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Thermochemical production of hydrogen from hydrogen sulfide with iodine thermochemical cycles

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ABSTRACT

With the goal of eventually developing a replacement for the Claus process that also produces H_2 , we have explored the possibility of decomposing hydrogen sulfide through a thermochemical cycle involving iodine. The thermochemical cycle under investigation leverages differences in temperature and reaction conditions to accomplish the unfavorable hydrogen sulfide decomposition to H_2 and elemental sulfur over two reaction steps, creating and then decomposing hydroiodic acid. This proposed process is similar to ideas put forth in the 1980s and 1990s by Kalina, Chakma, and Oosawa, but makes use of thermochemical hydrogen iodide decomposition methods and catalysts rather than electrochemical or photoelectrochemical methods.

Process models describing a potential implementation of this thermochemical cycle were created. Motivated by the process model results, experimentation showed the possibility of using alternative solvents to dramatically decrease the energy requirements for the process. Further process modeling incorporated these alternative solvents and suggests that this theoretical hydrogen sulfide processing unit has favorable economic and environmental properties.

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Introduction

Hydrogen sulfide is a toxic gas that is both naturally abundant, found in many hydrocarbon reserves [1,2], and is generated on a large scale by human activity, specifically the hydrodesulfurization of sulfur-rich hydrocarbons [3]. Both of these sources are increasing in magnitude as the environmental benefits of natural gas power generation are realized and as increasing numbers of nations impose stricter limits on the release of air pollutants such as sulfur dioxide [4].

Additionally, as hydrocarbon resources with lower sulfur content are depleted, higher sulfur content reserves are extracted to meet demand. H_2S poses a danger to human health [5,6] as do the species formed by its oxidation in the atmosphere [7]. Finding efficient ways to process hydrogen sulfide is important to protect human health, reduce carbon emissions, and enhance the profitability of previously marginal hydrocarbon resources.

The current widely used method for hydrogen sulfide processing is the Claus process [8]. This method produces elemental sulfur and water from hydrogen sulfide and

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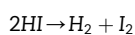
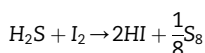
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accounts for the majority of elemental sulfur production in the world [9]. While effective in treating the hydrogen sulfide to protect human health, the Claus process extracts very little value from the hydrogen sulfide waste.

A process that could decompose hydrogen sulfide into hydrogen gas and elemental sulfur would be especially useful when the hydrogen sulfide was created by the reaction of hydrogen with a sulfur-rich hydrocarbons during hydrodesulfurization. By recovering and recycling the hydrogen gas originally used to desulfurize the hydrocarbon, the amount of hydrogen gas needed to treat a sulfur-rich hydrocarbon could be dramatically reduced. Given that natural gas reforming, the lowest cost and most widely implemented method of hydrogen gas generation, is inherently greenhouse gas emitting, reducing hydrogen gas consumption also reduces the environmental impact of the process. Similarly, large quantities of hydrogen sulfide present in natural gas resources or accumulated at other locations [10] are much less of liability if a valuable product such as hydrogen could be generated.

Many different approaches have been explored to find a method that could decompose hydrogen sulfide into sulfur and hydrogen gas. Some have tried direct [11,12] and catalyzed [13–15] thermal decomposition often coupled [16] with traditional Claus units. These approaches scale well but suffer from the need for high temperatures to achieve significant hydrogen generation. Others have explored electrochemical [17–19] photochemical [20–25] or some combination of these methods [26,27] to decompose hydrogen sulfide. These methods are possible at low temperatures but tend to scale very poorly. Thermochemical cycles have also been explored for their potential to decompose hydrogen sulfide. A modified Bunsen cycle applied to hydrogen sulfide decomposition has been proposed by Wang [28] with many of its key steps examined in detail [29,30]. However, key problems associated with the Bunsen cycle persist even in this hydrogen sulfide variant. None of these methods have achieved commercial implementation. Chakma and Zaman [31] and Reverbi and Fabiano [32] both have written comprehensive reviews on H_2 production from H_2S decomposition which can be referred to for more detailed information on the state of this technology.

We propose a low temperature thermochemical method to accomplish the decomposition of hydrogen sulfide to elemental sulfur and hydrogen gas. The decomposition is accomplished with two reaction and separation steps. The first reaction is performed at low temperatures in a solvent and the second reaction is performed over an activated carbon catalyst at temperatures at or below 500°C according the conditions suggested by Favuzza et al. in their study of HI decomposition [33].



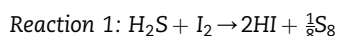
This proposed process is similar to ideas put forth in the 1980s by Kalina [17,18] and Oosawa [20] but makes use of more recently discovered thermochemical hydrogen iodide decomposition methods and catalysts rather than electrochemical or photoelectrochemical methods. Chakma and Zaman [31] also obliquely mention the potential for this type

of process in their review of hydrogen sulfide decomposition methods but they suggest that it should be accomplished by photochemical catalysts. Recent advances in the catalyzed decomposition of HI [34,35] mostly focused toward water splitting schemes, have led us to examine a potential thermochemical H_2S splitting scheme.

Thermochemical cycles

Thermochemical cycles accomplish chemical reactions that are unfavorable in a single step with a series of reaction and separation steps. This series of reactions involves other intermediates that are recycled such that if the stoichiometry of all reaction steps are summed each intermediate cancels out. Thermochemical cycles often also require that each reaction step is performed in distinct and specific conditions. In addition, thermochemical cycles typically accomplish the desired transformation at lower process temperatures compared to single step processes. Thermochemical cycles have been studied extensively in the context of splitting water [36] and have also been applied to H_2S decomposition [37–40].

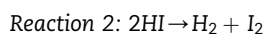
As we propose a new thermochemical cycle, we begin by summarizing what is known about each step of the proposed cycle in conditions relevant to the process.



At 25°C in the gas phase this reaction is extremely unfavorable with a ΔG_{rxn} of 35.4 kJ/mol. This is calculated assuming that each species is in their equilibrium form, for example sulfur is an orthorhombic crystal. However, if performed in water, the solvation of hydroiodic acid drives the reaction to consume the hydrogen sulfide with an overall ΔG_{rxn} of -71.6 kJ/mol. This implies that in the aqueous phase the thermodynamic limit of the reaction is the almost complete consumption of hydrogen sulfide.

Qualitative descriptions of this reaction in aqueous conditions have been described by various authors [41,42] but the reaction has little detailed analysis. Mehra and Sharma quantitatively characterize the reaction of hydrogen sulfide and iodine in the context of using iodine as a hydrogen sulfide absorbent [43]. In this characterization they measure the volumetric rate of absorption of hydrogen sulfide gas into an iodine solution at ambient conditions. They find that the reactive absorption happens extremely quickly, observed occurring at rates of 0.1 mol H_2S absorbed per m^2 gas-liquid interface per second. Kalina and Maas also observed the near complete conversion of hydrogen sulfide (from 25% to less than 1 ppm) at a flow rate of 880 cubic centimeters per min [18]. This was in basic conditions where iodine will be mostly oxidized to the iodate ion as was preferable for their electrochemical process.

The thermochemistry and observations of these authors support a model where hydrogen sulfide bubbled through a concentrated aqueous iodine solution will almost entirely react.



Hydrogen iodide decomposition is of great importance to many researchers investigating thermochemical cycles for

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