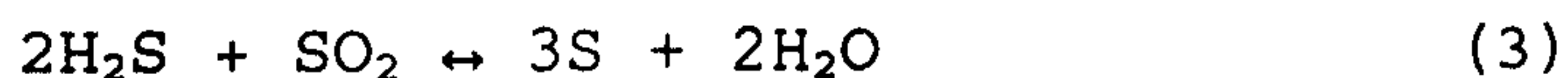
Claims:

1. A process for the production of elemental sulfur from an H₂S-containing acidgas stream, comprising

(a) oxidation of the H₂S with an oxygen-containing gas according to the chemical reaction



followed by the chemical reaction



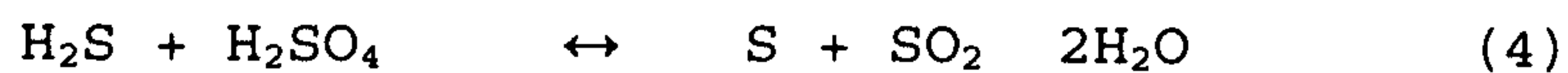
(b) removing the elemental sulfur so formed, by condensation at a temperature of about 120°C to prevent condensation of water vapour,

(c) passing the acidgas stream which is substantially oxygen-free to a catalytic converter, and repeating the chemical reaction (3) in the presence of a catalyst in two successive stages, a first stage at a temperature of about 280°C and a second stage at a temperature of about 260°C,

(d) removing the elemental sulfur so formed after each of said two successive stages, by condensation, wherein after step (b) removing the water vapor so formed, by dehydration by direct contact of the acidgas stream which is substantially water and oxygen free, with concentrated sulfuric acid of a concentration of about 82 to about 96 wt%, whereby the production of elemental sulfur in chemical reaction (3) is enhanced.

2. A process according to Claim 1, wherein reaction (2) is carried out in a furnace at elevated temperatures.
3. A process according to Claim 2, wherein reaction (3) is carried out in a catalytic converter.
4. A process according to Claim 3, wherein the catalyst is selected from the group consisting of alumina and titania.
5. A process according to Claim 3, wherein reaction (3) is repeated at successively lower reaction temperatures above the boiling point of water.
6. A process according to Claim 1, wherein each of the reactions (1) to (3) is adiabatic and approaches the equilibrium conversion limit for a given set of operating conditions.
7. A process according to Claim 1, wherein the water vapor is removed after removal of the elemental sulfur.
8. A process according to Claim 1, wherein the water vapor is removed after each reaction stage.
9. A process according to Claim 1, including the further step of reacting the concentrated sulfuric acid with hydrogen

sulfide at a temperature of from ambient to about 120°C according to the chemical reaction,



to further enhance the production of elemental sulfur.

10. A process according to Claim 3, wherein the process is continuous.

11. A process according to Claim 10, wherein unreacted H_2S and SO_2 in a ratio of 2:1, are continuously removed and recycled back to the catalytic converter.

12. A process according to Claim 11, wherein the oxygen source for reactions (1) and (2) is selected from the group consisting of oxygen-enriched air and pure oxygen.

13. A process according to Claim 8, wherein the elevated temperature is about 1100 °C.

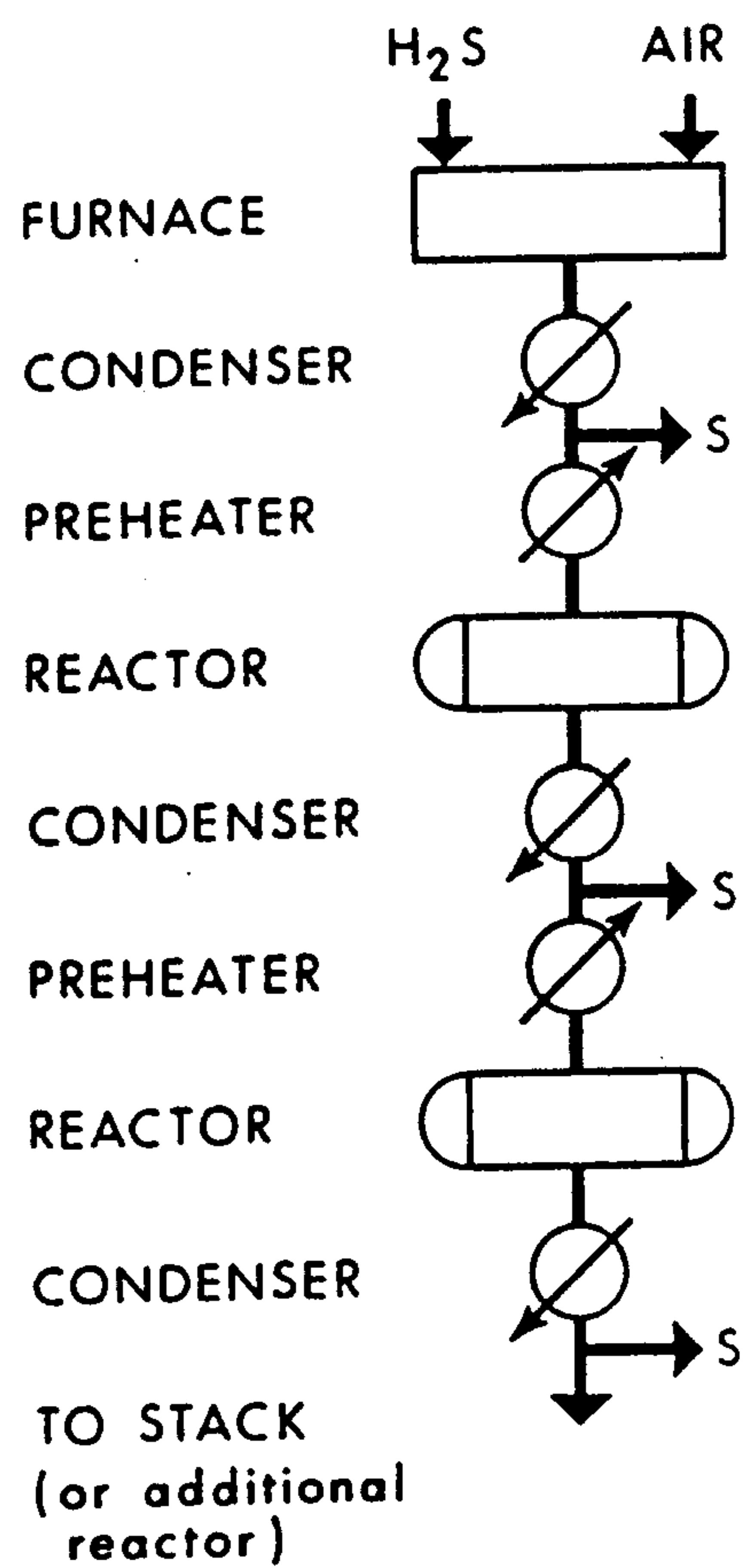


Figure 1 PRIOR ART

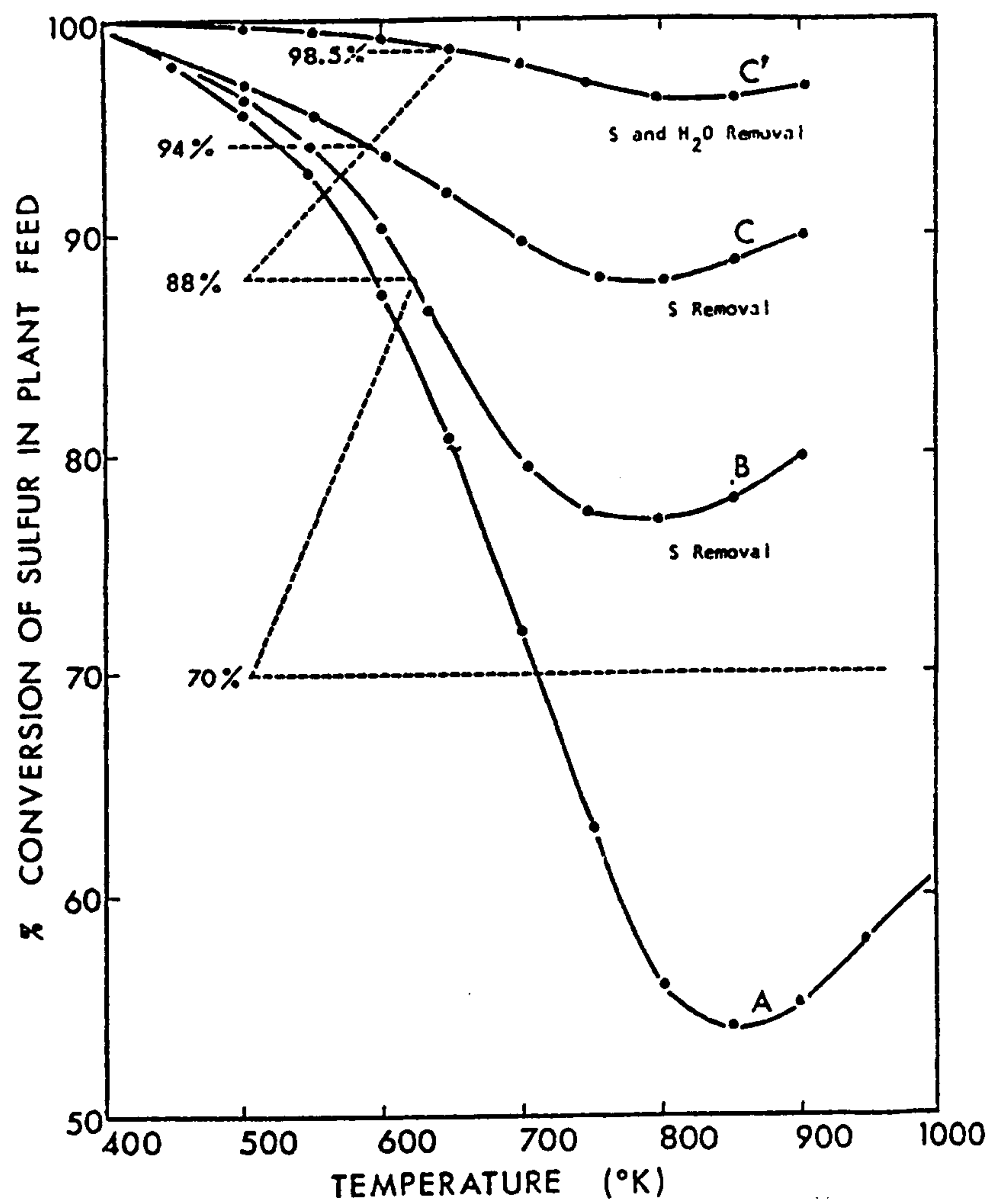


Figure 2

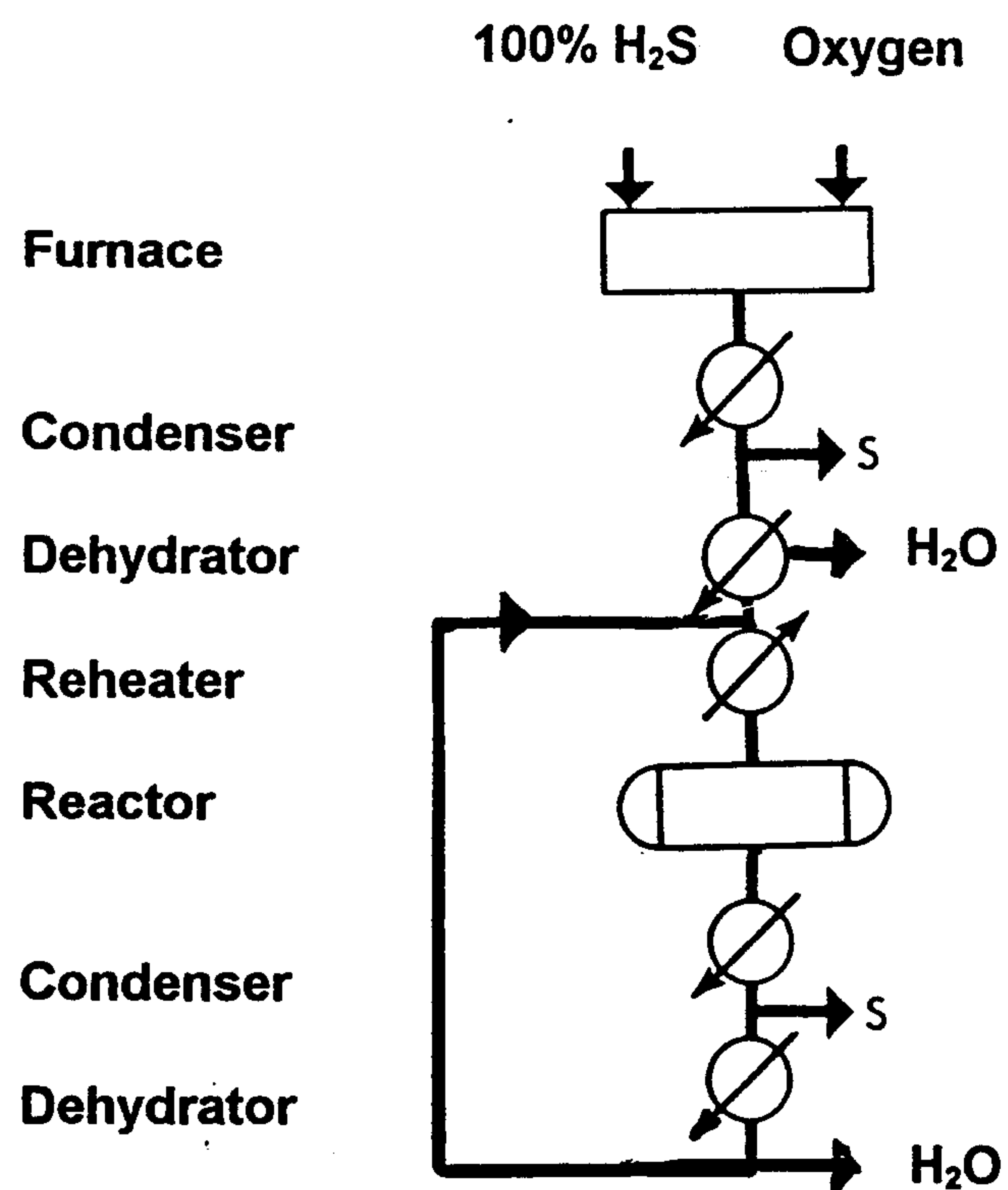


Figure 3.

100% H₂S

Oxygen

Furnace

Condenser

Dehydrator

Reheater

Reactor

Condenser

Dehydrator

