



- (51) **International Patent Classification:**
C01B 3/04 (2006.01) *C01B 3/50* (2006.01)
- (21) **International Application Number:**
PCT/CA2009/001562
- (22) **International Filing Date:**
29 October 2009 (29.10.2009)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (71) **Applicant (for all designated States except US):** HER MAJESTY THE QUEEN IN RIGHT OF CANADA AS REPRESENTED BY THE MINISTER OF NATURAL RESOURCES CANADA [CA/CA]; 580 Booth Street, 16th Floor, Ottawa, Ontario K1A 0E4 (CA).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** GALUSZKA, Jan [CA/CA]; 389 Vances Side Road, Dunrobin, Ontario K0A 1T0 (CA). IAQUANIELLO, Gaetano [IT/IT]; Via Annia Faustina 27, I-00153 Roma (IT).
- (74) **Agents:** GALE, Edwin J. et al.; KIRBY EADES GALE BAKER, Box 3432, Station D, Ottawa, Ontario K1P 6N9 (CA).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) **Title:** MEMBRANE-ASSISTED CONVERSION OF HYDROGEN SULPHIDE

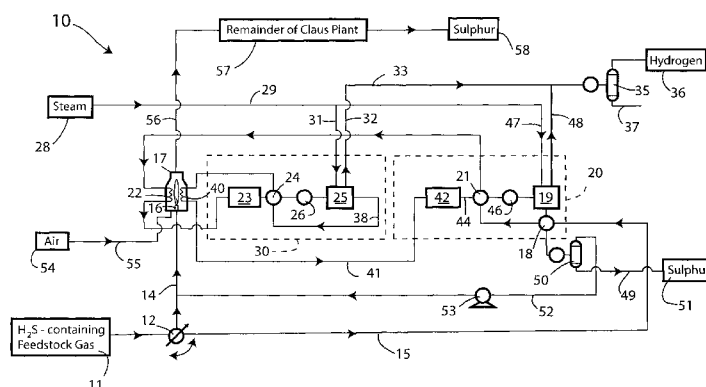


Fig. 1A

(57) **Abstract:** An exemplary embodiment of the invention provides a method of producing hydrogen from a feedstock gas containing hydrogen sulphide. The method involves partially thermally decomposing hydrogen sulphide in the feedstock gas to produce hydrogen and sulphur, and separating hydrogen from the sulphur and unreacted hydrogen sulphide. In particular, the feedstock gas is heated to a decomposition temperature of up to about 1000°C by heat generated in a thermal step of a Claus process operating to convert hydrogen sulphide to sulphur and water, thereby producing a decomposition gas containing hydrogen, sulphur and unreacted hydrogen sulphide, followed by separating hydrogen from the decomposition gas by hydrogen permeation through a hydrogen-permeable membrane, collecting the hydrogen thereby separated, and burning residual unreacted hydrogen sulphide in the thermal step of the Claus process. Apparatus for carrying out the method is also provided.

MEMBRANE-ASSISTED CONVERSION OF HYDROGEN SULPHIDE

TECHNICAL FIELD

5 This invention relates to the conversion of hydrogen sulphide to hydrogen and sulphur. More particularly, the invention relates to such conversion primarily for the production of hydrogen without CO₂ emission.

BACKGROUND ART

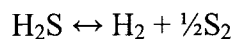
10 Large amounts of hydrogen sulphide are produced worldwide, mostly from amine scrubbing in the processing of natural gas and the refining of conventional oil deposits and oil from tar sands. This acidic gas (often referred to as “acid gas” or “sour gas”) is considered to be a waste stream and has to be treated. Hydrogen sulphide itself has limited industrial application and is considered to be an
15 environmental pollutant.

 In oil refineries and natural gas treating plants, when the sour gas stream contains amounts of H₂S greater than about 20% by volume, the H₂S is usually treated in the Claus process, whereby H₂S is oxidized to water and sulphur. This involves burning an H₂S-rich gas stream with a sub-stoichiometric quantity of air to produce
20 SO₂, and the hot gas is cooled to generate steam. Then the gas is passed over an alumina catalyst in a converter to react SO₂ with remaining H₂S to produce sulphur and water. This process is not economical when the price of sulphur (the primary product) is depressed, but nevertheless it is practiced to dispose of the H₂S in an environmentally acceptable manner.

25 Nevertheless, H₂S has potentially a much higher economic value if not just sulphur, but also hydrogen, could be recovered and recycled instead of being wasted in the form of water. Moreover, it would be highly desirable to convert H₂S to sulfur and hydrogen within the refinery and to return the recovered hydrogen to a heavy oil hydrogenation step which requires quantities of hydrogen, for example during the
30 treatment of bitumen and tar sand deposits. This would significantly improve hydrogen inventory and avoid associated carbon dioxide emissions, as well as avoiding the need for off-site treatment and associated transportation costs.

Refineries use hydrogen as a basic reagent in hydrocracking and in hydrotreating to produce fuels with low sulphur and low aromatics content. Hydrogen is also used in the chemical industry primarily in the synthesis of ammonia and methanol. Most of the hydrogen currently consumed is manufactured by steam methane reforming (SMR). This process requires large quantities of natural gas as both the feed gas and combustion fuel resulting in large amount of carbon dioxide being produced and discharged into the atmosphere, and thus contributing significantly to the “greenhouse” effect.

It is known that the heating of H_2S will dissociate the molecule according to the following reversible reaction:



but the decomposition reaction is strongly endothermic and very high temperatures are required to achieve satisfactory conversion yields, normally temperatures higher than 1000°C . The cost of such conversion is prohibitive due to energy demands and the need for exotic metallurgy to withstand the high temperatures. Accordingly, direct dissociation is not currently practiced on a commercial scale.

There is, therefore, a need for a more effective way of treating H_2S -containing gases, particularly acid gas produced within heavy oil refineries, to produce hydrogen suitable for industrial use without creating CO_2 emissions.

20

DISCLOSURE OF THE INVENTION

An exemplary embodiment of the invention provides a method of producing hydrogen from a feedstock gas containing hydrogen sulphide. The method involves partially thermally decomposing hydrogen sulphide in the feedstock gas to produce hydrogen and sulphur, and separating hydrogen from the sulphur and unreacted hydrogen sulphide. In particular, the feedstock gas is heated to a decomposition temperature of up to about 1000°C by heat generated in a thermal step of a Claus process operating to convert hydrogen sulphide to sulphur and water, thereby producing a decomposition gas containing hydrogen, sulphur and unreacted hydrogen sulphide, followed by separating hydrogen from the decomposition gas by hydrogen permeation through a hydrogen-permeable membrane, collecting the hydrogen

thereby separated, and burning residual unreacted hydrogen sulphide in the thermal step of the Claus process.

According to another exemplary embodiment of the invention, there is provided apparatus for producing hydrogen from a feedstock gas containing hydrogen sulphide. The apparatus includes a furnace for generating heat by combustion of fuel
5 sulphide. The apparatus includes a furnace for generating heat by combustion of fuel in a burner, a heat exchanger within the furnace for heating a feedstock gas comprising hydrogen sulphide passing through the heat exchanger, a reactor associated with the heat exchanger within which the hydrogen sulphide partially thermally decomposes to form a decomposition gas containing hydrogen, sulphur and
10 unreacted hydrogen sulphide, a separation device downstream of the reactor for separating hydrogen from the decomposition gas, and a vessel for collecting the hydrogen thus separated. In particular, the furnace forms part of a Claus apparatus used for conversion of hydrogen sulphide to sulphur and water, the hydrogen separation device is a membrane permeable to hydrogen, and the hydrogen separation
15 device is connected to the burner of the furnace for combustion of residual unreacted hydrogen sulphide following hydrogen separation therefrom.

Exemplary embodiments of the invention employ the Claus process to generate heat for the thermal decomposition of hydrogen sulphide and use a lower temperature thermal decomposition coupled with permeable membrane reaction and
20 separation to allow lower temperatures to be employed overall. The residual hydrogen sulphide is disposed of within the Claus process and its heat content is employed as a partial or complete energy source for the process. Relatively inexpensive materials may be used for the apparatus and there is normally no requirement for external energy and no generation of carbon dioxide.

25 The decomposition gas leaving the reactor is normally quenched, i.e. quickly reduced in temperature, to avoid back reaction of hydrogen and sulphur in the decomposition gas which may take place if the gas is allowed to cool slowly. This can be achieved by passing the decomposition gas through a suitable heat exchanger.

Preferably, before ultimately burning the residual hydrogen sulphide in the
30 thermal step, the decomposition gas containing unreacted hydrogen sulphide is heated at least one more time to the decomposition temperature of up to about 1000°C by heat generated in the thermal step, followed each time by further separation of

hydrogen by permeation through a hydrogen-permeable membrane and collection of the separated hydrogen. Preferably, there is only one more heating and separation step of this kind before the remaining unreacted hydrogen sulphide is burned in the thermal step.

5 In the decomposition steps, the temperature is preferably not raised above about 1000°C to avoid the need for expensive and exotic materials required to resist damage and degradation at such higher temperatures. The lower yield or conversion to hydrogen at such temperatures is compensated for by the hydrogen separation through the permeable membrane which removes one of the products of the
10 decomposition and produces a higher yield in subsequent decomposition steps, when such steps are carried out. The overall yield may therefore be kept reasonably high.

 During the hydrogen separation steps, the temperature is preferably made no higher than about 800°C to avoid loss of stability of the permeable membrane. Of course, this depends on the characteristics of the separation membrane, but
15 membranes capable of resisting temperatures higher than about 800°C without loss of stability are currently not available. The temperature is preferably kept within the range of about 500 to 800°C so that some appreciable decomposition of unreacted hydrogen sulphide takes place as hydrogen separation proceeds. Most preferably, the temperature is kept within the range of about 550 to 650°C, and generally at about
20 600°C.

 The hydrogen separation may be carried out in the absence or presence of a catalyst for accelerating decomposition of hydrogen sulphide to hydrogen and sulphur. The use of a catalyst is preferred so that equilibrium is reached quickly and the yield may be increased above that expected for the temperature because of the
25 removal of hydrogen.

 The decomposition reactions carried out at temperatures up to about 1000°C are also preferably conducted in the presence of a catalyst for accelerating decomposition of hydrogen sulphide to hydrogen and sulphur. The decomposition reactions are preferably carried out adiabatically (without heat input or removal) and
30 thus experience some temperature reduction during reaction in view of its endothermic nature. However, if the reaction is carried out in a vessel (heat exchanger reactor) located within a Claus furnace, additional heat may be supplied as

the reaction proceeds.

The decomposition and hydrogen removal steps are normally carried out a pressure in the range of about 1 to 10 atmospheres, although higher or lower pressures may be selected, if desired. Low pressures favour the decomposition reaction, but
5 may make hydrogen separation less efficient. An optimal pressure may therefore be selected, e.g. from within the above range. The pressure may also be increased downstream of the reactor but upstream of the membrane separator to optimize the main thermal reaction.

Following an initial start-up period, the residual unreacted hydrogen sulphide
10 (i.e. that remaining after all of the decomposition reactions and hydrogen separation steps, if more than one, have been carried out) may be used as the only (sole) hydrogen sulphide fuel for the thermal step of the Claus process. This is possible if sufficient residual unreacted hydrogen sulphide remains in the final residual gas to provide the necessary heat for the decomposition reactions and for the operation of
15 the Claus process. If the residual hydrogen sulphide is insufficient for this, it may be supplemented by diverting part of the feedstock gas directly to the Claus furnace. During start-up, such diversion is necessary to raise the temperatures of the apparatus and reactants to the operating range.

The burning of the hydrogen sulphide in the final gas stream is preferably
20 carried out in accordance with the Claus reaction so that sulphur can be recovered in subsequent steps. That is to say, the residual hydrogen sulphide is burned with a sub-stoichiometric quantity of oxygen to produce sulphur dioxide but with residual unreacted hydrogen sulphide, and, following cooling of these gases, the sulphur dioxide and hydrogen sulphide are reacted together in the presence of a catalyst to
25 produce sulphur and water. When these further steps are carried out, the products of the overall reactions are hydrogen, sulphur and water. This contrasts with the Claus process itself in which hydrogen sulphide is converted only to sulphur and water. The hydrogen thus produced may be collected and used for well-known purposes, such as hydrocracking of hydrocarbons.

30 Most preferably, after an initial period of start-up, the hydrogen sulphide from the final gas stream remaining after the final hydrogen separation is used as the sole source of heat for the two or more heating steps. This is possible because the amounts

of hydrogen sulphide thermally decomposed in the two or more heating steps are generally no higher than about 40% because the use of extremely high temperatures is avoided, so sufficient hydrogen sulphide remains in the final gas flow to generate heat for the heating steps and for the preferred further conversion of the products of combustion to sulphur and water. During the start-up period, when temperatures have to be raised to the operational levels, the feedstock gas is preferably divided into two parts. A first part is used for direct combustion to generate heat for the two or more heating steps, and a second part is subjected to the heating and hydrogen removal steps. After the start-up period (i.e. when the apparatus has reached stable operational temperatures), the separation of the feedstock gas into two parts may be terminated, so that all of the feedstock gas is subjected to the heating and hydrogen removal steps, and then proceeds to combustion. However, in cases where it is necessary to maintain a suitable supply of heat, the division of the feedstock gas after the period of start-up may be continued, but with a reduced amount of gas going to the first part. For example, during the start-up period, the first part of the feedstock gas (used for direct combustion) may amount to up to 80% by volume of the feedstock gas flow, with the second part (used for hydrogen production and eventual combustion) making up the remainder. More preferably, the start-up ratio is about 75% for the first part and about 25% for the second part. After the start-up period, the proportion of gas used for the first part (direct combustion) is reduced to zero or a low value necessary for sufficient heat generation (e.g. up to, and including, 50%, 40%, 30%, 20%, 10% or 5%). The actual amount retained for the first part depends on such considerations as the content of hydrogen sulphide in the feedstock gas (a higher percentage reduces the need for direct combustion), the number of heating and hydrogen removal steps, the efficiency of hydrogen sulphide combustion, etc.

The method may be carried out by modifying existing Claus apparatus, or by constructing new apparatus. Claus apparatus is often located within a heavy oil treatment facility, so the method of the invention lends itself to the production of hydrogen in such a facility where hydrogen is required for hydrocracking and other processes.

Another exemplary embodiment of the invention provides a method of generating hydrogen and sulphur from waste gas containing hydrogen sulphide, e.g.

so-called acid gas obtained from amine stripping in treatments for removing sulphur from hydrocarbons. The method involves on a start up dividing the waste gas into a first stream and a second stream, and feeding the first stream to a burner of a hydrogen sulphide combustion furnace, and feeding the second stream to a first heat
5 exchanger positioned in the furnace to receive heat from the burner to raise the temperature of the second stream to at least 900°C and to convert thermally some of the hydrogen sulphide to sulphur and hydrogen. The second stream is then quickly cooled to minimize reverse reaction between hydrogen and sulphur and passed through a membrane reactor at a temperature of 500 to 600°C to convert more of the
10 hydrogen sulphide to sulphur and hydrogen while removing at least some hydrogen through a hydrogen-permeable wall of the membrane to leave a retentate gas of depleted hydrogen content. The retentate gas is then fed to a second heat exchanger positioned in the furnace to heat the retentate gas to a temperature of at least 900°C and to convert thermally more of the hydrogen sulfide to hydrogen and sulphur to
15 produce a gas stream of reduced hydrogen sulphide content. This stream is again quickly cooled to minimize reverse reaction between hydrogen and sulphur and then hydrogen and sulphur are removed from the cooled gas stream of reduced hydrogen sulphide content, leaving a retentate gas stream containing unreacted hydrogen sulphide. The retentate gas stream is then replacing the first stream and is directed to
20 the burner of the furnace for combustion of the unreacted hydrogen sulphide therein. The combustion products are then treated for conversion to sulphur and water.

The exemplary embodiments make it possible to increase the hydrogen production from H_2S decomposition by using a new reactor architecture assisted by membrane where high temperature is preferably achieved in the catalytic reactors
25 and lower temperature in the membrane separator/reactors.

The use of a reactor that employs a membrane permeable to hydrogen makes it possible to shift the reaction towards the products and to improve the hydrogen production.

The operating temperature in the high temperature catalytic reactors may be at
30 least 900 °C and, at this temperature, the equilibrium value for the selected feed is 25%. The exemplary embodiments make it possible, at least on theoretical calculations, to increase the conversion from 25% to

- close to 40% for a higher flow in the membrane reactor shell of 1 L(STP)/min and a high H₂ membrane permeance of 8 cm³(STP)≅cm⁻²≅min⁻¹≅atm⁻¹;
- to about 39% for a flow of 0.5 L/m in the shell and a high membrane permeance of 8 cm³(STP)≅cm⁻²≅min⁻¹≅atm⁻¹; and
- 5 • to about 38% for a flow in the shell of 0.5 l/min and a H₂ membrane permeance of 5 cm³(STP)≅cm⁻²≅min⁻¹≅atm⁻¹.

It is also preferable to provide a catalyst inside the membrane reactor and to operate the reactor at about 600 °C. At this temperature, an equilibrium value for the decomposition reaction is about 4%. If the equilibrium is reached inside the
10 membrane reactor containing the catalyst, an additional shift toward the products will be expected because of the removal of hydrogen.

BRIEF DESCRIPTION OF THE DRAWINGS

Exemplary embodiments of the invention are described in the following with
15 reference to the accompanying drawings, in which:

Fig. 1A is a diagram showing apparatus and method steps for carrying out a first exemplary embodiment of the invention;

Fig. 1B is a diagram showing part of the apparatus of Fig. 1A, but with an example of additional apparatus provided for sulphur removal at an intermediate
20 stage;

Fig. 2 is a schematic diagram showing part of the apparatus of Fig. 1A in greater detail;

Fig. 3 is a graph showing the equilibrium conversion for H₂S as a function of temperature for a mixture containing 10 vol.% of H₂S;

25 **Fig. 4** is a graph showing the partial al pressure effect on equilibrium, calculated using Gaseq (Chemical equilibrium in perfect gases, Version 0.79);

Fig. 5 is a graph showing the dependence of the conversion of H₂S on the presence of H₂ or S₂ in a feed mixture at 900°C, calculated using Gaseq® (Chemical equilibrium in perfect gases, Version 0.79);

30 **Fig. 6** is a graph showing the activities of various catalysts at different GHSV values for 10% by volume of hydrogen in nitrogen;

Fig. 7 is a schematic diagram illustrating a high temperature reactor scheme;

Fig. 8 is a schematic diagram illustrating a combination of high temperature reactors and a membrane reactor;

Fig. 9 is a graph showing the decrease in H_2S conversion due to the presence of H_2 presence in a second high temperature reactor at $900^\circ C$, wherein the percentage of hydrogen sulphide is 7.5%;

Fig. 10 is a schematic diagram illustrating a membrane reactor scheme, wherein 1, 3 are tube side streams 2,4 are shell side streams;

Fig. 11 is a graph showing how much hydrogen is removed with changing rates of flow of gases through a membrane reactor; the parameters were:

Permeance $H_2 = 8 \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{min} \cdot \text{atm}$

Permeance ratio $H_2/H_2S = 100$

Permeance ratio $H_2/N_2 = 100$

Permeance ratio $H_2/\text{Air} = 100$

$Q_{\text{shell}} = 250 \text{ ml/min}$ (where Q_{shell} means gas flow through the shell);

Fig. 12 is a graph showing how much hydrogen is removed from a membrane reactor at different rates of gas flow through the shell; the parameters were:

Permeance $H_2 = 8 \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{min} \cdot \text{atm}$

Permeance ratio $H_2/H_2S = 100$

Permeance ratio $H_2/N_2 = 100$

Permeance ratio $H_2/\text{Air} = 100$

$Q_{\text{tube}} = 250 \text{ ml/min}$ (where Q_{tube} means gas flow through the tube);

Fig. 13 is a schematic diagram of a reaction scheme involving two high temperature reactors and a membrane reactor;

Fig. 14 is a graph showing the total conversion available at different shell flow rates with a flow of 250 ml/min in the tube side of the membrane reactor; the parameters were:

Permeance $= 8 \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{min} \cdot \text{atm}$

Permeance ratio $H_2/H_2S = 100$

Permeance ratio $H_2/N_2 = 100$

Permeance ratio $H_2/\text{Air} = 100$

$Q_{\text{tube}} = 250 \text{ ml/min}$;

Fig. 15 is a schematic diagram of a membrane reactor scheme;

Fig. 16 is a graph showing the amount of hydrogen removed in a membrane reactor at various values of hydrogen permeance; the parameters were:

Permeance ratio $H_2/H_2S = 100$

Permeance ratio $H_2/N_2 = 100$

5 Permeance ratio $H_2/Air = 100$

$Q_{tube} = 250$ ml/min

$Q_{shell} = 500$ ml/min; and

Fig. 17 is a graph showing the total conversion of hydrogen sulphide in a plant having a membrane reactor at different values of hydrogen permeance; the parameters

10 were:

Permeance ratio $H_2/H_2S = 100$

Permeance ratio $H_2/N_2 = 100$

Permeance ratio $H_2/Air = 100$

$Q_{tube} = 250$ ml/min

15 $Q_{shell} = 500$ ml/min.

DETAILED DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

An exemplary embodiment of the above method and an illustration of suitable apparatus 10 is shown schematically in the diagram of Fig. 1A. At the start-up of the apparatus, an acid gas (sour gas) feed 11 preferably containing at least 20% by volume of H_2S is divided at a variable directional valve 12 into a first feed gas part fed through pipe 14 and a second feed gas part fed through pipe 15. Pipe 14 leads directly to a burner 16 of an enclosed Claus furnace 17 for combustion represented by the flame symbol to generate heat. Pipe 15 carrying the second part of the sour gas stream leads first to a heat exchanger 18 for preheating by exchange of heat with a retentate gas from a membrane reactor 19 (described later) of a second conversion module 20 of the apparatus as indicated in broken lines. The preheated second feed gas part then passes through a second heat exchanger 21 to pick up further heat, this time from a reaction gas stream exiting a catalytic reactor 42 of the second conversion module 20. The further heated second feed gas part then passes through a heat exchanger 22, preferably in the form of one or more ceramic tubes, positioned within the Claus furnace 17 so that gas is heated to an elevated temperature, preferably in the

range of 900 to 1000°C, required for the H₂S decomposition reaction to take place with a moderate degree of conversion to hydrogen and sulphur, and from there to a reactor 23 containing a packed catalyst bed effective to accelerate the H₂S decomposition reaction. The reactor 23 is positioned in a first module 30 of the apparatus, although it should be understood that the term "module" may merely relate to a notional grouping together certain parts of the apparatus that function together during one stage or other of the reaction, rather than a collective physical assembly or unit (although the parts may form such a unit, if desired). In the reactor 23 of the first module 30, the hydrogen sulphide is partially converted into hydrogen and sulphur within a short residence time. Once the reaction gas leaves the catalytic reactor 23, it is quickly quenched to a lower temperature, e.g. below 700°C, at which temperature the rate of back conversion is quite low. This quenching may be carried out in heat exchanger 24 where heat is exchanged with retentate gas from a membrane reactor 25 used as a hydrogen separation device as described below. The reactants from high temperature reactor 23 are then increased in pressure by operation of a compressor 26, if desired, and the compressed gas is fed, preferably at a temperature in the range of 500 to 600°C, into the membrane reactor 25 provided with a gas permeable membrane that is permeable to and selective for hydrogen. The reactor 25 also has an outer shell (not shown) enclosing the exterior of the membrane, preferably provided in the form of numerous parallel tubes through which the gas flows. The exterior of the permeable membrane is swept with steam flowing through the shell from a steam supply 28 via pipes 29 and 31. The steam sweeps away hydrogen from the exterior of the permeable membrane and removes the hydrogen from the reaction zone. The hydrogen and steam mixture exits the shell of the membrane reactor 25 via pipe 32 and is fed via pipe 33 to a water-cooled condenser 35 which condenses the steam and leaves hydrogen in gaseous form. The gaseous hydrogen is collected in vessel 36 and the condensed water exits the condenser via pipe 37. Alternatively, instead of using steam to sweep hydrogen from the outside of the permeable membrane, the permeating hydrogen may be removed by lowering the pressure of the shell side of the membrane reactor by pumping out air and collecting the hydrogen gas. A pressure differential across the membrane favours the permeation of hydrogen.

The high temperature reactor 23 and membrane reactor 25 form the main components of the first conversion module 30 for conversion of H_2S to H_2 and S_2 , with removal and collection of the hydrogen component. The retentate gas from the membrane reactor 25, referred to here as the first retentate gas, contains unreacted hydrogen sulphide and small amounts of hydrogen that were not separated in the membrane separator as well as sulphur. The first retentate gas exits via pipe 38 and is fed to the heat exchanger 24, as previously noted, where it is preheated and, from there, to a second heat exchanger 40 positioned within the Claus furnace 17. Heat from the Claus burner 16 elevates the temperature of the gas for a second time, preferably to the range of 900 to 1000°C and the heated gas is then fed via pipe 41 to a second catalytic reactor 42 in the second conversion module 20. The second catalytic reactor 42 is similar to the first reactor 23 and contains a catalyst for the H_2S decomposition reaction. The hydrogen sulphide remaining in the first retentate gas from the reaction in the first conversion module 30 is partially converted in the catalytic reactor to hydrogen and sulphur. The reaction gases exit the catalytic reactor 42 via pipe 44 and are quickly quenched in heat exchanger 21 where, as noted earlier, heat is exchanged with the second part of the feedstock stream from pipe 14. The cooled reaction products are compressed by compressor 46 and are fed into a second membrane reactor 19 having, as in the case of membrane reactor 25, a permeable membrane that is porous to and selective for hydrogen, and an encircling shell (not shown) that receives a stream of steam from supply 28 via pipe 29 and pipe 47. Once again, the temperature of the gas in the second membrane reactor is preferably in the range of 500 to 600°C. As in the previous case, hydrogen penetrates the porous membrane and is swept away from the reaction zone by the flow of steam. The hydrogen and steam mixture exits the separator via pipe 48 and joins the mixture from membrane reactor 25 for delivery to the condenser 35 where there is separation into hydrogen and water as previously explained. The retentate gas from the membrane reactor 19, referred to here as the second retentate gas, contains unconverted hydrogen sulphide, sulphur and a small proportion of unremoved hydrogen. The second retentate gas exits the membrane reactor 19 and passes through heat exchanger 18 where it exchanges heat with the second part of the feedstock gas as previously

explained. The reactor 42 and membrane separator 19 form the main parts of the second conversion module 20 indicated by the dotted lines.

The cooled second retentate gas then proceeds to a separation apparatus 50 for the removal of sulphur, which is then delivered in liquid form through pipe 49 to collector vessel 51. The residual gas exiting the sulphur separator 50 contains unreacted H_2S and a small proportion of unremoved hydrogen, and this gas is fed via pipe 52 and pump 53 to the burner 16 of the Claus furnace 17 via pipe 14. As already noted, during the start-up operation, the valve 12 is positioned to divide the feedstock gas stream into first and second parts, with a first part being delivered directly to the Claus furnace 16 via pipe 14. Consequently, the first feedstock part and the residual gas from the second feedstock part are combined in pipe 14 for delivery to the Claus furnace 17.

After start-up, i.e. when the reactors and other equipment have reached steady operational temperatures, the valve 12 may be repositioned manually or automatically to reduce the amount of gas delivered through pipe 14 as the first part of the feedstock gas and, indeed, the first part may be entirely shut off by completely closing the valve for communication with pipe 14. This reduction or elimination of the first part is possible because the amount of hydrogen sulphide remaining unconverted in the final gas stream fed to the Claus furnace 17 through pipes 52 and 14 is generally sufficient to produce enough heat in the furnace to heat the gas in exchangers 22 and 40 to the required elevated temperatures and to allow for proper completion of the Claus process downstream of the furnace 17 (as will be described later). If the amount of unconverted hydrogen sulphide remaining in the second part of the feedstock gas is insufficient for this, the valve 12 may be positioned to reduce, but not entirely eliminate, the first part of the gas feedstock fed to pipe 14 after start-up. The amount of reduction may be based on outputs from temperature sensors (not shown) positioned at strategic points in the apparatus to check that effective temperatures are being maintained. The positioning and operation of such temperature sensors and the necessary adjustments may be carried out manually or automatically according to predetermined specifications. Generally speaking, lower temperatures in the catalytic reactors 23 and 42 and the membrane reactors 19 and 25 will lead to lower conversions of hydrogen sulphide to sulphur and hydrogen, and thus to increased

amounts of residual hydrogen sulphide in the final gas flow fed to the Claus furnace 17, thereby reducing the need for additional H₂S fuel from the first part of the gas feedstock fed directly to the furnace 17. To some extent, therefore, there is a tradeoff between greater hydrogen production when using higher conversion temperatures and
5 lower hydrogen production because of the need to divert some of the feedstock gas directly to the Claus furnace 17 for generation of those higher temperatures. With feedstock gases containing more than 20%, and preferably more than 25% by volume of hydrogen sulphide, and temperatures of 900 - 1,000°C in the reactors and temperatures of 500 - 600°C in the membrane reactors, it is generally possible to
10 circulate all of the feedstock gas through pipe 15 (i.e. so that the second gas part comprises 100% of the gas flow) after start-up, and to achieve up to about 40% or more of conversion of hydrogen sulphide to hydrogen.

Of course, should there be times when no hydrogen is needed, the second part of the feedstock gas may be shut off by valve 12 so that all of the feedstock gas goes
15 directly to the Claus furnace 17 for eventual conversion to sulphur and water.

In the Claus furnace 17, the burner 16 is fed with air or oxygen from a supply 54 via pipe 55 and the products of the H₂S combustion exit via pipe 56 and are thereby delivered to a remainder of a Claus plant 57 for the recovery of sulphur in vessel 58. This operation is described in more detail below with reference to Fig. 2 of
20 the accompanying drawings. In this exemplary embodiment, the furnace of the Claus reaction is used as a non-polluting source of heat for partial hydrogen sulphide decomposition, thereby avoiding the need for additional energy expenditure for the decomposition reaction and associated pollution.

If desired, one or both of the membrane reactors 19 and 25 may be packed
25 with a catalyst for the separation reaction. Although the reaction temperature within these membrane reactors is kept fairly low (e.g. in the range of 500 to 600°C), the decomposition reaction of hydrogen sulphide still takes place at these temperatures, but with relatively low conversion to hydrogen and sulphur. Nevertheless, the reaction equilibrium is shifted somewhat in favour of the decomposition products because of
30 the removal of hydrogen from the reaction zone via the permeable membrane. The optional presence of a catalyst in the membrane reactor also helps the

kinetics of the reaction for the formation of hydrogen within a reasonable residence time. Since the decomposition takes place as the hydrogen is being separated, the units 19 and 25 are referred to as "membrane reactors" rather than merely membrane separators. The use of higher gas pressures in these reactors favours the penetration of hydrogen through the membrane, but higher pressures undesirably shift the reaction equilibrium back towards the H_2S starting material. It may therefore be considered undesirable to use compressor 26 to increase the pressure of gas entering membrane reactor 25 of the first module 30. However, the gas entering the membrane reactor 19 of the second module 20 may already be at elevated pressure whether or not compressor 46 is used. Generally, an optimal pressure is employed that increases the permeation of hydrogen without disfavoring the decomposition reaction unduly.

As noted above, the temperature of the gases in the membrane reactors 19 and 25 is preferably selected to be in the range of 500 - 600°C. Higher temperatures favour the desirable decomposition of the H_2S and penetration of hydrogen through the membrane. However, many permeable membranes lose significant permeability above a certain high temperature, so such temperatures should be avoided and a maximum temperature around 600°C is considered suitable for most membranes. However, for membranes that are not deactivated by temperatures higher than 600°C, such higher temperatures may be employed in the membrane reactors, potentially up to the 1000°C maximum considered suitable for use in the catalytic reactors 23 and 42.

In the apparatus of Fig. 1A, sulphur is removed from the reaction circuit at only one location, i.e. at the condenser 50. This means that sulphur resulting from the partial decomposition of hydrogen sulphide in reactors 23 and 42 passes through the membrane reactors 25 and 19. This may be undesirable, particularly if a catalyst is present in the membrane reactors that is partially or fully deactivated upon contact with sulphur. If so, the sulphur may be removed in each reaction module before the reaction gases are fed to the membrane separators. To achieve this, it is necessary to cool the gases from the reactors to a temperature of 250°C or less (preferably 150 to 250°C), remove the condensed sulphur, and then reheat the gases to 500 - 600°C for delivery to the membrane reactors. This can be done in a modification of the apparatus as shown in Fig. 1B of the accompanying drawings. This modification is

shown for the second module 20, but may be used also for the first module 30. After leaving the second catalytic reactor 42, the reaction gases pass through heat exchanger 21 as in the apparatus of Fig. 1A, but then pass through a second heat exchanger 60 for exchange of heat with cold water passing through pipe 61. This cools the gases to about 700°C. The gases then pass through pipe 62 to a heat exchanger 63 where heat is exchanged with gases exiting a sulphur condenser 64. This cools the gases to about 250°C and from there they pass through pipe 65 to a further heat exchanger 66 where they lose further heat to cold water passing through pipe 67 and are cooled to about 150°C. At this temperature, liquid sulphur can condense in condenser 64 and exit through pipe 68 for collection in collection vessel 69. The gases remaining after the condensation of sulphur then exit the condenser 64 via heat exchanger 63 and are thereby heated (with further input from external means, if necessary) to a temperature of 600°C and are delivered through pipe 70 to compressor 46 and then to membrane reactor 19. Thus, the gases entering the membrane reactor 19 are free of sulphur but contain hydrogen for removal by the membrane. In such cases, the final sulphur condenser 50 of Fig. 1A may be omitted and the final gases fed directly to the Claus furnace 17 via pipe 52 and pump 53.

The illustrated method and apparatus is capable of achieving an acceptable conversion of H_2S to H_2 and S_2 while avoiding the use of extremely high temperatures, e.g. temperatures much above 1000°C, for the high temperature reactors and temperatures much above 600°C for the membrane reactors. This keeps capital expenditures for the plant within reasonable limits because conventional materials and apparatus may be employed. Moreover, in the above exemplary embodiment, the feedstock gas is subjected twice to a heating, quenching and hydrogen separation operations. It is found necessary to carry out two such operations in order to boost the conversion of hydrogen sulphide to hydrogen to an acceptable level. More than two of such operations may be employed, but with increasing apparatus cost and complexity, and with a possible reduction of the amount of residual hydrogen sulphide available for heat generation. Therefore just two such operations are most preferable. Tests carried out by the inventors (as detailed below) have demonstrated that about 25% of H_2S may be converted to H_2 and S_2 in the presence of a catalyst in a first reactor at a temperature of 900°C. If all the resulting hydrogen can be removed in the first

membrane reactor, and the resulting product stream is passed again to a second catalyst-containing reactor at 900°C, a theoretical conversion of 26.7% of the remaining H₂S may be attained in the second catalyst-containing reaction. The higher conversion of H₂S in the second reactor compared to the first is due to the effect of the lower concentration (and hence lower partial pressure) of H₂S in the gas introduced into the second reactor, which favours a shift in the equilibrium towards the decomposition products. If no hydrogen were to be removed between the first and second catalytic reactors, the equilibrium conversion of H₂S in the second reactor would be only 12%. In practice, the membrane reactor will not likely be 100% effective in hydrogen removal, but any amount of hydrogen removal increases the H₂S conversion in the second reactor. If the membrane reactor does indeed remove 100% of the hydrogen, a system as described above has a theoretical combined H₂S conversion rate of 43.75%, which is a rate that would require a temperature of much higher than 1000°C in a single stage conventional packed bed catalytic reactor.

Fig. 2 of the accompanying drawings is a schematic diagram showing apparatus for carrying out the remainder of the Claus process as represented by boxes 57 and 58 in Fig. 1A. As shown, the Claus furnace 17 feeds partially combusted gases to a steam generator 75 where cold water entering via pipe 76 is converted to steam exiting via pipe 77 due to heat exchange with the hot combustion gases. This cools the combustion gases that exit through pipe 78 and enter a sulphur condenser 80 for removal of any sulphur formed during the partial combustion in the furnace 17. Liquefied sulphur exits via pipe 81 and passes through collector pipe 84 to sulphur collection vessel 58. The retentate gas exits the condenser 80 via pipe 82 and is reheated in a heat exchanger 83 before entering a catalytic reactor 85 containing a packed bed of catalyst (e.g. alumina) 86 that reacts SO₂ and unreacted H₂S from the furnace 17 to form sulphur and water. This reaction is not complete, so the reaction gases are subjected to two further reactions in catalytic reactors 85a and 85b containing catalyst beds 86a and 86b following intervening sulphur removal in condensers 80a, 80b, and 80c, and reheating in exchangers 83a and 83b. The gases are fed between these units via pipes 87, 89, 90, 92 and 94, and the condensed sulphur is removed via pipes 88, 91 and 95 to be collected and delivered via pipe 84 to the vessel 58. The gas emerging from the final condenser 80c via pipe 96 is a tail gas that

may be suitable for release to the atmosphere, or may be collected in vessel 98 for further treatment. The process produces only sulphur and water as the products of the partial SO₂ combustion.

In the exemplary embodiments shown in Figs. 1A and 1B, the gas for the catalytic reactors 23 and 42 is heated in heat exchangers 22 and 40 located within the Claus furnace 17, while the reactors themselves are located outside the furnace. Alternatively, it is possible to locate the high temperature reactors within the Claus furnace, i.e. to pack the heat exchangers themselves with catalyst, thereby combining the functions of heating the gases and conducting the decomposition reaction in the presence of a catalyst. The advantage of such an arrangement is that there is no heat loss between the heat exchangers and the catalytic reactors as they are combined in the same units. The disadvantage is that access to the reactors for catalyst replacement or other servicing is more complicated.

In the following, details of the reactants and various parts of the apparatus are provided together with a brief explanation of the Claus process.

H₂S Feedstock

The exemplary embodiments of the invention are intended primarily to treat so-called "acid gas" which is H₂S produced by hydro-treating operations of hydrocarbons to remove sulphur, followed by amine scrubbing to remove the H₂S, and then H₂S stripping from the amines. The gas may typically contain up to 80% H₂S by volume, some CO₂ contained in the hydrocarbon source material (usually up to 8%) as well as residual saturated hydrocarbons (usually up to 5%). This gas may be used directly in the method and apparatus described above. Of course, other H₂S-containing source gases and even pure H₂S if desired may be employed. The gas should preferably contain little or no oxygen to cause oxidation of the H₂S content prior to combustion. The minimum content of H₂S is preferably in the region of 20% by volume.

Catalysts

The decomposition of H₂S into H₂ and S₂ is a temperature driven (strongly endothermic) reaction that takes place without requirement for catalysts. However,

the rate of reaction at temperatures below 1000°C is fairly slow, i.e. equilibrium yields are achieved in the order of seconds. It is therefore preferred to employ catalysts for reactions carried out at such temperatures so that equilibrium yields can preferably be attained within tens of milliseconds, i.e. times consistent with
5 reasonable residence times in reactors at desirable rates of flow.

Any catalyst capable of bringing the decomposition reaction to equilibrium in a short period of time will be effective for the reaction. Suitable catalysts include, but are not limited to, MoS₂, alumina, MoS₂-alumina, sulphided Ni-Mo, sulphided Co-Mo, Ni-W oxide, WS₂, Cr₂S₃, FeS₂, CoS₂, NiS₂ and V₂S₃. As many of these catalysts
10 are sulphur-containing compounds, they are resistant to deactivation by sulphur contained in the feedstock and reactant gases. These catalysts are discussed in a publication by P.D. Clark, et al., "Production of Hydrogen and Sulphur from Hydrogen Sulfide in Refineries and Gas Processing Plants, ASRL Quarterly Bulletin, 32, No. 1, 11-28, April-June, 1995 (the disclosure of which is specifically
15 incorporated herein by this reference).

The catalysts may be packed as particles within a tubular reactor or formed into a porous structured shape or body and, if necessary, supported on a suitable high temperature resistant inert support. Optimally, the catalyst and gas should have maximum contact without unduly impeding gas flow.
20

Reactors and Heat Exchangers

As mentioned in the above description, the high temperature reactors may be separate from the Claus furnace, in which case the gas is pre-heated by passing through a heat exchanger located within the Claus furnace, or the reactors may
25 themselves be located within the Claus furnace so that the functions of heat exchanger and reactor are combined.

The elements located within the Claus furnace must be able to resist the high temperature and harsh environment present within the furnace. Generally such elements are made of high temperature ceramics, e.g. alumina. High melting metals
30 may alternatively be used, but these must be heat resistant and resistant to attack by H₂S and SO₂ at high temperature. Such metals tend to be expensive and are therefore less preferred.

For reactors positioned outside the Claus furnace, the materials must merely be resistant to high temperatures of 1000°C or more, and to the chemical environment. Conventional cast materials, such as those used in the widely practiced steam reforming technology, may be employed.

5

Membrane Reactor

Clearly, the permeable wall of the membrane reactor should have high permeance to hydrogen and low permeance to H₂S and other gases (i.e. high selectivity for hydrogen) at the intended reaction temperatures. Such membranes are often referred to as permselective membranes. Preferably, the permeance to hydrogen is 2 cm³ (STP)/(cm² per minute per atm.) or more (the higher, the better), and more preferably 4 cm³ (STP)/(cm² per minute per atm.) or more. Permeance normally increases with temperature but, as noted above, the stability of a membrane may decline significantly at temperatures higher than a certain value (e.g. due to sintering or other heat-related physical changes). In terms of selectivity for hydrogen (which is normally expressed as a ratio of permeability to hydrogen compared to that to nitrogen), it is preferable to employ a membrane having a selectivity of 100 or more (H₂/N₂ ≥ 100). High permeance and selectivity (and good stability) at a temperature of 600 – 800°C (± 100°C) is preferred.

15

In view of the temperatures involved inorganic membranes are preferred. Ceramic membranes are more attractive than metal membranes since they are normally less expensive and are chemically stable (resistant to sulphur) while providing high permeability and selectivity for hydrogen. Suitable permeable membranes may be made from such ceramic materials as alumina (Al₂O₃), titania (TiO₂), zirconia (ZrO₂) and silica (SiO₂). Silica is particularly preferred because the SiO₄ tetrahedra can be connected together in various ways to prepare a large number of different amorphous or crystallized solids which can be microporous, mesoporous or macroporous. In particular, ultra- or super-microporous amorphous thin layers are suitable for molecular sieving (i.e. separation) applications. Such membranes may be made by such methods as chemical vapour deposition (CVD) on porous glass (e.g. Vycor®) substrates, by chemical vapour infiltration techniques (CVI) or by sol-gel processes. Ultramicroporous silica membranes provide energy efficient H₂ separation

20

25

30

because of their high flux, good selectivity and relatively good stability in harsh conditions. Membranes of this kind are already known and have been experimented with for application in industrial processes involving hydrogen separation, such as steam reforming of methane, dehydrogenation of alkanes, etc. More information
5 about membranes of this kind may be obtained, for example, from *Membrane Science and Technology Series, Inorganic Membranes: Synthesis, Characterization and Applications*, Reyes Mallada and Miguel Menendez (editors), Elsevier, Volume 13, 2008, pp. 60 to 64. The disclosure of this reference is specifically incorporated herein.

10 Metal membranes may be employed as alternatives to ceramic membranes, particularly if sulphur is removed from the decomposition gases before each membrane reaction step. Palladium membranes, which are known for hydrogen separation from natural gas, may be employed and several forms are sold by Johnson Matthey, Precious Metals Marketing, of Orchard Road, Royston, Hertfordshire, SG8
15 5HE, United Kingdom.

The effectiveness a hydrogen permselective membrane having given values of hydrogen permeance and selectivity depends on the hydrogen pressure difference across the membrane (ΔP), with higher pressure differences giving increased amounts of hydrogen penetration. This guides the selection of the operating parameters for the
20 membrane reactor. Effectively, to keep ΔP at its maximum value, the partial pressure of hydrogen on the outside of the membrane should be as low as possible. Hydrogen is therefore swept from the outside surface (the reactor shell) by employing a flow of a condensable gas, such as steam, or is pumped away by a vacuum pump. If hydrogen is removed from the shell by a flow of gas, the ratio flow rate through the
25 shell should preferably be as high as practically possible in order to improve yields.

The surface area of the membrane should also be as large as possible to assure maximum penetration of H_2 . The reactor may therefore be designed in the form of numerous tubular membranes packed into a surrounding shell with the reactants fed through the tubular membranes and a non-reactive gas flowing through the shell over
30 the outer surfaces of the membranes.

Reaction Pressures

Since the number of molecules increase as H_2S decomposes to H_2 and S_2 , Le Chatelier's principle favours the use of low pressures for the decomposition reaction to move the equilibrium towards the formation of decomposition products. However, the gases have to be moved through the apparatus, so pressures above atmospheric are normally required and, moreover, the penetration of hydrogen through the permeable membrane is favoured by higher pressures. It is therefore desirable to optimize the pressures to avoid undue suppression of the decomposition reaction and to maximize the separation of hydrogen while keeping the flow rates acceptable. Generally, pressures of 1 to 10 atmospheres are employed, but this depends to some extent on the architecture of the apparatus, and higher or lower pressures may be acceptable in some cases.

Claus Process

During the treatment of natural gas or other hydrocarbons, H_2S is usually separated from the host material using amine extraction. The amines are then recovered for re-use by amine stripping and the resulting gas contains mainly H_2S and some CO_2 . The Claus process is then employed to convert the H_2S to S_2 and H_2O , as previously explained. This conversion is carried out in two distinct stages, namely a thermal step and a catalytic step. In the thermal step, part of the H_2S is oxidized with air or oxygen in a combustion furnace at high temperatures (e.g. 1000 to 1400°C). The main product is SO_2 , but some of the H_2S remains unreacted because less than stoichiometric amounts of oxygen are employed, and some elemental sulphur is formed. In the catalytic step, the remaining H_2S is reacted with the SO_2 previously produced at lower temperatures (e.g. about 200 – 350°C) over a catalyst to form sulphur and water. The reaction does not go to completion, so several reaction stages are employed, and residual amounts of H_2S in the final tail gas is often removed in a specialized tail gas treatment unit. The catalyst employed is normally Al_2O_3 having a surface area preferably in the range of 200 to 300 m^2/g .

In the thermal step, sufficient air or oxygen is typically supplied to burn about one third of the total H_2S to SO_2 . The goal is to obtain a stoichiometric ratio of H_2S to SO_2 for the conversion to sulphur in the subsequent catalytic step.

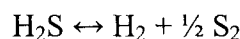
Further information about the Claus process and apparatus may be obtained, for example, from *Ullmanns Enzyklopadie der Technischen Chemie*, Verlag Chemie, 4th Edition (1982), vol. 21, pp 8 to 26 (the disclosure of which is incorporated herein by reference).

5 In the exemplary embodiments of the present invention, the thermal step of the Claus process is used as a source of heat for the decomposition of H₂S to H₂ and S₂ (a strongly endothermic reaction), and the unconverted H₂S from the decomposition reaction is used as a fuel in the thermal step, possibly the sole fuel source after start-up. Thus, the Claus process is employed both as a source of heat and as a means of
10 converting unreacted H₂S to sulphur, all without any emissions of CO₂.

EXAMPLES AND CONSIDERATIONS

Decomposition of Hydrogen Sulphide

15 H₂S decomposition is a reversible reaction controlled by thermodynamic equilibrium:



20 Figure 3 shows the thermodynamically allowable H₂S equilibrium conversion as a function of temperature (for 10 vol.% H₂S in nitrogen). The reaction is highly endothermic and at 600°C the conversion is about 4%. At temperatures of 900°C to 1000°C, the conversion ranges from about 24% to about 36%.

 As the total number of moles increases during the decomposition reaction,
25 increase of pressure has a negative effect on conversion as shown in Fig. 4.

 Since H₂S decomposition is a reversible reaction, the conversion is also negatively influenced by the presence of one or both products of its decomposition in the reaction mixture. Tables 1 and 2 below and Fig. 5 show the influence of hydrogen or sulphur presence in the mixture at 900 °C.

Table 1
Equilibrium conversion values with H₂ in feed mixture at 900 °C

NO SULPHUR	IN			conversion		OUT, <i>Sulphur free</i>		
	N ₂	H ₂ S	S ₂		Sulphur	N ₂	H ₂ S	H ₂
%	90	10	0	24.73	1.22	90.00	7.53	2.47
	87.5	10	2.5	13.46	0.67	87.50	8.65	3.85
	85	10	5	7.04	0.35	85.00	9.30	5.70
	80	10	10	2.40	0.12	80.00	9.76	10.24

5

Table 2
Equilibrium conversion values with S₂ in feed mixture at 900 °C

10

NO H ₂	IN			conversion		OUT, <i>Sulphur free</i>		
	N ₂	H ₂ S	S ₂		Sulphur	N ₂	H ₂ S	H ₂
%	90	10	0.2	23.48	1.358	89.980	7.667	2.353
	87.5	10	0.5	22.13	1.584	89.980	7.803	2.217
	85	10	0.8	20.924	1.827	89.919	7.971	2.109
	80	10	1	20.222	1.991	89.899	8.058	2.043
	88	10	2	17.48	2.849	89.796	8.420	1.784

Figure 5 shows that at up to 1 vol.% concentration, the influence of hydrogen or sulphur present in the reaction mixture on the H₂S conversion is similar. However, as the concentration increases, hydrogen has a greater effect than sulphur. Up to 7% difference in the H₂S conversions could be observed between 2 – 7 vol.% of H₂ or S₂ in the reaction mixture.

For instance, considering a feed mixture containing 10% of H₂S diluted in N₂, the 25% equilibrium conversion for pure H₂S at 900 °C could be decreased to 12% if 3% of hydrogen is present and to 15.5% for the same amount of sulphur in the mixture.

Decomposition Catalysts

Catalytic decomposition of H₂S was studied in a high temperature reactor to establish an effective catalyst and a usable range of the reaction conditions. Quartz

25

chips and four different formulations were tested that included Al_2O_3 fresh and calcined at 800°C , MoS_2 powder, and alumina supported Pt and MoS_2 between 700 - 1000°C and with a gas hourly space velocity (GHSV) in the range of 20000 - 900000 h^{-1} . The total feed flow rate was between 0.25 - 1.2 l/min and H_2S was
5 diluted in N_2 giving compositions between 5 - 100% at atmospheric pressure.

Fig. 6 shows H_2S conversions at 900°C and 800°C for the feed stream containing 10% H_2S in N_2 . The H_2S conversions with quartz chips were below 2% and they are not shown in the figure.

At 900°C $10\%\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst showed the best performance as H_2S
10 conversions were in a narrow range between 21 - 25% for a wide range of GSHV values between 5000 - 70000 h^{-1} . The lowest contact time was about 5 ms corresponding to GSHV of 700000 h^{-1} . All the other catalysts were able to bring the system to either equilibrium or nearly equilibrium but in a much narrower range of GSHV values. A practical range of GSHV values was between 5000 h^{-1} and
15 100000 h^{-1} .

At 800°C , again $10\%\text{MoS}_2/\text{Al}_2\text{O}_3$ gave the best results but equilibrium conversion was not reached. At 18000 h^{-1} GSHV (contact time of 0.2 seconds) gave conversion of 14% versus 15% required. It was verified that sintering of the catalysts did not play any role in these data.

20 The observed conversion decrease below GSHV of 5000 h^{-1} could most likely be ascribed to the efficiency of sulphur removal. Apparently for lower flows sulphur is not transported fast enough out of the reaction zone allowing reverse reaction to proceed and limiting kinetically the H_2S conversion.

In conclusion $10\%\text{MoS}_2/\text{Al}_2\text{O}_3$ at 900°C and contact time of 5 ms gave a
25 desirable 25% of H_2S conversion.

Table 3 below in conjunction with Fig. 7 summarize the concentrations of the inlet and outlet streams for the catalytic reactor. It is to be noticed that the product stream is sulphur free.

Table 3
Feed and product stream compositions for a conventional reactor, T=900°C

	%	
	IN	OUT
H ₂ S	10	7.5
N ₂	90	90
H ₂	0	2.5
S ₂	0	1.25

5

Membrane assisted catalytic H₂S decomposition: High Temperature reactors and Membrane reactor/separator (MRS)

10 Fig. 8 shows the scheme of a plant containing two high temperature reactors and a membrane separator/reactor having a hydrogen-permeable silica membrane. The impact of this arrangement and the relevant operating parameters on the H₂S conversion is analyzed.

It is theorized that the location of the MRS between the two high temperature
15 reactors allows a shift in equilibrium by selective removal of hydrogen. Moreover, if a decomposition catalyst is loaded into the membrane separator/reactor an additional gain in the H₂S conversion can be achieved.

The products of H₂S decomposition at 900°C from the first high temperature reactor are stripped of sulphur, then fed to the tube side of the membrane
20 separator/reactor. Sulphur is condensed at the exit of the first high temperature reactor minimizing a possible adverse impact on the silica membrane. A portion of hydrogen in the product stream from the first high temperature reactor is selectively permeated to the shell side of the membrane where it is recovered as a hydrogen-rich stream. The hydrogen-depleted stream exiting the tube side of the membrane,
25 containing H₂S, N₂ and H₂, is fed into the second high temperature reactor.

An objective of this consideration is to predict the impact of the membrane on the conversion of H₂S in the second high temperature reactor. In the above description, the impact of the H₂S reaction products on the thermodynamically allowable conversion of H₂S is assessed. Different scenarios are analyzed in relation
30 to the efficiency of hydrogen removal in the membrane separator/reactor and sulphur stripping.

It was experimentally shown that 25% of H_2S was converted in the first high temperature reactor when a feed of 10% of H_2S in N_2 was used with 10% $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst at 900°C . The resulting product stream contained 2.5% of H_2 and 7.5% H_2S . This stream would enter the membrane separator/reactor and, depending on the performance of the membrane, the stream exiting the membrane separator/reactor and entering the second high temperature reactor could have a H_2 concentration ranging from 0% as a best-case to 2.5% for a worst-case scenario. For a feed stream having 7.5% H_2S in N_2 entering the second high temperature reactor, a theoretical equilibrium conversion of H_2S is 26.7% and this could be attained if H_2 is not present in the feed mixture. It should be noted that the higher equilibrium conversion in the second high temperature reactor compared to the first high temperature reactor is due to the effect of lower concentration (7.5% vs. 10%) and hence partial pressure of H_2S . If no H_2 is removed by the membrane, and taking into account the removal of S_2 after the first high temperature reactor, the equilibrium conversion of H_2S in the second high temperature reactor will be only 12%. Therefore, depending on the hydrogen removal efficiency of the membrane, different theoretical equilibrium conversions of H_2S can be predicted for the second high temperature reactor as shown in Figure 9.

If the membrane removes all the H_2 produced in the first high temperature reactor, the plant containing the two high temperature reactors and the membrane separator/reactor would give a net combined H_2S conversion of 43.75%.

Evaluation of membrane separator/reactor performance

It is assumed that total flow needed for effective high temperature reactor operation is 250 ml/min to assure good sulphur transport from the reaction zone and allowed good pressure control inside the high temperature reactor. The composition for the inlet flow to the tube side of the membrane separator/reactor (product stream from the first high temperature reactor) is given in Table 5 below. Typical membrane operating characteristics for 500°C are given in Table 4 and the scheme of membrane separator/reactor is shown in Fig. 10. Microsoft Excel Solver was used to estimate the impact of different flow ratios in the MRS on the composition of the exit stream. The results are listed in Tables 6 to 9 below.

It should be noted that membranes giving higher H_2/N_2 permeance ratios than that given in Table 4, which may be desirable, will correspondingly have lower permeance for H_2 . A typical H_2 permeance for membranes having a H_2/N_2 permeance ratio of approximately 400 would be in the range of 4 to 5 $cm^3(STP)/(cm^2$ per min per atm). It should also be noted that H_2 permeance at 600°C, which is the intended temperature of operation, is typically higher than at 500°C.

Table 4
Membrane Parameters

Permeance H_2	8	$cm^3(STP)/(cm^2 \cdot min \cdot atm)$
Permeance ratio H_2/H_2S	100	
Permeance ratio H_2/N_2	100	
Permeance ratio H_2/Ar	100	
Membrane length	12	cm
Membrane o.d.	1	cm
Membrane area	38	cm^2

Table 5
Composition of the inlet flow to the membrane

	%	
	1	2
H_2S	7.5	0
N_2	90	0
H_2	2.5	0
Ar	0	100

Table 6
Stream composition at the exit of the MRS
at high sweep flow

Tube = 250 ml/min	%	
Shell = 250 ml/min	3	4
H_2S	7.5	0.1
N_2	89.9	1.1
H_2	1.4	1.1
Ar	1.2	97.7

Table 7
Stream composition at the exit of the MRS
at low sweep and low tube flow

Tube = 100 ml/min	%	
Shell = 100 ml/min	3	4
H ₂ S	7.4	0.2
N ₂	88.4	2.6
H ₂	1.3	1.2
Ar	2.9	96

5

Table 8
Stream composition at the exit of the MRS
at low sweep and high tube flow

Tube = 250 ml/min	%	
Shell = 100 ml/min	3	4
H ₂ S	7.5	0.2
N ₂	89.5	2.6
H ₂	1.8	1.8
Ar	1.2	95.4

10

Table 9
Stream composition at the exit of the MRS
at high sweep and low tube flow

Tube = 100 ml/min	%	
Shell = 250 ml/min	3	4
H ₂ S	7.4	0.1
N ₂	88.9	1.1
H ₂	0.7	0.7
Ar	3	98.1

15

Tables 6 and 7 report data predicted for equal gas flows in tube and shell, for high and low flow rates respectively. Tables 8 and 9 report the data predicted for different combinations of flows. It is clear that a higher ratio of the sweep flow to the flow on process side (stream 3) gave the most effective hydrogen removal as shown in Table 9. Figure 11 shows the predicted percent of H₂ removed with respect to tube flow for a fixed shell flow of 250 ml(STP)/min. Figure 12 shows the predicted

20

percent of hydrogen removed with respect to rate of sweep flow rate on the shell side for a fixed tube flow rate of 250 ml(STP)/min.

As shown in Figure 11, the percent of H₂ removed by the membrane decreases for increasing tube flow rates for a fixed shell flow rate of 250 ml(STP)/min. For example, when the tube flow rate is doubled from 100 ml(STP)/min to 200 ml(STP)/min, the percent H₂ removed by the membrane drops from 50.5% to about 33.5%. Whereas at an even lower tube flow of 75 ml(STP)/min it is possible to remove 77% of the H₂. Figure 12 shows that by increasing the shell flow from 75 ml(STP)/min to 500 ml(STP)/min, for a fixed tube flow rate of 250 ml(STP)/min, the percent of H₂ removed by the membrane increases from 23.4% to 56.2%, effectively, more than doubling the efficiency of the membrane. By increasing the shell flow from 500 ml(STP)/min to 1000 ml(STP)/min, an additional 6.5% H₂ may be removed.

Therefore, for a membrane assisted catalytic plant having an initial feed flow of 250 ml(STP)/min of flow, and a membrane having characteristics as shown in Table 4, a sweep flow rate of 500 ml(STP)/min would be required in order to reach an acceptable hydrogen removal rate, and consequently to reach an acceptable overall conversion. Table 10 shows the gas stream compositions for the membrane assisted catalytic plant for a shell sweep flow rate of 500 ml(STP)/min. The scheme of the plant is shown again in Figure 13. A total conversion of H₂S of 38.4% is predicted, and assuming a selectivity of 100% to H₂, a yield of H₂ of 38.4% is predicted.

TABLE 10
Concentration of Flows in the Plant

Tube = 250 ml/min	%, sulphur free				
Shell = 500 ml/min	1	2	3	4	5
H ₂ S	10	7.5	7.5	6.07	0.04
N ₂	90	90	90.2	90.17	0.54
H ₂	0	2.5	1.1	2.6	0.7
S ₂	0	1.2	0	0.72	0
Ar	0	0	1.2	1.21	98.72

Gas concentrations are reported sulphur free while the concentration of sulphur on the total products is also reported in bold.

Operating conditions are:

T in conventional reactor = 900 °C

Flow fed in the first catalytic reactor = 10% H₂S, 90% N₂

Conversion in first conventional reactor = 0,25

5 Conversion in second conventional reactor = 0.19

Figure 14 shows the total conversion of H₂S predicted with varying shell sweep flow rates for an initial feed flow rate of 250 ml(STP)/min.

As discussed above, the best operating conditions in the membrane reactor
 10 with a permeance value for H₂ of 8 cm³(STP)/cm²*min*atm and with tube flow of 0.250 l/m are attainable with high flow in the shell side. With a 500 ml(STP)/min sweep flow rate, it is theoretically possible to produce 55% more H₂ than with a conventional reactor. In summary, the membrane plus the second catalytic reactor makes it theoretically possible to increase the H₂S conversion from the equilibrium
 15 value at 900°C of 25% to about 39%.

Permeance dependence

The H₂ permeance shown in Table 4, which was used in the above estimations for permeance and conversion, is a “best-case” permeance for the membrane.

Membranes having lower H₂ permeances in the range of 4 to 5 ml(STP)*cm⁻²*min⁻¹*atm⁻¹ at 500°C could be produced more reproducibly. The membrane scheme
 20 is shown in Figure 15, wherein:

1, 3 are tube side streams
 2, 4 are shell side streams

25

and

1 is the outgoing flow from the first high temperature reactor: H₂ 7,5%,
 N₂ 90%, H₂ 2,5 %
 2 is Ar at 100%.

30

Using the feed composition given for stream 2 in Table 10, and using a tube flow rate of 250 ml(STP)/min and a shell sweep flow rate of 500 ml(STP)/min, the permeate (shell exit) and retentate (tube exit) stream compositions were estimated using Microsoft Excel Solver for membranes having different H₂ permeances.

35 The predicted exit stream concentrations are given in Table 11. The percentage H₂ predicted to be removed by membranes having different H₂

permeances and the corresponding overall H₂S conversions for membrane assisted catalytic conversion of H₂S are shown in Figures 16 and 17, respectively.

For a membrane having a H₂ permeance of $8 \text{ cm}^3(\text{STP}) \cong \text{cm}^{-2} \cong \text{min}^{-1} \cong \text{atm}^{-1}$, 56.2% H₂ is predicted to be removed with a corresponding membrane assisted H₂S conversion of approximately 39%. A membrane assisted H₂S conversion of 36% is
5 predicted for a membrane have a permeance of $2 \text{ cm}^3(\text{STP}) \cong \text{cm}^{-2} \cong \text{min}^{-1} \cong \text{atm}^{-1}$ and a conversion of 37.5 to 38 is predicted for the more practical range of permeance of 4 to $5 \text{ cm}^3(\text{STP}) \cong \text{cm}^{-2} \cong \text{min}^{-1} \cong \text{atm}^{-1}$.

Table 11
Flow Concentrations inlet and outlet the membrane
at different permeance values

Tube = 250 ml/min			Shell = 500 ml/min		Stream 3 (tube exit)				Stream 4 (shell exit)			
H ₂ permeance, cm ³ (STP)* cm ⁻² * min ⁻¹ * atm ⁻¹	Permeance ratio H ₂ /H ₂ S	Permeance ratio H ₂ /N ₂	Permeance ratio H ₂ /Ar		H ₂ S	N ₂	H ₂	Ar	H ₂ S	N ₂	H ₂	Ar
2	100	100	100		7.52	90.27	1.90	0.30	0.01	0.14	0.30	99.55
4	100	100	100		7.53	90.35	1.52	0.60	0.02	0.27	0.50	99.21
6	100	100	100		7.53	90.30	1.27	0.91	0.03	0.40	0.62	98.94
8	100	100	100		7.51	90.17	1.11	1.21	0.04	0.54	0.70	98.72

CLAIMS:

1. A method of producing hydrogen from a feedstock gas containing hydrogen sulphide, which method comprises partially thermally decomposing hydrogen sulphide in the feedstock gas to produce hydrogen and sulphur, and separating hydrogen from the sulphur and unreacted hydrogen sulphide, characterized in that the feedstock gas is heated to a decomposition temperature of up to about 1000°C by heat generated in a thermal step of a Claus process operating to convert hydrogen sulphide to sulphur and water, thereby producing a decomposition gas containing hydrogen, sulphur and unreacted hydrogen sulphide, followed by separating hydrogen from the decomposition gas by hydrogen permeation through a hydrogen-permeable membrane, collecting the hydrogen thereby separated, and burning residual unreacted hydrogen sulphide in said thermal step of the Claus process.
2. A process according to claim 1, characterized in that, before burning said residual unreacted hydrogen sulphide in said thermal step of the Claus process, said decomposition gas containing unreacted hydrogen sulphide is heated at least one more time to said decomposition temperature of up to about 1000°C by heat generated in said thermal step, followed each time by further separation of hydrogen by hydrogen permeation through a hydrogen-permeable membrane and collection of the separated hydrogen.
3. A process according to claim 2, characterized in that said decomposition gas containing unreacted hydrogen sulphide is heated only one more time to said decomposition temperature of up to about 1000°C, followed by said further hydrogen permeation and collection, before said residual unreacted hydrogen sulphide is burned in said thermal step of the Claus process.
4. A process according to claim 2 or claim 3, characterized in that said heating of said decomposition gas containing unreacted hydrogen sulphide said one more times to said decomposition temperature of up to about 1000°C is carried out in the

presence of a catalyst for accelerating decomposition of hydrogen sulphide to hydrogen and sulphur.

5. A process according to any one of claims 1 to 4, characterized in that said feedstock gas is heated to said decomposition temperature of up to about 1000°C in the presence of a catalyst for accelerating decomposition of hydrogen sulphide to hydrogen and sulphur.

6. A process according to any one of claims 1 to 5, characterized in that said hydrogen permeation is carried out at a temperature up to about 800°C.

7. A process according to any one of claims 1 to 6, characterized in that said hydrogen permeation is carried out at a temperature in a range of about 500 to 800°C.

8. A process according to any one of claims 1 to 7, characterized in that said hydrogen permeation is carried out at a temperature in a range of about 550 to 650°C.

9. A process according to any one of claims 1 to 8, characterized in that said hydrogen permeation is carried out in the presence of a catalyst for accelerating decomposition of hydrogen sulphide to hydrogen and sulphur.

10. A process according to any one of claims 1 to 8, characterized in that said feedstock gas is heated to a decomposition temperature in a range of 900 to 1000°C.

11. A process according to any one of claims 1 to 10, characterized in that said process is carried out at a pressure in a range of about 1 to 10 atmospheres.

12. A process according to any one of claims 1 to 11, characterized in that said heating of said feedstock gas and said separating of hydrogen are carried out adiabatically.

13. A process according to any one of claims 1 to 12, characterized in that, following an initial start-up period, said residual unreacted hydrogen sulphide is the only hydrogen sulphide used for said thermal step of the Claus process.
14. A process according to any one of claims 1 to 12, characterized in that said feedstock gas is a second part of a gas flow containing hydrogen sulphide, and a first part of said gas flow is fed directly to said thermal step of the Claus process.
15. A process according to any one of claims 1 to 14, characterized in that sulphur is separated from said residual unreacted hydrogen sulphide before said residual hydrogen sulphide is burned in said thermal step of the Claus process.
16. Apparatus for producing hydrogen from a feedstock gas containing hydrogen sulphide, which apparatus comprises a furnace for generating heat by combustion of fuel in a burner, a heat exchanger within the furnace for heating a feedstock gas comprising hydrogen sulphide passing through the heat exchanger, a reactor associated with the heat exchanger within which said hydrogen sulphide partially thermally decomposes to form a decomposition gas containing hydrogen, sulphur and unreacted hydrogen sulphide, a separation device downstream of the reactor for separating hydrogen from the decomposition gas, and a vessel for collecting the hydrogen thus separated, characterized in that the furnace forms part of a Claus apparatus used for conversion of hydrogen sulphide to sulphur and water, the hydrogen separation device is a membrane permeable to hydrogen, and said hydrogen separation device is connected to said burner of said furnace for combustion of residual unreacted hydrogen sulphide following hydrogen separation therefrom.
17. Apparatus according to claim 16, characterized in that said hydrogen separation device is connected to said burner of said furnace via at least one more combination of a heat exchanger within the furnace, a reactor for decomposition of hydrogen sulphide and a hydrogen separation device comprising a membrane permeable to hydrogen.

18. Apparatus according to claim 16 or claim 17, characterized in that said heat exchanger and said reactor form a single unit within said furnace.

19. Apparatus according to claim 16, claim 17 or claim 18, characterized in that said reactor contains a catalyst for accelerating a decomposition reaction of hydrogen sulphide to hydrogen and sulphur.

20. Apparatus according to any one of claims 16 to 19, characterized in that said separation device contains a catalyst for accelerating a decomposition reaction of hydrogen sulphide to hydrogen and sulphur.

21. Apparatus according to any one of claims 16 to 20, characterized in that a variable valve is provided upstream of said furnace for directing a first part of a feedstock gas flow directly to said burner and a second part of said gas flow to said heat exchanger, and for varying relative proportions of said first part to said second part.

1/10

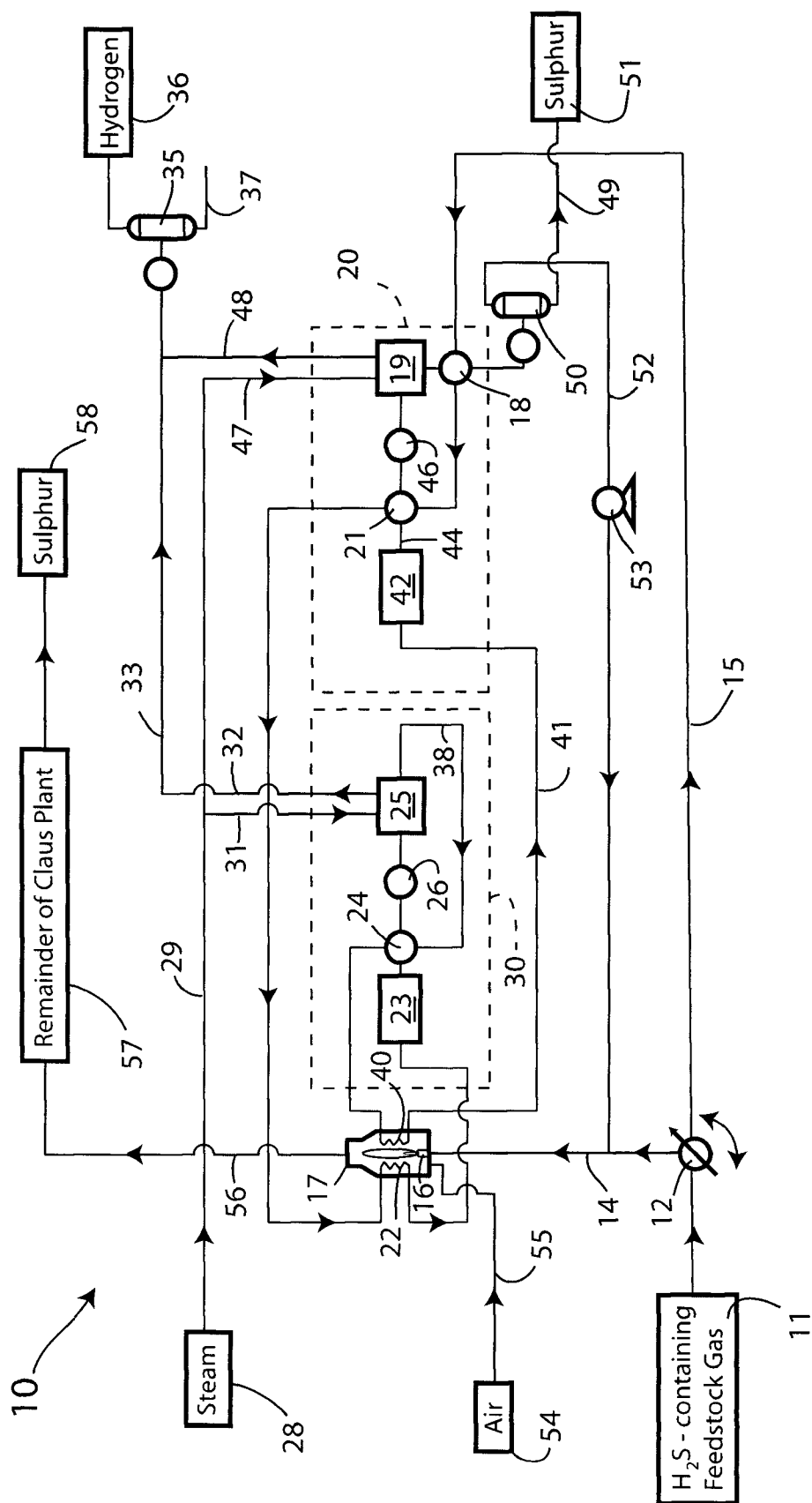
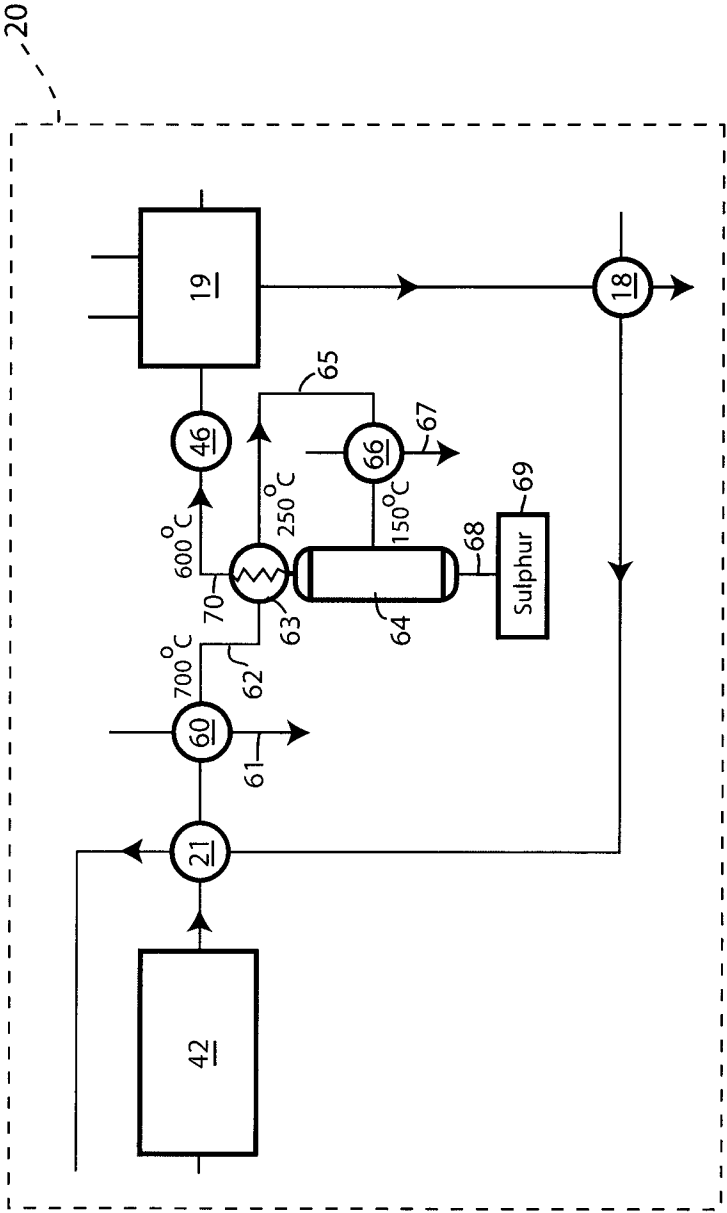


Fig. 1A

Fig. 1B



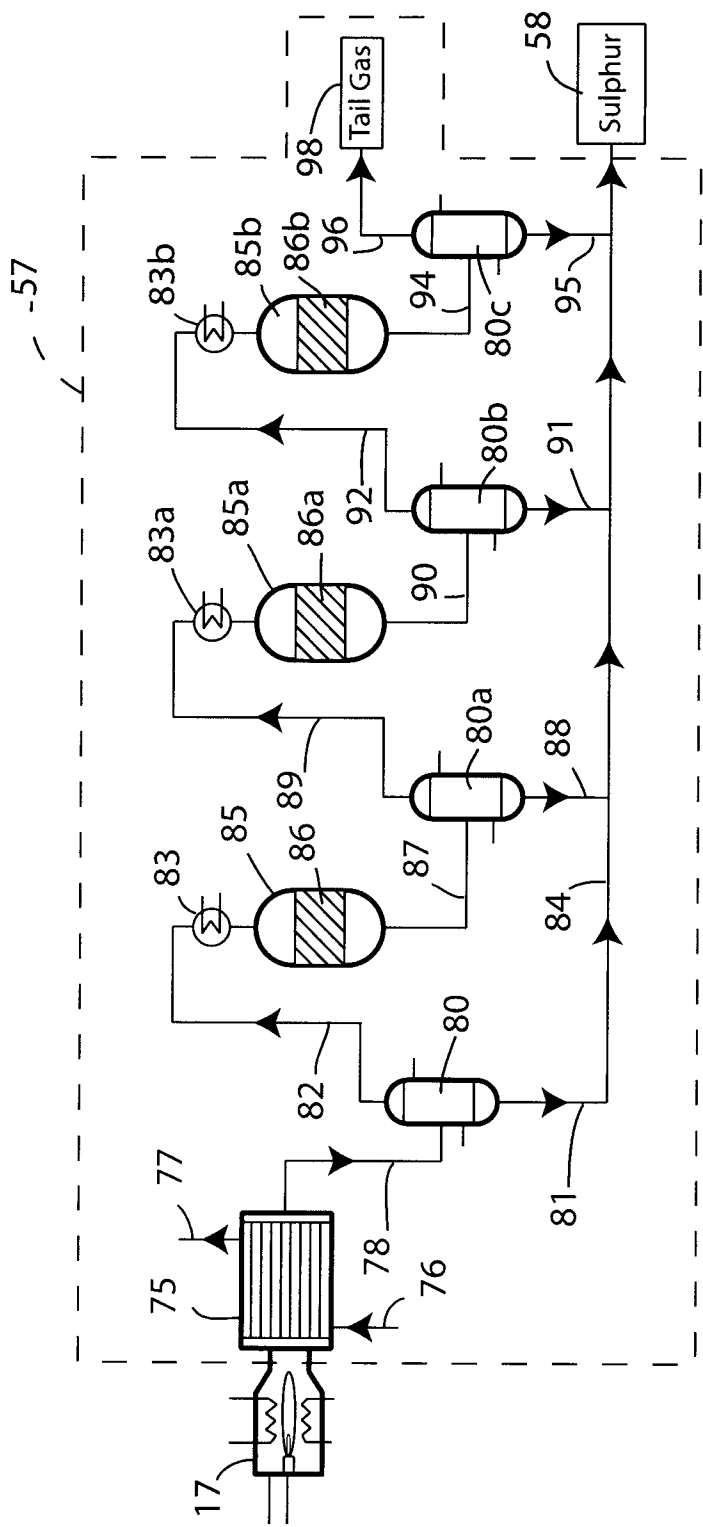


Fig. 2

4/10

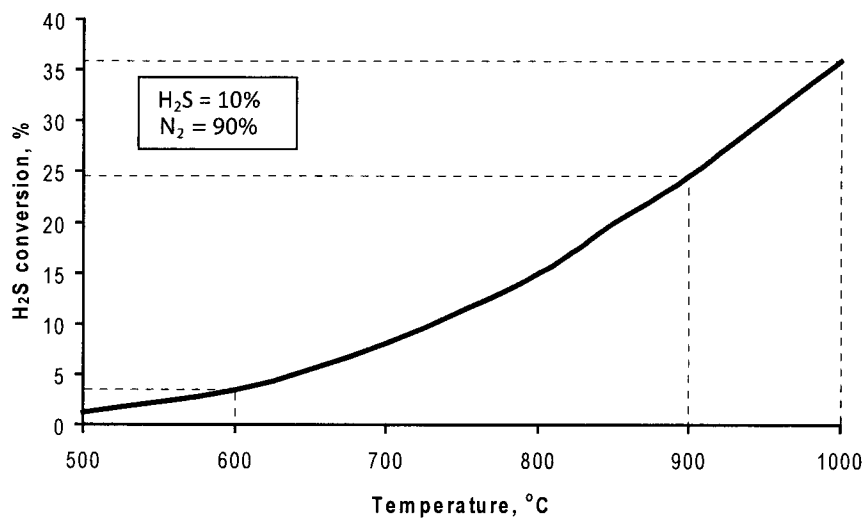


Fig. 3

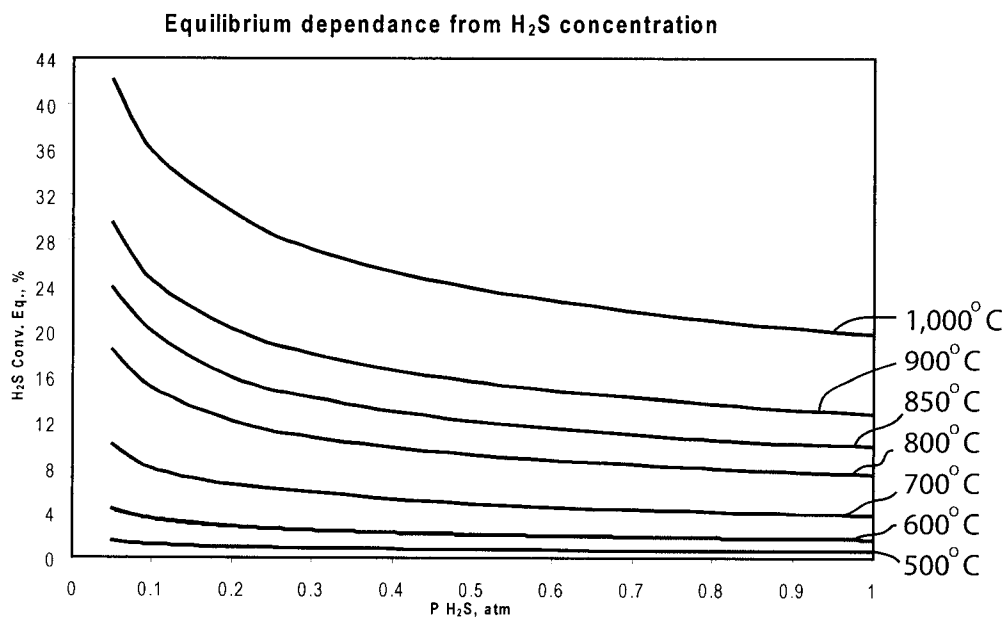


Fig. 4

5/10

Influences on H₂S conversion of H₂ and S₂ separately

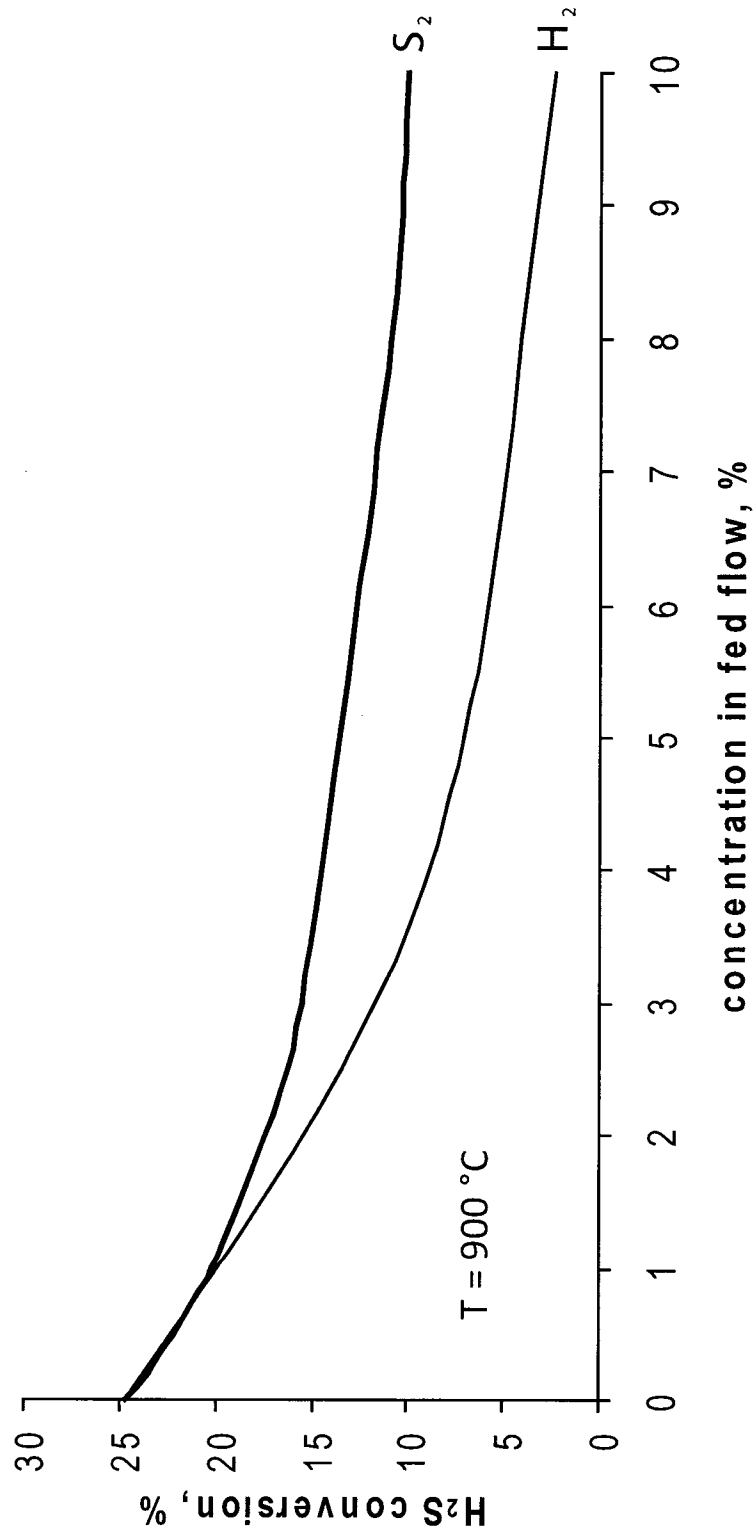


Fig. 5

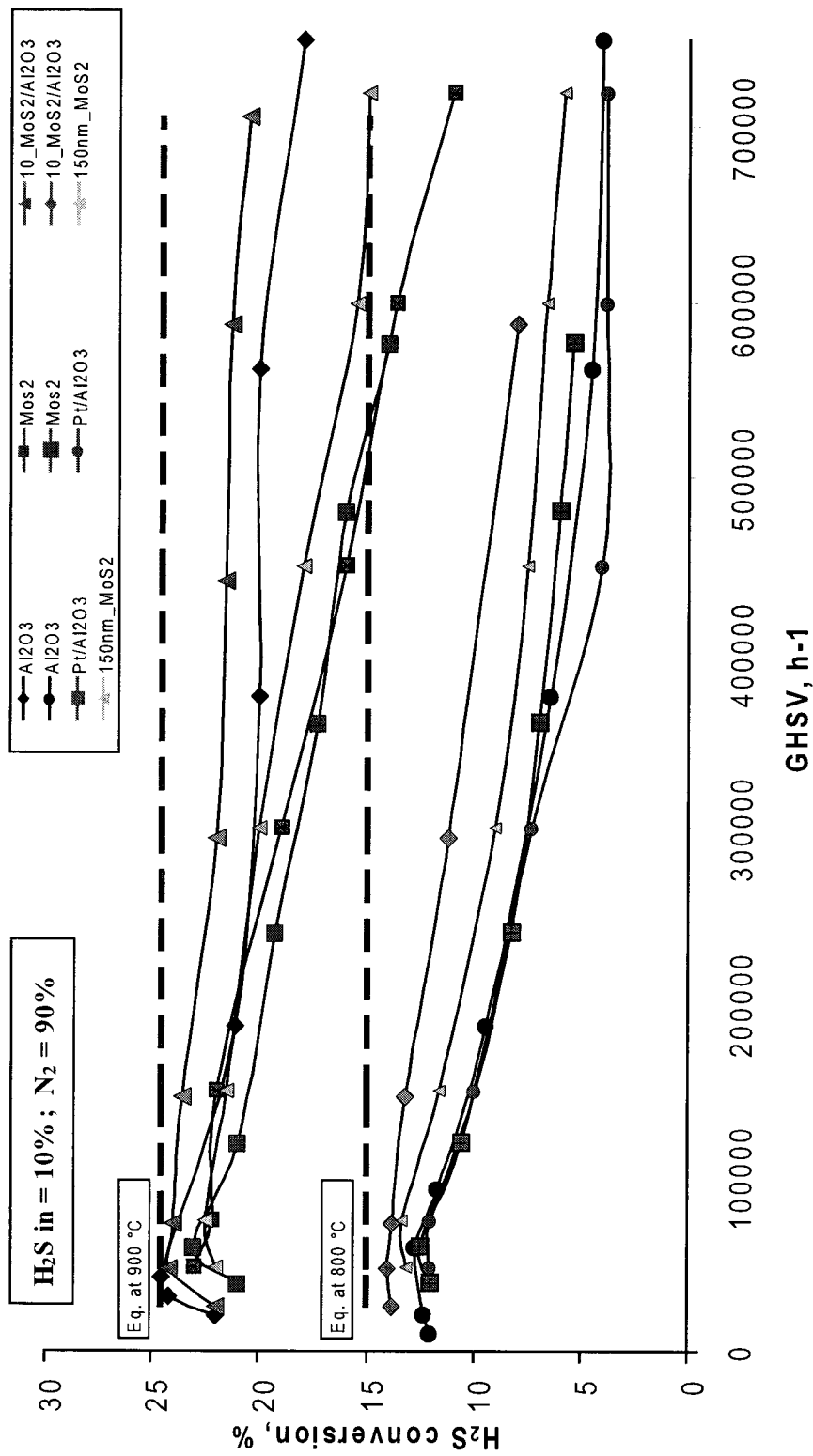


Fig.6

7/10

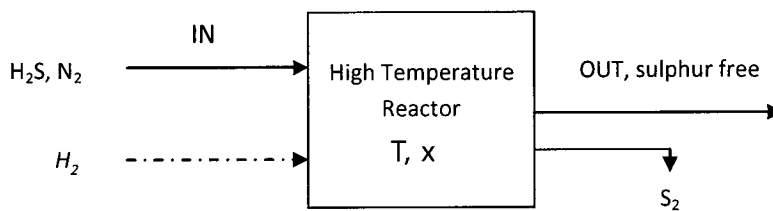


Fig. 7

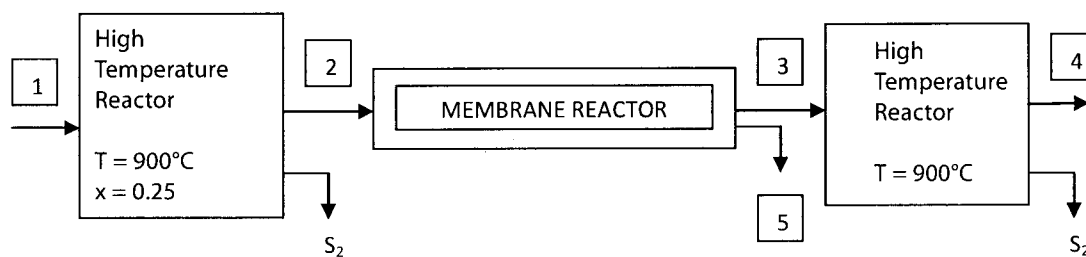


Fig. 8

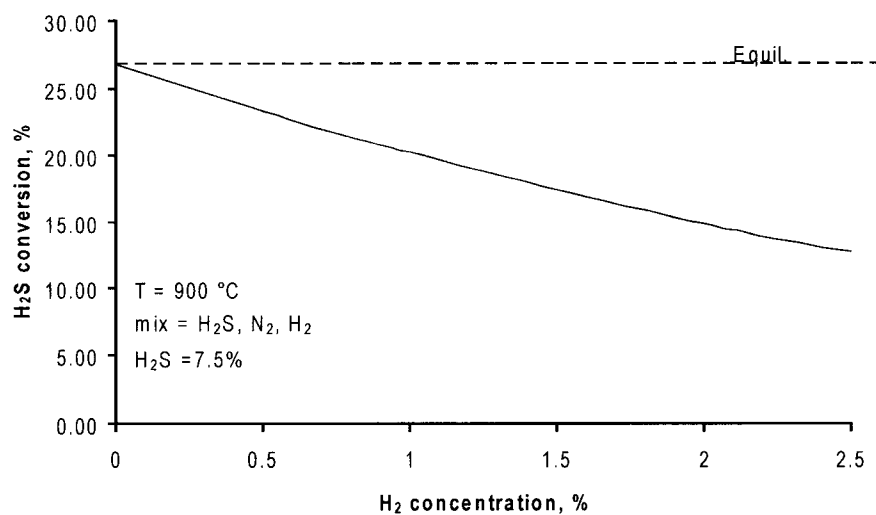


Fig. 9

8/10



Fig. 10

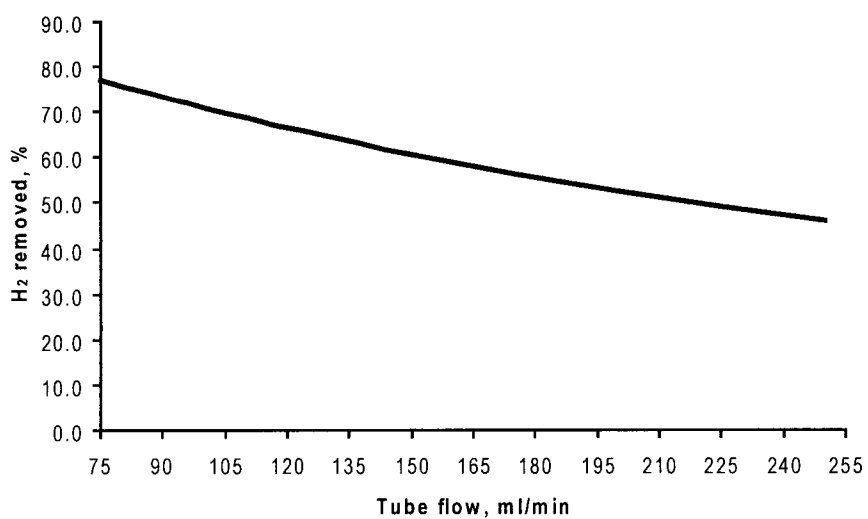


Fig. 11

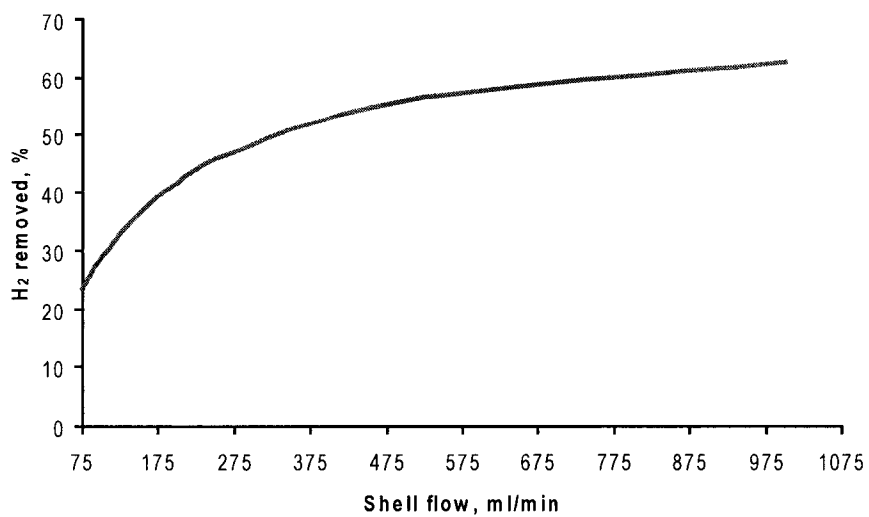


Fig. 12

9/10

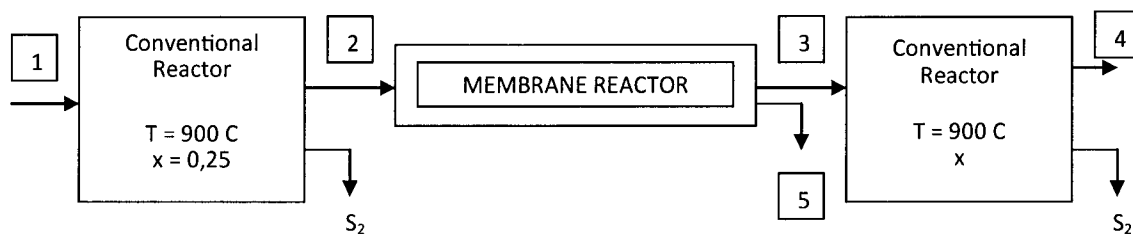


Fig. 13

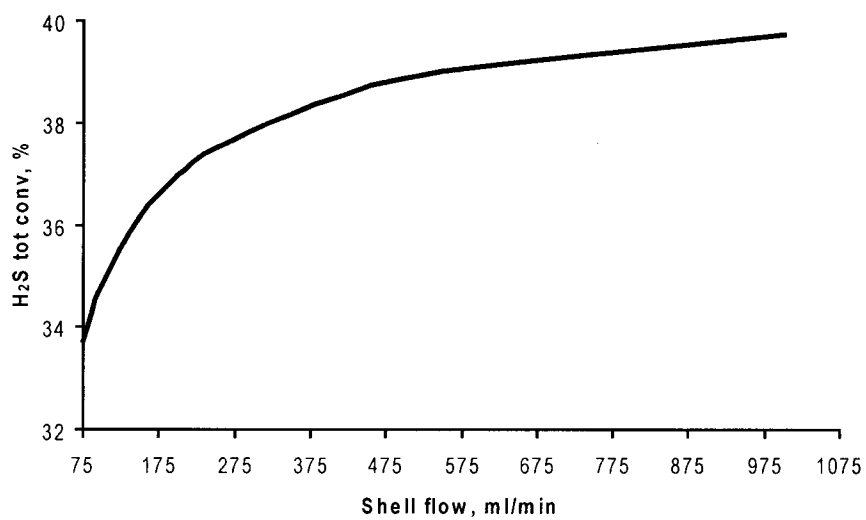


Fig. 14



Fig. 15

10/10

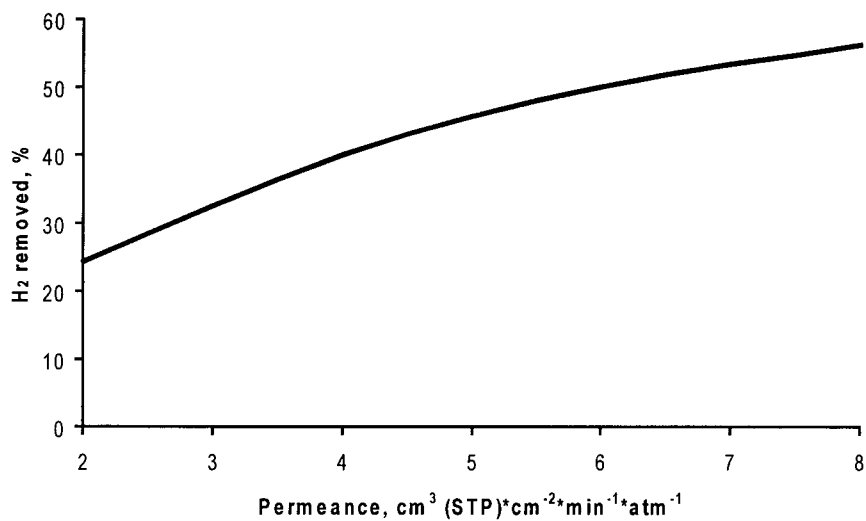


Fig. 16

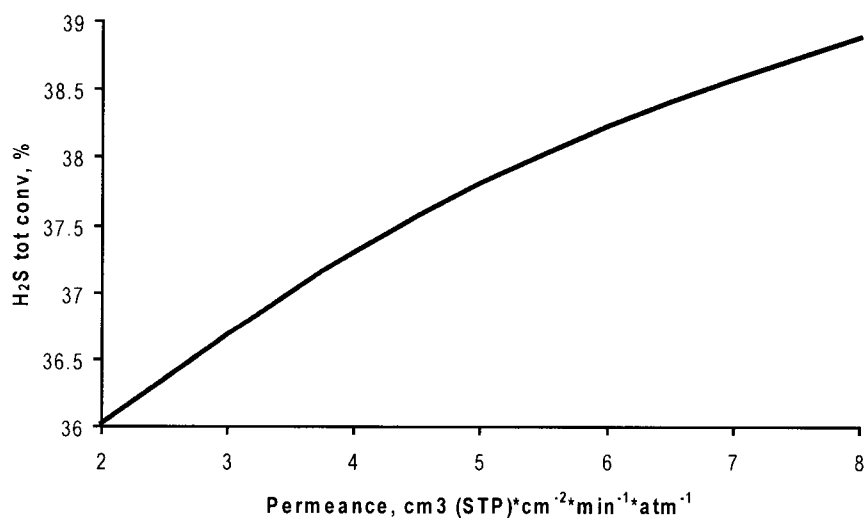


Fig. 17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2009/001562

A. CLASSIFICATION OF SUBJECT MATTER IPC: C01B 3/04 (2006.01) , C01B 3/50 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC (2006.01): C01B 3/04, C01B 3/50 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Databases: EPOQUE (Epodoc, English Full-Text), TotalPatent, Canadian Patent Database, SCOPUS Keywords: hydrogen, hydrogen sulfide, hydrogen sulphide, H2S, decompos*, dissociat*, claus, furnace, heat*, thermal, membrane, separat*		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	CLARK et al., "Production of Hydrogen and Sulfur from Hydrogen Sulfide in Refineries and Gas Processing Plants", ASRL Quarterly Bulletin, Volume XXXII, Number 1, April-June 1995, Pages 11-28.	1-8, 10-19, 21 9, 20
X A	COX et al., "Economics of thermal dissociation of H ₂ S to produce hydrogen" International Journal of Hydrogen Energy, July 1998, Volume 23, Issue 7, Pages 531-544.	1-8, 10-19, 21 9, 20
A	US 4,302,434 (HELLMER et al.) 24 November 1981 (24-11-1981) *whole document*	1-21
A	US 4,461,755 (DALEY et al.) 24 July 1984 (24-07-1984) *whole document*	1-21
A	US 4,481,181 (NORMAN) 6 November 1984 (06-11-1984) *whole document*	1-21
A	US 4,575,453 (REED) 11 March 1986 (11-03-1986) *whole document*	1-21
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 29 June 2010 (29-06-2010)	Date of mailing of the international search report 21 July 2010 (21-07-2010)	
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer Philip Gbor (819) 934-9091	

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/CA2009/001562

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/0031607 A1 (STREICHER) 13 February, 2003 (13-02-2003)	1-21

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2009/001562

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US4302434A	24-11-1981	DE2915210A1	16-10-1980
		FR2453826A1	07-11-1980
		GB2047221A	26-11-1980
		JP55140704A	04-11-1980
US4461755A	24-07-1984	CA1215820A1	30-12-1986
US4481181A	06-11-1984	US4481181A	06-11-1984
US4575453A	11-03-1986	US4575453A	11-03-1986
US2003031607A1	13-02-2003	DE10218815A1	31-10-2002
		FR2824060A1	31-10-2002
		FR2824060B1	30-05-2003
		US6780396B2	24-08-2004