PRODUCTION OF HYDROGEN BY SUPERADIABATIC DECOMPOSITION OF HYDROGEN SULFIDE

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Abstract
The Gas Technology Institute, in collaboration with the University of Illinois at Chicago and industrial partners, including UOP, has been developing an innovative noncatalytic, thermochemical process for the production of hydrogen and elemental sulfur from hydrogen sulfide in H$_2$S-containing waste gases. The key feature of this process is the superadiabatic reactor, where partial oxidation of H$_2$S in the feed gas is carried out in a cylindrical vessel packed with a porous ceramic medium with a high thermal capacity. The intensive heat exchange between the filtrating and burning gas mixture, and the porous medium through the highly developed internal surfaces permits the accumulation of combustion energy in the solid matrix. As a result, flame temperatures can be significantly higher than the adiabatic temperature for the mixture.

This process has potential to produce economically viable quantities of hydrogen through the superadiabatic partial oxidation of H$_2$S in the feed at very high temperatures, which can be achieved without the input of external energy, and with no additional carbon dioxide (CO$_2$) emissions. GTI has envisioned a process comprising the superadiabatic H$_2$S decomposition reactor, product/byproduct separation schemes, hydrogen purification, and tail gas cleanup. With funding from the U.S. Department of Energy, GTI, and UIC, work has so far concentrated mainly on the superadiabatic reactor, and has comprised computational modeling and experimental studies to demonstrate the technical and economical feasibility of the superadiabatic H$_2$S decomposition concept, using H$_2$S-N$_2$-O$_2$ gas mixtures.

Theoretical (numerical modeling) studies at UIC and collaborative experimental investigations by GTI and UIC researchers on the generation of hydrogen-rich gases from hydrocarbons via the superadiabatic partial oxidation have shown the high potential of this approach. It has been shown that stable self-sustained flames could be generated using H$_2$S-containing gases as a feedstock in the range of equivalence ratios from 2 to 5 with hydrogen output at about 20%. The performed experimental and numerical studies analyzed chemical and thermal structures of the H$_2$S-containing gases/air flames stabilized in an inert porous medium. The agreement between the groundwork experimental data developed to-date and modeling predictions is quite reasonable.

To carry out a rigorous process evaluation, GTI has designed and constructed a state-of-the-art superadiabatic H$_2$S decomposition reactor system. This reactor is currently being operated to demonstrate the technical feasibility of the superadiabatic decomposition process, to evaluate the agreement between modeling predictions and experimental results, and to reassess the economic potential of the process.
As a logical extension of our ongoing process development efforts, GTI plans to undertake a combination of lab-scale and pilot-scale work to address several issues, which are critical for successful demonstration and future commercialization of the superadiabatic H₂S decomposition process:

- Fate of feed gas impurities (i.e., CO₂, CH₄, etc.) in the product gas, and their effect on reactor performance, especially with respect to hydrogen yield;
- Product/byproduct separation schemes to separate the unreacted H₂S for recycle (to maximize the overall H₂S conversion), the hydrogen product for purification, and the tail gas for cleanup;
- Construction and operation of a pilot-scale superadiabatic reactor system to provide for a more practical evaluation of the process and to develop large-scale data permitting more realistic engineering and economic analysis; and
- Construction of an integrated superadiabatic H₂S decomposition system for field-testing at an industrial site, such as an oil refinery.

Introduction

In recent years, hydrogen sulfide (H₂S) has come to be regarded as a mineral from which two valuable products (hydrogen and sulfur) can be extracted. Technology is well established for the recovery of the sulfur component, with the Claus process being the most prominent. Although this technology also produces a low-quality steam, it does not fully utilize the potential of H₂S as a resource for hydrogen.

Hydrogen is currently needed in large quantities, and is projected to be the fuel of choice for a number of advanced technologies that are being pursued. The greatest need for hydrogen continues to be as a feedstock in the synthesis of ammonia and methanol, in the desulfurization and hydrocracking in oil refineries, and in the upgrading of various hydrocarbon resources such as heavy oil and coal.¹ There is a growing need for hydrogen as the fuel cell technology is being introduced into the utility and transportation sectors.

Globally, the predominant method of hydrogen production is through the steam reforming of natural gas. Other established methods include partial oxidation of residual oil, coal gasification, and water electrolysis. Because of the increasingly important status of hydrogen as a fuel, many other exotic approaches have been investigated, such as high-temperature electrolysis of steam, thermal cracking of natural gas, thermochemical water splitting, solar photovoltaic water electrolysis, and plasma decomposition of water. These technologies can be classified as thermal, thermochemical, electrochemical, photochemical, and plasmochemical methods. A recent comprehensive review has been made to bring to focus the possibilities and limitations in each of these areas.¹

Because of the significant amounts of H₂S available worldwide, efforts have been made in recent years for the production of hydrogen, in addition to sulfur, from H₂S through a number of approaches. It is widely recognized that the most direct process of converting hydrogen sulfide into hydrogen and sulfur is through thermal decomposition (catalytic or noncatalytic). However, because of energy considerations, this approach has been considered impractical at temperatures exceeding about 927°C (1200K). In addition to being endothermic, the equilibrium of the thermal decomposition of H₂S at these temperatures is relatively low, and the reaction does not proceed to an industrially important extent.² As indicated in Figure 1, showing the predicted conversion of H₂S decomposition based on thermodynamic equilibria, conversion is
only about 20% at 1000°C and 38% at 1200°C. Temperatures exceeding 1375°C are needed to drive the H₂S decomposition reaction to conversions > 50%. Because of these limitations and other considerations, such as environmental regulations on sulfur emissions, any process for the recovery of hydrogen, in addition to sulfur, from H₂S based on thermal decomposition or dissociation, has to overcome a number of technical (and economical) hurdles. These include:

- Low yields even at high temperature (equilibrium limited)
- To maximize H₂ production, it is necessary to recycle unreacted H₂S
- Need to separate product gases
- Unless conversion is reasonably high, large recycle streams have to be dealt with
- Rapid quenching of product gas may be necessary to block any recombination of H₂ and S₂ (decomposition reaction is reversible)
- Fate of impurities in feed gas has implications on emissions, tail-gas cleanup, product purity

Because of the high-energy demands for thermal dissociation, other approaches were evaluated where attempts were made to carry out the decomposition reaction with equilibrium shift, such as by preferential removal of reaction products by membranes and thermal diffusion columns. Despite the advances made in these areas, no method of hydrogen sulfide decomposition can be considered commercially feasible today.

**Figure 1. Pure H₂S Decomposition Reaction as a Function of Temperature**

Working with the University of Illinois at Chicago (UIC) and other industrial partners, including UOP and BP Amoco, the Gas Technology Institute (GTI) has been developing an innovative process that promises to overcome the limitations of the noncatalytic thermal decomposition approach. In this process operation at significantly high temperatures is made possible and economical by oxidation of part of the H₂S to provide the energy required for the decomposition reaction to proceed to a significant extent. Partial oxidation of H₂S in the H₂S-containing fuel gas is carried out in the presence of an inert, porous, high-capacity medium and the intense heat exchange results in flame temperatures that significantly exceed the adiabatic flame temperature of the gas mixture. By coupling the partial oxidation of H₂S in the porous medium with the H₂S decomposition, temperatures as high as 1400°C (1673K) can be achieved.
economically within a reaction zone without the input of external energy, and therefore, no additional CO\(_2\) emissions. In this reaction zone, the self-sustaining conditions are very favorable for the decomposition reaction to proceed to an industrially significant extent, within a slowly propagating thermal wave (Figure 2). The superadiabatic partial oxidation concept is depicted in Figure 3 for a given set of operating conditions (i.e., 20% H\(_2\)S in the feed gas, 12 cm/s gas velocity, etc.). It is clearly seen that in this case, for equivalence ratios > 1.5, the temperature achieved greatly exceeds the adiabatic temperature of the gas mixture. (Equivalence ratio is defined as the molar ratio of O\(_2\) supplied to the O\(_2\) that is stoichiometrically required to burn all the H\(_2\)S.) It is conceivable that higher temperatures than shown in Figure 3 can be achieved by manipulating the operating conditions.

One process envisioned for application of the superadiabatic decomposition concept for the conversion of H\(_2\)S in an H\(_2\)S-rich waste stream to high-purity hydrogen and elemental sulfur is illustrated in Figure 4. H\(_2\)S-rich acid gas from an H\(_2\)S-selective amine system is mixed with a substoichiometric volume of air or enriched air before entering the decomposition reactor. Gases exiting the reactor would include the H\(_2\)S decomposition products, hydrogen and sulfur vapor, as well as unreacted H\(_2\)S, water vapor, sulfur dioxide, and any contaminants. The exit stream would be cooled by heat exchange with recycled H\(_2\)S and possibly the acid gas feed. Sulfur vapor would be removed in a conventional sulfur condenser as a molten product, generating additional steam. The remaining H\(_2\)S, H\(_2\), N\(_2\), SO\(_2\), etc. would be separated in a series of gas separation devices such as the separation membranes shown. Recycle of unconverted H\(_2\)S would be employed to maximize conversion.

Figure 2. Propagating Superadiabatic Partial Oxidation Wave
In addition to a practical superadiabatic decomposition reactor design, an economical means for separation of unreacted H$_2$S and product hydrogen from residual water and other contaminants in the product gas stream is a critical consideration in the overall system design. Membrane technologies, including polyamide membranes, ceramic membranes, and other high temperature hydrogen separation membranes are being developed for similar applications. The remaining system components would be either similar to those in the Claus plant (sulfur condensation and recovery) or consist of conventional equipment (blowers, heat exchangers, pumps, etc.). Depending on acid gas components and the membrane systems selected, additional equipment such as knockout drums, coalescing filters, and guard beds may also be required to protect the membranes.

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**Figure 3. Partial Oxidation Temperature of H$_2$S (Gas Velocity= 12 cm/s)**

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**Figure 4. Conceptual Process Design for Hydrogen Production Based on the Superadiabatic Decomposition Concept**
One possible design concept for the superadiabatic reactor for the decomposition of $\text{H}_2\text{S}$ is shown in Figure 5. $\text{H}_2\text{S}$ and oxidant are premixed, introduced at one end of the U-shaped reactor shown, and then passed into the reaction zone. Decomposition products exit the other end, giving up heat rapidly to the cooler ceramic packing. The flame front advances slowly to a control point, at which time the three-way valve positions are switched to reverse the flow, and the flame front begins to move in the other direction. A procedure is required to avoid contamination of the product stream with residual $\text{H}_2\text{S}$ at the time of flow reversal. This can be done by purging the upstream zone with a fuel-air mixture (either natural gas-air or hydrogen-air from the products) for a short time just prior to flow reversal.

Integration of this switching-reactor concept into the process concept of Figure 5 would require a second recycle heater. A single sulfur condenser and membrane separation train would be used, with feed and reaction product streams switched from one end of the reactor to the other to maintain the moving flame front within the required control boundaries.

Another possible reactor design concept would employ a moving bed of ceramic beads to stabilize the combustion wave position and avoid the complications of the switching reactor configuration. While this approach introduces solids-handling issues into the design, they would involve relatively small amounts of solids transported for a short distance at manageable temperatures.

To date, GTI’s efforts have been focused on issues involving the superadiabatic decomposition reactor, and have included reactor modeling; design, construction, and operation of a suitable reactor system; and assessment of process economics and market analysis. Process development efforts are reviewed below. In addition, several issues are discussed, with reference to the conventional technologies for sulfur recovery (i.e., Modified Claus + Tail-Gas Cleanup) and hydrogen production (i.e., steam methane reforming), highlighting the potential superiority (technical and environmental performance, and economic benefits) of the superadiabatic decomposition process over these well-established technologies.

![Figure 5. Conceptual Design for SAC-Based $\text{H}_2\text{S}$ Decomposition Reactor](image_url)
Superadiabatic H\textsubscript{2}S Decomposition Reactor Modeling

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. UIC has developed a numerical model to describe the wave characteristics in a coordinate system moving together with the wave front. In this work thermal waves in H\textsubscript{2}S/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. UIC has developed a chemical kinetic mechanism that is specific to the partial oxidation of H\textsubscript{2}S, where the products of the superadiabatic decomposition are predominantly hydrogen (H\textsubscript{2}) and elemental sulfur (S\textsubscript{2}). The chemistry in the combustion wave is modeled and species and temperature profiles are predicted.

Groundwork numerical modeling of the superadiabatic decomposition reactor has been performed, identifying key process parameters. These parameters include fuel gas composition (i.e., H\textsubscript{2}S-rich and H\textsubscript{2}S-lean), oxidant composition (air/enriched air/oxygen), equivalence ratio, superficial gas velocity, feed gas temperature (pre-heating effect), and product gas quenching (to avoid recombination of H\textsubscript{2} and S\textsubscript{2}). Qualitative and quantitative determinations were made of the effects of these parameters, individually and in combination, on the performance of the superadiabatic decomposition reactor for production of hydrogen and elemental sulfur.\textsuperscript{4,5} The effect of steam (one of the products) addition to the initial mixture on enhancing the reactor performance, with respect to hydrogen and elemental sulfur production, was also assessed. In addition, the separation of unreacted H\textsubscript{2}S from the product gas and recirculation was investigated as a means for maximizing the overall conversion of H\textsubscript{2}S in the feed stream.

The major findings appear to indicate that by optimizing the porous body reactor configuration, equivalence ratio, and gas velocity, the overall H\textsubscript{2}S decomposition in a single pass can be as high as 50\%, with a conversion of H\textsubscript{2}S to the desirable product hydrogen (H\textsubscript{2}) reaching a level of 30\%. This reactor performance can be obtained using equivalence ratios in the range of 10 to 15, while maintaining an interstitial gas velocity greater than 100 cm/s. For these high values of equivalence ratio and filtration velocity, the partial oxidation temperature is considerably higher than the adiabatic temperature. Such high temperature promotes the decomposition of H\textsubscript{2}S, the hydrogen (H\textsubscript{2})/water (H\textsubscript{2}O) selectivity, and the elemental sulfur (S\textsubscript{2})/sulfur dioxide (SO\textsubscript{2}) selectivity. Given that in a single pass the H\textsubscript{2}S decomposition can reach up to 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\textsubscript{2}S. It can be shown that in 4 to 5 passes nearly total H\textsubscript{2}S decomposition into sulfur can be realized, with recovery of 30-40\% of the hydrogen component.

The most optimum scenario in the results of the numerical modeling 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\textsubscript{2}S conversion of 50\%, with a hydrogen (H\textsubscript{2})/water (H\textsubscript{2}O) selectivity of 57/43 and an elemental sulfur (S\textsubscript{2})/sulfur dioxide (SO\textsubscript{2}) selectivity of 99/1.

Technical Feasibility Demonstration

The application of ultra-rich superadiabatic partial oxidation in inert porous media for hydrogen generation is a novel area of research and technology. Theoretical (numerical modeling) studies at UIC and collaborative experimental investigations (Figures 6 and 7) by GTI and UIC
researchers on the generation of hydrogen-rich gases from hydrocarbons via the superadiabatic partial oxidation have shown the high potential of this approach. This concept was initially evaluated as a fuel-reforming approach at UIC. Premixed methane-air superadiabatic flames demonstrated conversion of fuel to hydrogen that exceeds 60%. More importantly for the proposed work, stable self-sustained flames were generated using hydrogen sulfide as a feedstock in the range of equivalence ratios from 2 to 5 with hydrogen output close to 20%, as shown in Figure 8. The performed experimental and numerical studies analyzed chemical and thermal structures of the hydrogen sulfide/air flames stabilized in an inert porous medium. As shown in Figure 9, the agreement between the groundwork experimental data developed so far and modeling predictions is quite reasonable.

Figure 6. GTI’s Preliminary Experimental Unit

Figure 7. UIC’s Superadiabatic Partial Oxidation Reactor
To carry out a rigorous demonstration of the technical and economical feasibility of the superadiabatic H$_2$S decomposition concept, GTI has designed and constructed a state-of-the-art superadiabatic H$_2$S decomposition reactor system (Figure 10 and Figure 11). A complete description of this reactor facility and capabilities is provided elsewhere. This lab-scale reactor is currently being operated to demonstrate the technical feasibility of the superadiabatic decomposition process, to evaluate the agreement between modeling predictions and experimental results, and to reassess the economic potential of the process.
Figure 10. Overall Arrangement of GTI’s Newly-Constructed Lab-scale H₂S Superadiabatic Decomposition Reactor

Figure 11. Superadiabatic H₂S Decomposition Reactor Details
Superadiabatic Decomposition Process Advantages over Conventional Technologies

Obviously, the major advantage of the superadiabatic decomposition process is the recovery of hydrogen in addition to elemental sulfur. Unlike the Claus process which uses a catalyst, requiring replacement every two years or so, the superadiabatic decomposition process is noncatalytic. The superadiabatic decomposition process is also less stringent than the Claus process from the point of view of the required feed gas conditioning. In addition, the potential exists for eliminating costly tail gas cleanup. In the Claus process, tail gas cleaning doubles the plant cost and adds considerable complexity to the process lineup. Furthermore, because of the very high operating temperatures in the superadiabatic decomposition process, problems related to benzene and ammonia in the Claus furnace will not be an issue. These issues are discussed in more detail below.

SO₂ Emissions
Clearly, because part of the H₂S is oxidized to generate heat, some SO₂ will inevitably form. At first glance, this can seem as a critical issue. However, as indicated by the modeling predictions, the operating conditions can be regulated such that the S₂/SO₂ selectivity is as high as 99/1. Therefore, SO₂ is not expected to form to a significant extent. Furthermore, SO₂ is an internal stream, which will be eventually separated from the product hydrogen for recirculation into the reactor or isolation from the gas stream. In addition, even if SO₂ is present in the tail gas, this will not lead to a situation that is worse than the Claus process (Figure 12), where about 3% of the sulfur in the feed gas ends up in the tail gas. Tail gas cleanup in the Claus process is a costly operation, and its cost can offset the value of the sulfur being recovered. Depending on the performance of the gas separation devices that will be employed for product/byproduct separation in the superadiabatic decomposition process, the amount of SO₂ in the tail gas can be expected to be significantly less than those seen in the Claus Process. Furthermore, the revenue from the valuable hydrogen product can absorb the cost of any further tail gas cleanup in the superadiabatic decomposition process.

![Figure 12. Modified Claus Process and Tail-Gas Cleanup Unit](image-url)
Source of H₂S and Feed Conditioning
Previously, GTI made a market assessment that showed a significant amount of H₂S is available worldwide. The superadiabatic decomposition process was determined to be most suitable for treating refinery gases, where the process can be co-located with a real need for hydrogen.⁴

The superadiabatic decomposition process is potentially suitable for treating gases containing H₂S at levels as low as 10%. Therefore, conditioning of the feed gas will certainly not go beyond what is currently practiced or required by the Claus process for waste H₂S treatment and sulfur recovery. In the Claus process, H₂S is first separated from the host gas stream using amine absorption and the feed gas to the Claus furnace must contain 40 to 50% H₂S. In addition, because no need exists to selectively remove CO₂, feed gas pre-treatment or conditioning can be readily accomplished in a simple amine plant using inexpensive solvents; whereas expensive solvents, such as MDEA or Acid Gas Enrichment (AGE) are required for producing an acceptable Claus feed.

Cost of Hydrogen Production
It remains premature to make a meaningful assessment of the cost of hydrogen production from the process at such an early stage of development. A real need exists for developing experimental data to determine the product gas composition. This way we can develop a better idea of product/byproduct separation schemes and provide “closure” for the various process components. In early estimates, GTI’s superadiabatic decomposition process was determined to compare favorably with the existing commercial Claus process.⁴ In this comparison, GTI used the major equipment required for the superadiabatic decomposition process versus that for the Claus process and concluded that the superadiabatic decomposition process required the same or fewer reactors and produces a valuable hydrogen gas product that the Claus process does not, while producing the same amount of sulfur. On that basis, the superadiabatic decomposition process cost is concluded to be potentially comparable to the Claus process. Therefore, any valuable product that can be produced from SAC over that of Claus is essentially ‘free’.

To indicate the good prospects for the superadiabatic H₂S decomposition process, two systems aiming to accomplish the same goal of economically producing hydrogen from H₂S, were selected. These systems have undergone significant development and are considered to have acceptable capital costs and good prospects for large scale hydrogen production (provided an economic way to separate the hydrogen product can be devised).⁸

The first system, shown in Figure 13, was a scheme investigated at the University of Calgary, and is essentially a stand-alone facility with natural gas supplying all the energy required for dissociation. All the fresh feed, plus the recycle H₂S, goes to the decomposition reactor. This reactor comprises a set of ceramic tubes containing catalyst, operating at about 1100°C, installed in a gas-fired furnace.
The cost of producing $\text{H}_2$ was cited at $1160/\text{ton}$ ($3.08/\text{Mscf}$) for this natural gas-fired system, compared to $670/\text{ton}$ ($1.78/\text{Mscf}$) for a comparatively sized Claus plant plus steam methane reformer. However, the portion of the $\text{H}_2$ cost attributable to natural gas fuel for the decomposition reactor was $727/\text{ton}$, or 63% of the total.\(^8\) The superadiabatic decomposition reactor, on the other hand, does not use natural gas under normal operating conditions, and is a self-sustaining process obtaining all of the necessary heat from oxidation of a small portion of $\text{H}_2\text{S}$ in the feed. In addition, in the GTI process, significantly higher temperatures can potentially be achieved, leading to improved $\text{H}_2$ yields.

Figure 14 shows another scheme that was proposed by Alberta Sulphur Research Ltd. (ASRL) as a retrofit to existing Claus plants (Figure 15). A portion of the acid gas feed is passed through “cracking” coils placed in the reaction furnace, where considerable heat is generated. The product stream is rapid-quenched on exiting the reactor, and then cooled further to condense the sulfur. The gas is then compressed and the $\text{H}_2$ separated using a membrane facility. Unreacted $\text{H}_2\text{S}$ is recycled and fed to the Claus reaction furnace. Very favorable results have been reported on this system, as highlighted below:

- Laboratory experiments with a 90/10% by volume mixture of $\text{H}_2\text{S}$ and $\text{CO}_2$ without catalyst showed that conversions of 26 and 28% were obtained at the typical Claus furnace temperatures of 1100 and 1200°C. Contacts times of only fractions of a second were needed.

- When pure $\text{H}_2\text{S}$ was passed through the “cracking” coils at a coil operating temperature of about 1200°C, $\text{H}_2$ yields of 34 to 36% were observed. For $\text{H}_2\text{S}$-$\text{CO}_2$ mixtures, $\text{H}_2$ yields were about 19, 24, and 28% for 70, 80, and 90% $\text{H}_2\text{S}$.

- To avoid flame stability problems, up to 25% of the feed could be safely directed through the “cracking” tubes for an acid gas consisting of 83% $\text{H}_2\text{S}$, 10% $\text{CO}_2$, 1% $\text{CH}_4$, and balance $\text{H}_2\text{O}$. 
Figure 14. Thermal Decomposition using Heat from Claus Reaction Furnace – ASRL Scheme

Figure 15. ASRL’s Thermal Cracking of H₂S in Modified Claus Furnace
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