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HYDROGEN PRODUCTION BY SUPERADIABATIC COMBUSTION OF HYDROGEN SULFIDE

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Abstract

In a two-phase program, the Gas Technology Institute (GTI), UOP and BP Amoco in an advisory role, and the University of Illinois at Chicago (UIC) are developing a process for the thermal decomposition of H_2S in H_2S-rich waste streams to high-purity hydrogen and elemental sulfur. The novel feature of this process is the superadiabatic combustion (SAC) of part of the H_2S in the waste stream to provide the thermal energy required for the decomposition reaction. The SAC process being developed will offer a more economical alternative to conventional technology (i.e., Claus Process) which, although it recovers elemental sulfur, wastes the more valuable hydrogen component as water.

In Phase 1, a one-dimensional numerical model has been developed for rich and ultra-rich filtration combustion of H_2S/air mixtures over a range of equivalence ratios, flow rates, and other packed bed parameters. Particular consideration is given to the optimization of hydrogen production via ultra-rich superadiabatic combustion of hydrogen sulfide. Model predictions have offered valuable guidelines for the preparation of a design and cost estimate of a suitable bench-scale reactor testing system to be assembled and tested in Phase 2 of the program. Modeling efforts also made possible the identification of key SAC process parameters and the preparation of a detailed parametric testing plan for Phase 2. The chemical kinetic mechanisms used in the formulation of this preliminary model will be updated based on direct comparison with the experimental data that will be obtained in Phase 2, further enhancing the reliability of the model.

Introduction

Hydrogen sulfide (H_2S) is present in the industrial world chiefly as an undesirable byproduct of fossil fuel processing, including natural gas, petroleum, and coal. These produce unwanted combustion products and so must be removed either from the fuel or from the combustion products. In natural gas, H_2S is the primary sulfur component, along with lower levels of hydrocarbon sulfides (mercaptans). In petroleum, H_2S appears at various stages in the refining process, and it must be removed to facilitate the production of low-sulfur liquid fuels. H_2S also appears in coal gasification and is generally removed prior to fuel gas utilization.

The conventional technologies in use to decompose H_2S (Claus, Superclaus, and variations thereof) produce elemental sulfur as a byproduct, which sells for about $30/ton. The hydrogen present in the original H_2S leaves the process as water. At the same time, hydrogen is in demand at petroleum refineries and other facilities such as ammonia synthesis plants. The value of hydrogen in these applications exceeds its fuel value, and so it may be worthwhile to recover the hydrogen as H_2 from the H_2S, if an economical and reliable process can be found to do so.

In this project, GTI, UOP and BP Amoco in an advisory role, and the University of Illinois at Chicago (UIC) are developing a process for the thermal decomposition of H_2S in H_2S-rich waste streams to high-purity hydrogen and elemental sulfur. The original conceptual layout of the SAC process is shown in Figure 1. The novel feature of this process is the superadiabatic combustion (SAC) of part of the H_2S in the waste stream to provide the thermal energy required for the decomposition reaction, as indicated by the following two reactions:

$$H_2S + \tfrac{1}{2} O_2 \rightarrow S\downarrow + H_2O; \qquad \Delta H = -94{,}800 \text{ Btu/lb-mol} \qquad (1)$$

$$H_2S \rightarrow S\downarrow + H_2 \qquad \Delta H = +8{,}877 \text{ Btu/lb-mol} \qquad (2)$$

Each molecule of H_2S reacting with oxygen can provide enough energy to dissociate up to 10 additional molecules of H_2S. While this chemistry offers an attractive way to decompose H_2S, it cannot be done using conventional burners because the adiabatic temperature is not sufficient to support the reaction kinetics. However, the SAC reactor can support this reaction because the temperature obtained at rich conditions is much higher with SAC than with conventional combustion.

Superadiabatic combustion (SAC), also known as filtration combustion, consists of combustion of a fuel gas-oxidant mixture in a porous ceramic medium with a high thermal capacity.[1] The intense heat exchange between burning gas mixture and the porous medium permits the accumulation of combustion energy in the solid matrix. As a result, the flame temperatures developed can be much higher than the adiabatic temperature for the mixture in free air. Using an H_2S-rich stream as both the fuel and hydrogen source, the high SAC flame temperature promotes rapid thermal decomposition of most of the H_2S to hydrogen and elemental sulfur.

Successful development of SAC technology for acid gas treatment in refining, natural gas sweetening, and IGCC power generation applications can result in the recovery of significant quantities of hydrogen from acid gas waste streams that would otherwise be lost as water vapor in conventional sulfur recovery processes. Recovery of hydrogen as a byproduct of sulfur

recovery offers the potential for hydrogen production at very low or even negative cost, with no additional carbon dioxide emissions to the environment. Further benefits include the elimination of sulfur recovery catalyst and chemical costs, and the cost and environmental liability of spent catalyst and chemical disposal.

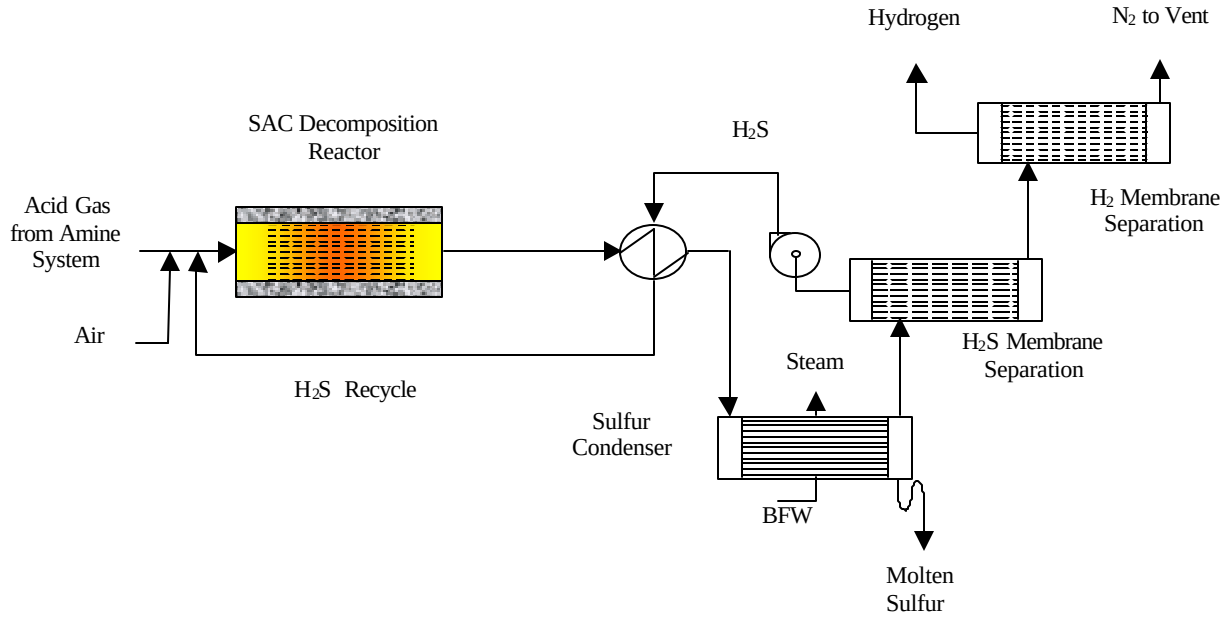

Figure 1. Conceptual Process Design for SAC-Based H_2S Decomposition/Hydrogen Recovery System

This research program is divided into two phases. In Phase 1, a one-dimensional numerical model has been developed for rich and ultra-rich filtration combustion of H_2S/air mixtures over a range of equivalence ratios, flow rates, and other packed bed parameters. Particular consideration is given to the optimization of hydrogen production via ultra-rich superadiabatic combustion of hydrogen sulfide. Model predictions have offered valuable guidelines for the preparation of a design and cost estimate of a suitable bench-scale reactor testing system to be assembled and tested in Phase 2 of the program. Modeling efforts also made possible the identification of key SAC process parameters and the preparation of a detailed parametric testing plan for Phase 2. The chemical kinetic mechanisms used in the formulation of this preliminary model will be updated based on direct comparison with the experimental data that will be obtained in Phase 2, further enhancing the reliability of the model.

Reactor Modeling

In this work filtration combustion waves in hydrogen sulfide (H_2S)/air mixtures are modeled within the one-dimensional approach, taking into account multi-step chemistry and separate energy equations for the gas and solid phases. The superadiabatic wave propagation is a complex phenomenon, and many factors that influence wave properties, in particular the heat loss rate and the interfacial heat exchange or effective heat conductivity of the porous medium, must be accurately specified. A numerical model was developed to describe combustion wave

characteristics in a coordinate system moving together with the wave front. Two chemical kinetic mechanisms have been used. The first mechanism was developed by Frenklach's group[2] and is applicable under combustion conditions (i.e., moderately high equivalence ratios); the second kinetic mechanism has been developed at UIC to describe more accurately the partial oxidation of H_2S (i.e., ultra-high equivalence ratios).[3] The products of partial H_2S oxidation, hydrogen (H_2) and elemental sulfur (S_2), are dominant for ultra-rich superadiabatic combustion, which is essentially a fuel reforming reaction. The chemistry in the combustion wave is modeled and species and temperature profiles are predicted.

Preliminary numerical modeling of the SAC reactor has been performed. The parameters considered in the modeling effort included fuel gas composition (i.e., H_2S-rich and H_2S-lean), oxidant composition (air/enriched air), equivalence ratio, superficial gas velocity, feed gas temperature (pre-heating effect), and product gas quenching. The major conclusions from the modeling predictions obtained are:

- In oxygen-enriched air (i.e., 30% O_2-N_2 gas mixture), conversions of H_2S to hydrogen and elemental sulfur are better than when pure oxygen is used as the oxidant.

- Product gas quenching can substantially increase the selectivity of H_2S conversion to H_2; however, the selectivity of H_2S conversion to elemental sulfur decreases. For example, at typical filtration velocities ranging from 20 to 30 cm/s, equivalence ratios of about 2-3, and oxygen-enriched air containing about 20-40% O_2, H_2S conversion to hydrogen is about 20% and H_2S conversion to elemental sulfur is about 60%. With quenching of product gas, H_2S conversion to hydrogen and elemental sulfur is about 35% and 25%, respectively.

- Water addition to the initial mixture does not improve the reactor performance with respect to hydrogen and elemental sulfur production.

- When air is used as the oxidant, conversion of H_2S to H_2 decreases as filtration velocity increases. In contrast, when pure oxygen is used as the oxidant, increasing the filtration velocity plays a positive role.

- SAC reactor performance can be significantly improved by separating and recirculating unreacted H_2S in the product gas.

Based on the developed numerical model, optimization studies of hydrogen production were conducted by varying the characteristics of the ultra-rich superadiabatic waves. The major findings appear to indicate that by optimizing the porous body reactor configuration, equivalence ratio, and filtration velocity, the overall H_2S decomposition in a single pass can be as high as 30-50%, with a conversion of H_2S to the desirable product hydrogen (H_2) reaching a level of 30%. This reactor performance can be obtained using equivalence ratios in the range of 10 to 15, while maintaining a filtration velocity greater than 100 cm/s. For these high values of equivalence ratio and filtration velocity, the combustion temperature is considerably higher than the adiabatic temperature, which is in fact too low for combustion to take place in the gas phase. Such high temperature promotes the decomposition of H_2S, the hydrogen (H_2)/water (H_2O) selectivity, and the elemental sulfur (S_2)/sulfur dioxide (SO_2) selectivity. Given that in a single pass the H_2S

decomposition can reach 30-50%, the overall process performance can be substantially improved, with respect to hydrogen production, by membrane separation of product gases and recirculation of unreacted H_2S. It can be shown that in 4 to 5 passes nearly total hydrogen sulfide decomposition into sulfur can be realized, with recovery of 30-40% of the hydrogen component.

The most optimum scenario in the results of the computer modeling to-date indicate that, with feed gases entering the reactor at ambient temperature, a maximum temperature of 1631 K (1394°C or 2541°F) can be achieved in the SAC reactor, resulting in an overall H_2S conversion of 50%, with a hydrogen (H_2)/water (H_2O) selectivity of 57/43 and an elemental sulfur (S_2)/sulfur dioxide (SO2) selectivity of 99/1.

These predictions have offered valuable guidelines for the preparation of a design and cost estimate of a suitable bench-scale reactor testing system to be assembled and tested in Phase 2 of the program. Modeling efforts also made possible the identification of key SAC process parameters and the preparation of a parametric testing plan for Phase 2. The chemical kinetic mechanisms used in the formulation of this preliminary model will be updated based on direct comparison with the experimental data that will be obtained in Phase 2, further enhancing the reliability of the model.

Lab-Scale Testing System Design

To develop the necessary experimental data to demonstrate the technical and economical viability of the SAC reactor unit, a bench-scale testing system has been designed for H_2 production from thermal decomposition of up to 1,400 standard cubic feet per hour (SCFH) of H_2S-oxidant gas mixture. Schematic diagrams of the P&ID for this system are shown in Figure 2. In the proposed testing system, predetermined amounts of feed gas components are mixed and delivered to a packed-bed reactor where H_2S is converted to H_2 and S at high temperatures. Hot off-gas leaving the reactor is cooled with a cooling medium in a condenser where sulfur vapor (S(g)) is condensed and collected. Cooled gas is then scrubbed with a caustic solution where H_2S and sulfur dioxide (SO_2) are removed and the cleaned gas is discharged to the atmosphere.

The bench-scale SAC reactor system consists of a fuel gas/oxidant conditioning system to generate appropriate inlet gas mixtures, a packed-bed reactor, a sulfur condenser and recovery subsystem, an exit gas scrubbing subsystem, and equipment for sampling and analysis of H_2S decomposition products. The major equipment for the proposed lab-scale testing system includes: a gas mixing chamber, a reactor, a thermal fluid cooler, a thermal fluid pump, a sulfur condenser, a gas scrubber, a caustic tank, a recirculating caustic pump, and a makeup caustic pump. The information required for design, engineering, procurement and installation of this system including the system description, equipment design, and equipment specifications has been prepared in a design package.

Important features of the designed bench-scale SAC reactor system include:

- A reactor diameter of 6 inches (15 cm) is used so that the data generated from the bench-scale testing can be used for future scale-up design.

- A minimum gas residence time of 2 seconds in the packed-bed of the reactor (based on the maximum superficial gas velocity) is used to ensure complete conversion of the H_2S decomposition reaction.

- The designed reactor is capable of processing up to 1,400 SCFH of total feed gas mixture containing H_2S and oxidant.

- The estimated pressure drop across the packed-bed at maximum gas throughput ranges from 0.7 to 1.6 psi at average gas temperatures ranging from 1000 to 2500°F (538 to 1371°C).

- The reactor consists of a vertical, cylindrical carbon steel shell (21-inch ID x 21.5-inch OD x 72-inch H) lined with 6-inch thick rigid fibrous ceramic insulation. An impervious ceramic tube (6-inch ID x 7-inch OD x 72-inch H) containing 99+% alumina is used as the inner reactor tube to contain the inert pellets and reactor gases.

- A 30 kW 3-zone, silicon carbide or molybdenum disilicide electric heater is located in the space between the ceramic tube and the insulation to provide auxiliary heat for cold startup and temperature control.
- Support and hold-down plates are used to support and contain the inert pellets and ceramic insulation.
- High-temperature gaskets are used in the ceramic-metal joints and the flanged connections to prevent any leakage of reactor gases.

During Phase 2 of this program, GTI, UIC, and industry advisors UOP and BP Amoco will construct the bench-scale unit and conduct parametric testing to validate the SAC concept. The computer model developed in Phase 1 will be updated with the experimental data and used in future scale-up efforts. The process design will be refined and the cost estimate updated. Market survey and assessment will continue so that a commercial demonstration project can be identified.

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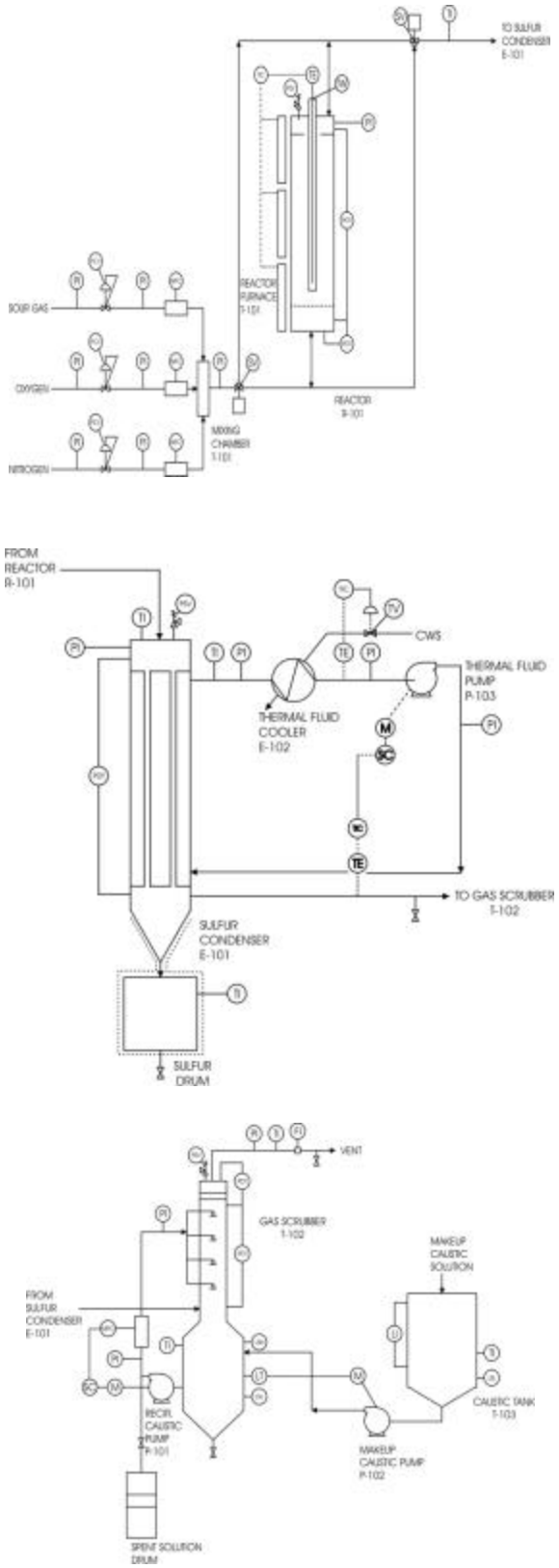

Figure 2. P&ID for the Bench-Scale SAC Reactor Testing System