

FINAL REPORT

TECHNOECONOMIC ANALYSIS OF AREA II HYDROGEN PRODUCTION

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OVERALL OBJECTIVES & RATIONALE

The aim of this work was to assess issues of cost, and performance associated with the production and storage of hydrogen via following three feedstocks: sub-quality natural gas (SQNG), ammonia (NH₃), and water. Three technology areas were considered:

- 1) Hydrogen production utilizing SQNG resources,
- 2) Hydrogen storage in ammonia and amine-borane complexes for fuel cell applications,
- 3) Hydrogen from solar thermochemical cycles for splitting water.

This report summarizes our findings with the following objectives:

- Technoeconomic analysis of the feasibility of the technology areas 1-3.
- Evaluation of the hydrogen production cost by technology areas 1.
- Feasibility of ammonia and/or amine-borane complexes (technology areas 2) as a means of hydrogen storage on-board fuel cell powered vehicles.

For each technology area, we reviewed the open literature with respect to the following criteria: process efficiency, cost, safety, and ease of implementation and impact of the latest materials innovations, if any. We employed various process analysis platforms including FactSage chemical equilibrium software and Aspen Technologies AspenPlus and HYSYS chemical process simulation programs for determining the performance of the prospective hydrogen production processes.

I. SUMMARY OF RESEARCH FINDINGS

This report has been organized into the following three sections, given as attachments to this report each of which describes our findings for one of the above mentioned task areas:

Attachment 1 - Thermochemical, CO_x-Free, H₂S reformation of methane.

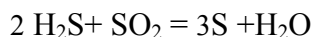
Attachment 2 - Analysis of hydrogen production using ammonia and ammonia-borane complex for fuel cell applications.

Attachment 3 - Analysis of solar thermochemical water splitting cycles for hydrogen production.

An updated summary of the findings for all three above-mentioned task areas follows.

I-1. Thermochemical, CO_x-Free, H₂S Reformation of Methane

Approximately one-third of the U.S. natural gas (NG) resource is low or sub-quality gas (SQNG) that does not meet specifications for pipeline transport. There are 10,000 SQNG wells in Texas alone and vast amounts of hydrogen sulfide (H₂S) are located beneath the Gulf of Mexico and other places (*e.g.* Black Sea). Typical specifications call for gas with no more than four parts per million of hydrogen sulfide content. Some SQNG can be blended with higher quality gas to meet market requirements. However, much of the sub-quality gas is too costly to upgrade and simply shut in. Hydrogen sulfide concentration in SQNG can be as high as 90% by volume. In natural gas processing, H₂S is viewed as a pollutant requiring treatment and removal. Presently, H₂S is separated from hydrocarbon gases by amine adsorption and regeneration producing acid gas containing 10-90% by volume H₂S. When hydrogen sulfide concentrations exceed 40%, gas is treated (or "sweetened") in the Claus plant. That is, a portion of the H₂S is burned to make SO₂, and then recombined with the main H₂S stream in a catalytic reactor to produce elemental sulfur and steam according to the following reaction:



Elemental sulfur is sold as a feedstock for sulfuric acid manufacture. In Claus process, hydrogen in the H₂S is converted to water vapor. Furthermore, since Claus units do not convert all the H₂S to sulfur, tail gas cleanup units are needed to remove traces of SO₂ before the off-gases can be vented to atmosphere. It would be advantageous to perform H₂S conversion in a manner so that to recover and recycle its hydrogen content. The market for the recovered hydrogen is readily available as each year U.S. refineries spend a quarter of billion dollars to produce H₂ needed for hydrodesulfurization of refinery products. The hydrodesulfurization process generated more than 5.5 million tons of H₂S waste gas in 1996 in the U.S. alone. As the quality of the crudes being processed in the U.S. continues to decline, more and more H₂ is required for the hydrodesulfurization of refinery products. The recovery of H₂ from the refineries' waste stream can provide a significant fraction of the H₂ now used for petroleum refining and upgrading.

Thus, the impetus for this study above was to determine the potential for improving the overall economics of the H₂S reformation of natural gas (particularly CH₄) to hydrogen and carbon disulfide (CS₂, instead of CO₂, as in the steam-methane reformation process). In this task, we addressed the following questions:

1. What is the magnitude of the H₂S resource, *i.e.* how much hydrogen can be realistically recovered from H₂S present in the sub-quality natural gas and Claus-type processes?
2. Today, the benchmark process for hydrogen production is catalytic reforming of methane (CH₄) with steam. Is there a sulfur analog to steam methane-reforming (SMR) process? In other words, is it technically feasible to reform CH₄ with H₂S (instead of H₂O) yielding H₂ and CS₂ (instead of CO₂)? If so, is the technology available and what are the costs?
3. What are the potential outlets for CS₂ product and economics of H₂S/CH₄ reformation?

An updated summary of our findings for the Task I is given below:

1. According to the U.S. Geological Survey (USGS) estimate of the petroleum potential of the Alaska's Arctic National Wildlife Refuge (ANWR) - 1002 area, the total quantity of technically recoverable oil in the 1002 area (excluding State and Native areas) is 7.7 BBO (mean value), which is distributed among 10 plays (<http://pubs.usgs.gov/fs/fs-0028-01/fs-0028-01.htm>). USGS estimates put most of the oil in the western, undeformed part of the ANWR - 1002 area, in a number of accumulations rather than a single large one. Estimates of economically recoverable oil, expressed by probability curves, show increasing amounts of oil with increasing price. At prices less than \$13 per barrel, there is no commercially viable oil to be found, but at a price of \$30 per barrel, between 3 and 10.4 billion barrels of oil (BBO) may be available. Assuming 46.2% yield of gasoline from one barrel of crude oil, this is equivalent to about 6.5-22.5 quads of energy (assuming: 1 BBO= 2.1610512 quads). The economic analysis by USGS for ANWR - 1002 area oil included the costs of finding, developing, producing, and transporting oil to market based on a 12 percent after-tax return on investment, all calculated in constant 1996 dollars.

Based on the magnitude of H₂S resource recoverable from the lower 48 US sub-quality NG (SQNG) sweetening and hydrodesulfurization operations, we estimate that the energy value of H₂ extracted from the H₂S-rich feedstocks can exceed 10 quads. Considering the added energy value of the sweetened gas made available by a H₂S-CH₄ process (**Attachment 1** provides a complete Task I report that also appears at the this URL: <http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/30535bq.pdf>), we found that the amount of energy that can be recovered from SQNG wells within lower 48 US is comparable to that estimated to be available from the ANWR reserves - at a price of about \$30 per barrel or less.

2. Viable bi-functional catalysts are available commercially that catalyze H₂S-methane reformation reactions, efficiently. In particular, Cr₂S₃ and Ce₂S₃ are catalytically active in dissociating H₂S. These catalysts remain stable at temperatures as high as 1000°C (1273 K), resulting in H₂S reaction with the carbon precursors that form on their surfaces.
3. Economic analysis of the H₂S-methane reformation process based on the sulfided catalysts indicates that the process can be a viable alternative to the present day Claus process and associated Tail Gas Cleanup Units (TGCU). The cost of hydrogen produced by the H₂S-methane reformation process depends on the price of the co-produced CS₂ that varies between \$0.04 and \$0.23/lb (1995 US\$). This is shown in the Figure 1 below. The lower limit of the CS₂ price range corresponds to the price of recovered sulfur (\$0.04 to \$0.15/lb depending on purity). The upper limit corresponds to the price of CS₂ in the conventional markets. As the market value of CS₂ increases, the cost of hydrogen decreases, accordingly. At CS₂ prices above approximately \$0.10/lb, the revenue generated by selling CS₂ would be more than enough to offset the cost of hydrogen production.
4. Production of H₂SO₄ provides the best large-scale near-term niche market for consumption of CS₂ by-product from the H₂S-CH₄ reformation process. Other large-scale applications for sulfur generated from CS₂ include its use in road fills.

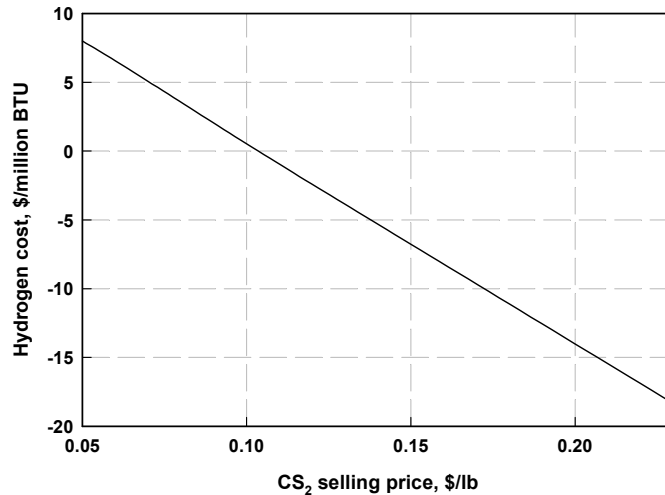


Figure 1- Comparison of CS₂ Selling Price and H₂ Cost.

I-2. Analysis of Hydrogen Production Using Ammonia and Ammonia-Borane Complex for Fuel Cell Applications

The goal for Task II effort was to determine the feasibility of using ammonia (NH₃), as a chemical carrier for hydrogen for mobile and stationary fuel cell applications. Of especial interest were issues related to the cost, safety, and performance of ammonia for the onboard hydrogen production using compact thermocatalytic reformers. The following facts constitute the rationale for conducting this analysis:

- Ammonia is readily available and a commodity product of the chemical industry with world production capacity exceeding 140 million tons.
- Ammonia is excellent hydrogen rich carrier- contains 17.8 wt% hydrogen.
- Price of anhydrous liquid ammonia (LNH₃) is about \$180 per short ton (May 2001, f.o.b. Gulf Coast) or less than \$7.50 per million BTU of hydrogen contained in ammonia.
- Technology for transportation, distribution, storage and utilization of ammonia is well established and widely available.
- Anhydrous LNH₃ can be stored under moderate pressure (about 370 psig) and its physical attributes mimic those of liquid propane.
- Anhydrous LNH₃ packs 40% more energy per unit volume than liquid hydrogen (with consideration of energy requirement for NH₃ decomposition but not for fuel preheating and evaporation). Anhydrous liquid ammonia stores 30% more energy per unit volume than LH₂ (taking into account the energy required for both NH₃ evaporation and splitting).
- Explosion limits for NH₃-air mixture (at 0°C, 101.3 kPa) is very narrow (*i.e.* 16 – 27 vol % NH₃) compared to that for H₂-air mixture (*i.e.* 18.3 – 59 vol % H₂).
- Autoignition temperature for NH₃ is 651°C, which is higher than that for H₂ (*i.e.* 585°C).

- Thermocatalytic decomposition of ammonia into hydrogen and nitrogen is a well-established technology.
- Ammonia used as hydrogen source for fuel cell power plants does not give rise to CO_x or NO_x emissions into the atmosphere.
- Just 16% of the available energy stored in ammonia is needed to split NH₃ into N₂ and H₂ (without consideration of fuel preheating and evaporation).
- Hydrogen from ammonia can be more readily used to operate alkaline fuel cells (AFCs) that are among the most developed, least costly and highly efficient fuel cell power plants.
- There was no U.S. DOE EERE Hydrogen Program funded effort on this subject.

In particular, our objectives were to address the following questions:

1. Where and when did the concept of "ammonia economy" come to being? How much ammonia is needed to meet the energy requirements of the U.S. transportation sector? What are the ramifications of implementing an ammonia economy? What are the main issues involving ammonia production, storage and distribution? What are the health and safety implications of widespread ammonia production and use, especially as transportation fuel in automobiles?
2. Can NH₃ be converted to hydrogen safely, efficiently and cost effectively? If so, is the technology available and adaptable for use in the future fuel cell powered vehicles?
3. Can the potential difficulties with the direct implementation of ammonia economy be overcome? If not, are there ways to mitigate the shortcomings of direct ammonia use as the transportation fuel in the U.S. markets?

According to the mineral commodity data compiled by the USGS, in 2000, 24 companies at 39 plants in the U.S. were producing ammonia. During the same year, the U.S. domestic ammonia production totaled nearly 15.8 million metric tons. More than half the U.S. ammonia production capacity is located in three States of Louisiana, Oklahoma, and Texas due to their large reserves of natural gas, the main domestic feedstock. The United States is the world's second largest NH₃ producer and consumer - behind China. In 2000, the U.S. ammonia consumption totaled slightly over 20 million metric tons, of which about 88% was for fertilizer use.

The concept of using ammonia as a hydrogen carrier is not new and has been discussed for almost 40 years. During early 1970s when the concept of "Hydrogen Energy Economy" was being widely debated, it was envisioned that ammonia would provide a perfect storage medium for hydrogen produced from the ocean thermal energy conversion (OTEC) plantships. In the early 1980s, Strickland at the Brookhaven National Laboratory (BNL) conducted a systems study to determine the economic prospects of using anhydrous liquid ammonia, produced by OTEC, as a hydrogen carrier for annual H₂ demand of 10-100 million standard cubic feet (SCF). He showed that OTEC NH₃ was competitive with H₂ made at the point of use via water electrolysis, steam reforming of natural gas, or OTEC LH₂, in the upper fifth of the use range. In another BNL study, three alternative transportation fuels (ATFs) were compared with respect to the input energy required for their production from NG, their H₂ storage capacity and cost per unit

of energy contained (\$/million BTU). The ATFs chosen were LH₂, hydrogen produced by steam reformation of methanol (MeOH), and via thermocatalytic dissociation of anhydrous LNH₃. The BNL results showed that LNH₃ had considerable advantage over MeOH and LH₂, coming very close to matching gasoline performance as a motor fuel.

The work of Strickland at BNL was complemented by the efforts of Ross at the Lawrence Berkeley National Laboratory (LBNL). In the early 1980s, Ross conducted a detailed experimental and analytical study on the use of indirect NH₃-air alkaline fuel cells (AFCs) for vehicular applications. Again, the impetus for his work was the belief that ammonia provided a feasible storage medium for H₂ produced from non-fossil sources, *e.g.* by the off-land OTEC or remote solar-thermal facilities. According to Ross, anhydrous LNH₃ provides an excellent medium for H₂ storage, even though energy is required to evaporate and dissociate NH₃ resulting in somewhat lower efficiencies. LBNL results showed the advantages of AFCs relative to acidic electrolyte fuel cells, *i.e.* 2-3 times higher power density and a factor of 2 lower components costs resulting in 4-6 times lower total power plant costs. In addition, the ammonia dissociation reaction and power characteristics of an alkaline fuel cell operating on cracked ammonia and air was determined. For a single cell unit, results obtained by Ross indicated that thermal efficiencies in the range of 34-44% at power densities of 1-2.2 kW/m² (using 1980s electrode technology) were possible.

As the 1980s drew to close and with the demise of non-fossil hydrogen production technologies as a near-term reality, ammonia disappeared as a viable hydrogen storage medium from the U.S. DOE programs. This is so because, in general, OTEC would be roughly twice as expensive as conventional energy forms due to the high capital cost of OTEC plants made under existing designs. It is often stated that a \$40/barrel oil cost would be necessary to spur investors into seriously considering OTEC technology. The total energy efficiency is lower with ammonia as the H₂ carrier versus methanol. Thus, if methane is the primary fuel, then methanol is the liquid fuel of choice for fuel cells, especially PEMFCs.

Presently, DOE's fuel cell for transportation program is focusing on the use of fossil fuels and for that reason ammonia is not presently considered as a viable H₂ carrier in that program. The NH₃ scenario was unique to the OTEC project, where the electrical energy would be generated at a remote location and it was not feasible to install either power lines or a hydrogen pipeline to the shore. Conversion to NH₃ and then shipping to shore seemed the most attractive way to store and transport the OTEC hydrogen. Using ammonia directly in a fuel cell then coupled nicely with that approach. In short, for non-fossil based solar produced hydrogen (see Task 3), NH₃ can still be a feasible storage medium and viable liquid fuel for fuel cells, in particular AFCs.

Among the persistent advocates of employing AFCs for automotive applications and LNH₃ as a high density H₂ storage medium are Kordesch and colleagues at the Technical University (TU) - Graz, Austria. According to Kordesch, using commercial off-the-shelf materials, an ammonia cracker can be fabricated providing on demand H₂ on-board fuel cell vehicles. In addition, ammonia is a more desirable fuel for AFCs, as the small

amounts of unconverted NH_3 that remains in the dissociated gas would not harm their function. Traditionally, the main problem with AFC technology has always been the problem with H_2 storage. In acid fuel cells, hydrogen can be stored as methanol and by steam reforming MeOH onboard the required H_2 for the fuel cell operation will be provided. The carbon oxides generated from the steam reformation of methanol do not present a problem to the acid fuel cell function. In the case of an alkaline fuel cell, the electrolyte would react with CO_2 forming problematic insoluble carbonate.

Considerable attention has been given to steam reforming of MeOH as a process for the generation of H_2 for fuel cells. Nonetheless, a comparison of the economics for H_2 production via NH_3 decomposition for alkaline fuel cells versus methanol reformation for acid fuel cells shows that ammonia decomposition is a more attractive process from an economic standpoint. Commercial ammonia is prepared at 99.5% purity (the impurity is mainly water which is harmless), whereas the higher alcohol impurities present in commercial methanol can result in production of contaminants during reforming that can lead to poisoning of the catalyst. Thus, the decomposition of ammonia appears to be an excellent choice for production of hydrogen for alkaline fuel cells as well as acid fuel cells if the unreacted NH_3 in the hydrogen stream is removed below an admissible level.

Earlier studies on ammonia decomposition catalysts and systems are given in a number of reviews. Briefly, NH_3 as fuel for AFCs requires no shift converter, selective oxidizer or co-reactants such as water as in other hydrocarbon or alcohol fuel cell power devices. Ammonia as a source of hydrogen permits a simple decomposition reactor design, simple operation and a low overall device weight and size. Catalysis plays a major role in ammonia decomposition. Among metal catalysts, ruthenium and iridium are the most active for NH_3 dissociation under mild conditions. Other compounds that exhibit high activity for NH_3 cracking include alloys such as Fe-Al-K, Fe-Cr, La-Ni (-Pt) and La-Co (-Pt). In general, noble metal containing catalysts are not used in the commercial processes due to high cost. The supported Ni catalyst has been widely used in industry but the required ammonia dissociation temperature can be as high as 1000°C . Transition metal nitrides and carbides, such as Mo_2N , VN, and VC_x , have also been tested for NH_3 decomposition. Tests, to date, show that the catalytic action of nitrides and carbides is similar to those of noble metals with respect to the reactions involving hydrogen.

The use of transition metal catalysts such as NiMo alloy has been tested for ammonia synthesis. However, ammonia decomposition on nitrated NiMo and other potentially interesting transition metal nitride catalysts have not been reported for NH_3 dissociation. Generally, NH_3 decomposition reaction is carried out at high temperatures, so $\alpha\text{-Al}_2\text{O}_3$ was used as the catalyst support. It has also been shown that the nitrated $\text{MoN}_x/\alpha\text{-Al}_2\text{O}_3$ and $\text{NiMoN}_x/\alpha\text{-Al}_2\text{O}_3$ are very active for NH_3 dissociation. For example, the ammonia conversion for $\text{NiMoN}_x/\alpha\text{-Al}_2\text{O}_3$ can be higher than 99% even at 650°C , and reaches a maximum of 99.8% when the atomic ratio of Ni/(Ni + Mo) is close to 0.60. This temperature is much lower than that required by the commercial catalysts such as the ICI's 10%-wt Ni on Al_2O_3 catalyst "47-1", Haldor Topsøe's triply promoted iron-cobalt catalyst "DNK-2R" or SÜD-Chemie 27-2, nickel oxide on Al_2O_3 . Recent XRD characterization of NiMo catalysts indicates that whenever the $\text{NiMo}/\alpha\text{-Al}_2\text{O}_3$ catalyst is

in oxidized form or nitrated form, it converts to the nitrated forms under the prevailing NH_3 dissociation conditions. The high activity of the nitrated $\text{MoN}_x/\alpha\text{-Al}_2\text{O}_3$ and $\text{NiMoN}_x/\alpha\text{-Al}_2\text{O}_3$ catalyst is mainly attributed to the nitrated phases, such as Mo_2N and $\text{Ni}_3\text{Mo}_3\text{N}$.

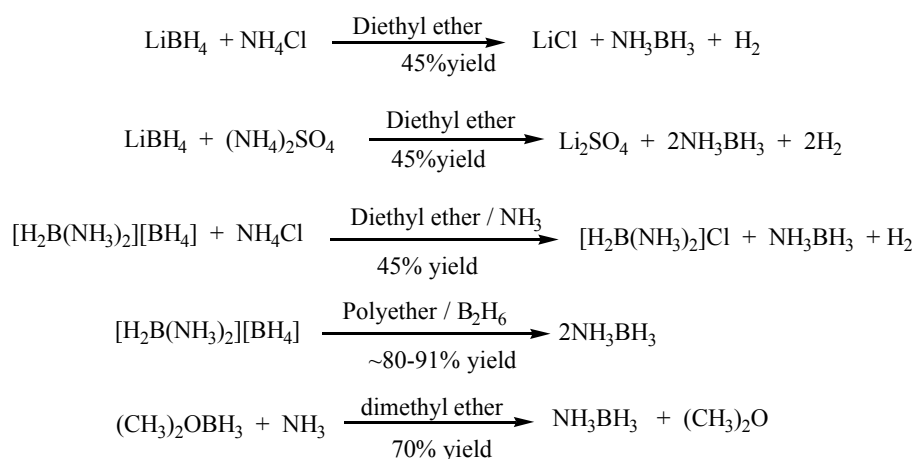
In addition to a number of University and government laboratories engaged in the development of new catalysts for ammonia dissociation, there are several companies involved in developing small NH_3 decomposition reactors. For example, with the support of Electric Auto Corporation (EAC), researchers at the Technical University (TU) - Graz have developed an 11.5 kW ammonia cracker that has a simple design and high efficiency. The work at the TU- Graz has involved improvement of commercially available catalyst materials (*i.e.* SÜD-Chemie 27-2, nickel oxide on alumina) and by addition of noble metals. Best results were obtained by simple addition of ruthenium salts to the nickel oxide catalyst. The catalyst pellets were crushed and sieved to obtain an average particle size of 1-1.5 mm. This was followed by the deposition of 0.3 g ruthenium per 100 g of nickel oxide catalyst. No cost data could be found on any of the TU-Graz/EAC ammonia dissociation reactors.

Unfortunately, despite all the benefits discussed above, the extreme toxicity of ammonia makes it difficult to envision its widespread use in the near future as a viable transportation fuel. In addition, due to the economic and energy efficiency considerations, it would be desirable to find a system that eliminates the need for dissociation devices or reactors onboard fuel cell powered vehicles.

These challenges were the focus of the Task II analysis. A paper describing Task II findings was presented at the 14th World Hydrogen Energy Conference in Montreal, Canada on June 10, 2002 (paper entitled "*Ammonia and Ammonia Adducts as Hydrogen Energy Storers on Board Fuel Cell Vehicles*") and given as **Attachment 2**. The complete task report is posted at URL: <http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/33098sec5.pdf>. Also, a more recent Task II follow on paper entitled "*Hydrogen Storage in Ammonia-Borane Complexes*," has been published in the *Proceedings of the 15th World Hydrogen Energy Conference*, held in Yokohama, Japan, June 26 - July 2, 2004. The following summarizes Task II findings:

One approach to mitigate the toxicity and other issues involving the on-board use of ammonia is to complex NH_3 with other hydrides so that the resulting compound is stable but not toxic and does not require storage under sub-ambient temperatures. A class of compounds (with generalized formula $\text{B}_x\text{N}_x\text{H}_y$) known as amine-boranes and some of their derivatives meet these requirements. The simplest known stable compound in this group is ammoniaborane, H_3BNH_3 (or borazane).

Ammoniaborane has a maximum hydrogen content of about 19.6-wt%, which is on the volumetric energy density basis about 4.94 kWh/L compared with 2.36 kWh/L for liquid hydrogen. At room temperature and atmospheric pressure, it is a white crystalline solid, stable in water and ambient air. Ammoniaborane can be synthesized through several procedures according to following Scheme:



There are alternative ways for preparing H_3BNH_3 that includes reaction of diborane with ammonia, decomposition of diborane diammoniate ($\text{H}_2\text{B}(\text{NH}_3)_2\text{BH}_4$) in ethers, base displacement by NH_3 on reactive Lewis salts of BH_3 , and reaction of NaBH_4 with ammonium carbonate in THF. Attempts to use most ammonium salts in liquid ammonia, ethers, or other inert solvents, give low H_3BNH_3 yields when reacted with hydroborate ion. The synthetic reaction of interest is the symmetric elimination of hydrogen from H_4BNH_4 , which is the principal reaction taking place in warm, dilute liquid ammonia solutions but side reactions hinder achieving a reasonable reaction rate. When ammonium sulfamate is used, reaction with NaBH_4 gives high yields (typically 70%) of H_3BNH_3 at a useful rate since $\text{HN}_4\text{SO}_3\text{NH}_2$ and NaBH_4 are both soluble in liquid ammonia.

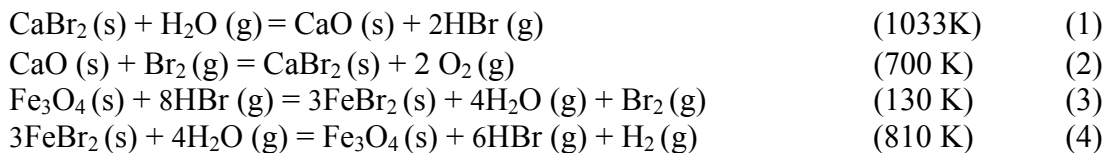
I-3. Analysis of Solar Thermochemical Water-Splitting Cycles for Hydrogen Production

A large hydrogen market already exists in the U.S. and elsewhere and it is growing rapidly to provide increasing amounts of hydrogen to oil refineries for upgrading heavy crude oils especially as the quality of the crude continues to decline. This hydrogen market is expected to continue growing at about 10%/yr, doubling by 2010 and doubling again by 2020. To transition to a "Hydrogen Economy" would take still more hydrogen. Serving all the US transportation energy needs with hydrogen would multiply current hydrogen demand by a factor of at least 18. To provide for all non-electric energy needs of the U.S. would require a factor of about 40 over current hydrogen production levels.

In the course of past thirty years or so, many process schemes have been devised to generate hydrogen from water. In particular, thermochemical water splitting cycles have been shown to achieve high overall heat-to-hydrogen energy conversion efficiencies. Presently, there are two prospective high temperature heat sources suitable for thermochemical process interface. They are solar thermal concentrator and central receiver systems, and nuclear power plants (*i.e.* high temperature gas-cooled reactors, HTGR). The nuclear option is not of direct interest to this work. The high flux, high temperature heat sources considered here are the solar concentrator/receiver systems.

The aim of the Task III analysis was to assess the state-of-the-technology for the thermochemical hydrogen production based on cycles/processes for splitting water. A systematic evaluation of the prospective cycles/processes were conducted with respect to the thermodynamic considerations, reaction kinetics, reactor and process design aspects, cost and performance considerations, safety issues, and possible environmental impact of the prospective cycles. In particular, two processes were analyzed in details: UT-3 and Westinghouse thermochemical water splitting cycles. Based on this analysis, we devised a new water splitting cycle based on sulfur ammonia system.

The UT-3 cycle (developed by Kameyama and Yoshida at the University of Tokyo, Japan) is a gas-solid cycle based on two pairs of hydrolysis (endothermic) and bromination (exothermic) reactions performed in four reactors arranged in series. In the process, only solid and gas reactants/products are used and the maximum temperature achieved is 1033 K. The cycle involves the following four gas-solid reactions:



The UT-3 process is one of the most studied thermochemical hydrogen production cycles in the world. We note that the UT-3 cycle had been envisioned originally for coupling to the advanced nuclear power reactors, *i.e.* high-temperature gas cooled nuclear reactors (HTGR). The reported cycle efficiency is in the range of 40 to 50%. UT-3 cycle operates by only changing the direction of the flow of reactant gas while the solid reactants remain fixed in the reactors. Other cycles including the so-called "sulfur family" cycles do not possess this superb operational advantage. However, in order to maintain the solid reactants in fixed bed reactors, the process gases have to flow, intermittently, in opposite directions. One reactor has to perform an endothermic hydrolysis reaction for about two hours and then switch and allow an exothermic reaction involving bromine to occur for the next two hours while the direction of flow changes. The requirement of reversing the gas flow and reactant compositions (with an intermediate purge) makes the process relatively inflexible and possibly difficult to control. The reaction 1 of the UT-3 cycle has been the slowest reaction, kinetically, of the four reactions involved, thus, being the rate-limiting step for the entire cycle. Since it is necessary, for the continuous operation of the cycle, that all of the reactions proceed at the same rate, the slow rate of calcium bromide hydrolysis does adversely affect the overall process efficiency. The following summarizes some of the more specific issues that required further development and refinement in this cycle.

1. Reactions 1 and 4 are endothermic hydrolytic reactions that require input heat. In contrast, reactions 2 and 3 are exothermic processes requiring heat removal from the reactors. Conducting both endothermic and exothermic reactions in one reactor is complex as two sets of heat exchangers are required, one for cooling and the other for heating bed materials.

2. Each cycle reportedly takes about two hours. When a new cycle begins, it takes time to reach a new steady state. The transient periods so created will reduce overall thermal efficiency of the process. Complicated heating and cooling is necessary to minimize the effects of transient periods leading to higher operational and capital costs.

3. As the heat transfer fluid as well as sweeping gas for the reaction products in the fixed bed reactors, the UT-3 process uses high temperature steam in excess as carrier gas and circulating media. Because the high temperature steam carries high heat duties, cooling the steam will result in excessive energy loss. To mitigate this, in the UT-3 cycle, the product hydrogen and oxygen are not separated from steam using common two-phase separators and instead membrane separation has been suggested. Molar concentrations of hydrogen and oxygen in the stream are low, typically less than 1% and 0.5%, respectively. Separating such a low concentration gases from steam via membranes is not very efficient. In addition, handling the large amount of steam required consumes energy causing parasitic power losses. To improve the separation efficiency, one can either increase total pressure or increase membrane surface area. Increasing total pressure in the system can reduce the conversion due to La Chatier effect, as the higher total pressure is unfavorable for hydrogen production. The reported hydrogen permeation of a support silica membrane is of the order of 10^{-7} to 10^{-8} mol m⁻² s⁻¹ Pa⁻¹ at 600 °C, while nitrogen permeation is below 10^{-11} mol m⁻² s⁻¹ Pa⁻¹. For example, to allow hydrogen production at a rate of 25 mol/s and a total pressure of 2.0 MPa, the membrane area required will be 125-1,250 m². To separate 12.5 mol/s of oxygen will require even larger membrane surface area. In all likelihood, the UT-3 cycle will involve hydrogen separation from a more complex mixture of H₂O, HBr and H₂, requiring even larger membrane surface areas.

4. UT-3 is a heterogeneous process involving gas-solid reactions. As noted above, the same reactor in the process has to perform both endothermic (hydrolysis) and exothermic (bromination) reactions. This dual operation complicates UT-3 reactor design considerably. This is so because endothermic reactions benefit from good heat isolation while exothermic reactions favor a reactor design that allows rapid heat removal from the reaction zone. These reactor design requirements are in conflict with one another.

5. Another important issue involves the lifetime of the UT-3 reactants/catalysts. Experimental results have shown that the rate of bromination decreases with cycling. (e.g. Fe₃O₄ → FeBr₂). Ideally, no solid reactants were to be consumed in the UT-3 reactions. However, in practice, this is not the case and effects of side reactions, attrition and reaction kinetic considerations become significant.

Proof-of-concept experiments for the UT-3 cycle have been carried out in Japan by testing a pilot unit named "MASCOT" (Model Apparatus for Studying Cyclic Operation in Tokyo) that produced H₂, continuously, at a rate of about 3 L·h⁻¹. The cyclic conversion of oxides to bromides and back generates major density variations. To handle that, the reactants CaO and Fe₃O₄ having a mean particle size of 0.5 μm were embedded in a matrix before pelletizing and loading into the reactors. The use of pellets as in the MASCOT plant is impractical because it results in doubling the quantity of material

needed in the process by addition of CaTiO_3 as well as continuous preparation of reactants. This is costly in terms of raw materials, process energetics and the overall hydrogen production efficiency.

It has been suggested recently by researchers at the Commissariat à l'Énergie Atomique, CEA-Marcoule, France (<http://www.waterstof.org/20030725EHECO1-95.pdf>), that fluidized bed reactors are better fit to UT-3 cycle. Unlike fixed bed reactors, they provide continuous stirring of the reactants, preventing sintering of solids and enhancing the reaction kinetics. In addition, it has been pointed out that UT-3 cycle could benefit from combining reactions 1 and 2 in a single fluidized bed reactor (*i.e.* reactants to include both water and bromine).

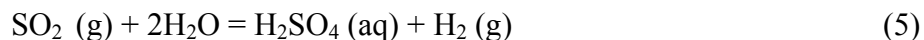
If a single reactor is used and the reactive gas enters the reactor at a temperature above 200°C with an $\text{H}_2\text{O}/\text{Br}_2$ molar ratio above 40 and subsequently heated to a temperature below 650°C , there is no risk of melting or sintering CaBr_2 or CaO-CaBr_2 eutectic mixture. In the fluidized bed reactor, Br_2 reacts first with CaO to form CaBr_2 , which then reacts with H_2O . The final equilibrium state reached is characterized by a CaO/CaBr_2 ratio that depends on the initial reactant composition and the reactor size. The differential fluidization of the products leads to decoupling of the reactions 1 and 2 since CaBr_2 is denser than CaO . Reactions 1 and 2 occur mainly in the upper and lower portion of the reactor, respectively.

The reactor off-gas stream contains a mixture of water, bromine, HBr and O_2 . Separation of products is accomplished by condensation of the $\text{HBr}/\text{H}_2\text{O}$ azeotrope (for HBr recovery without entraining Br_2 , which is not particularly soluble in water at this temperature). Further lowering the temperature to 50°C allows re-condensation of the $\text{H}_2\text{O}/\text{Br}_2$, recovering oxygen gas. Finally, the purified reactants are heated and returned to the reactor. A possible side reaction in the CEA scheme involves the formation of hypobromous acid HOBr directly from water and Br_2 . This species is unstable under ultraviolet light, and a radiation source such as solar would hinder its formation. CEA modification of UT-3 cycle by coupling reactions 1 and 2 would simplify the system and improve the cycle efficiency through better heat recovery. CEA researchers show that, based on the recovery of 65% of the total recoverable heat, a thermal efficiency of roughly 40% is achievable less the energy necessary for compression of the reactor outlet gas and for maintaining gas flow.

The original UT-3 cycle intended for coupling with HTGR. Later, a new version (*i.e.* adiabatic UT-3) was conceived for coupling with a solar heat source. In the new cycle, all four reactions are carried out, continuously, in adiabatic equipment where steam (or steam + nitrogen) is used as a vector. The adiabatic UT-3 cycle is conceptually simple. During sunshine hours, the energy is supplied to the process directly from the solar receiver. During dark periods, it is supplied from a thermal storage reservoir where the high temperature heat is stored during sunshine hours. The reported overall thermal and exergetic efficiencies of the solar/UT-3 cycle were estimated at 49.5% and 52.9%, respectively.

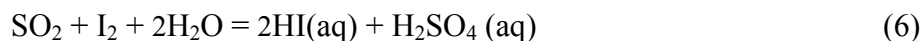
In short, there still remains several challenges with UT-3 cycle requiring further development including: 1) hydrogen and oxygen separation via membranes resulting in possible scale-up difficulties; 2) hydrogen and oxygen are produced at subatmospheric pressures and require compression during the process; 3) solid reactants/catalysts attrition may occur in non-steady state operation of the cycle; and 3) the fact that potential for the cycle efficiency improvement is limited by the melting point of CaBr_2 .

Unlike the UT-3 process, the Bowman-Westinghouse cycle is a two-step hybrid (*i.e.* "heat plus work") cycle, in which sulfur dioxide is electrolytically oxidized to produce H_2 and sulfuric acid as follows:

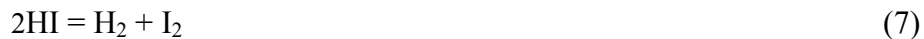


The product, sulfuric acid, is then concentrated and vaporized into sulfur trioxide; the later is then reduced to sulfur dioxide and oxygen. By compressing sulfur dioxide, oxygen is separated and sulfur dioxide is then recycled into an electrolyzer where a new cycle begins. This cycle, originally proposed by Bowman, is the basis of the so-called "Westinghouse cycle" and Mark 11 cycle developed at the Commission of the European Communities Joint Research Center (JRC), Ispra, Italy. The Bowman-Westinghouse cycle is a "hybrid" thermochemical cycle. In the hybrid cycles, there is always a compromise between the extent of acid concentration and required cell voltage. For the Mark 11 cycle, an electrolytic cell operating at 0.55 V would produce an acid solution of 50 wt% at 90°C. The cell voltage increases to 0.62 V for an acid concentration of about 55 wt%. Variations of the Bowman-Westinghouse cycle include the following sulfur family cycles:

- Sulfur-Iodine cycle: Bunsen reaction involving iodine and thermal decomposition of hydroiodic acid (HI) - In addition to acid decomposition step, the following reactions are employed:



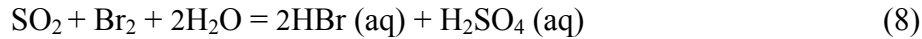
Followed by thermal decomposition of hydroiodic acid:



This cycle, proposed by Norman, is the basis of the General Atomic (GA) and JRC-Mark 16 cycles. The Sulfur-Iodine cycle is an all-liquid/gas process. If reactants in the Bunsen reaction are used in a stoichiometric ratio, the yield is very poor. To improve the kinetics and facilitate separation of the reaction products into two liquid phases, the reaction must be carried out using a large amount of excess water and I_2 . Excess water causes the physical separation and thermal decomposition of HI to be very energy-intensive. Researchers at RWTH Aachen have further improved on the GA process by devising a new scheme for direct decomposition of hydroiodic acid and eliminating the need for phosphoric acid as extraction agent for HI. The result is improved energetic and an overall efficiency of about 50% estimated.

The advantages of the S-I cycle are: 1) all fluid continuous process, chemicals all recycled and no effluents; 2) reactions all have been demonstrated; and 3) offers one of the highest efficiency quoted for any water-splitting process, *i.e.* 52%. The challenges still remaining are: 1) requires high temperature, 800°C; 2) has not been demonstrated as an integrated closed loop cycle; and 3) process cost and economics are unknown.

- Cycles based on the bromine and electrolysis of hydrobromic acid (HBr) - In addition to decomposition of sulfuric acid, the cycle includes the following reactions:



Followed by the decomposition of hydrobromic acid via an electrochemical step:



Again, this cycle, originally conceptualized by the late Bowman, is the basis of the Mark 13 hybrid cycle developed at the JRC, Ispra, Italy. The electrolytic decomposition of HBr requires a cell voltage of approximately 0.80 V (for acid concentration of 75 wt%). This voltage is higher than the electrolytic step in the Westinghouse cycle, but still less than direct water electrolysis.

These sulfur family cycles (especially, the S-I thermochemical water-splitting cycle) are envisioned to couple to the Modular Helium Reactor (H₂-MHR) for H₂ production and just as the UT-3 cycle, they are not truly intended for solar power interface. Unlike these water-splitting cycles, the SynMet process, conceived at the Paul Scherrer Institute in Switzerland, has been developed from the beginning for direct interface with solar central receivers. A brief description of SynMet process is given below:

SynMet process for solar co-production of zinc and syngas - The idea behind this process is to combine ZnO-reduction and CH₄-reforming processes within a novel solar reactor. It consists of a gas-particle vortex flow confined to a solar cavity-receiver that is exposed to concentrated solar irradiation. A 5-kW reactor has been built at the Paul Scherrer Institute (PSI) and tested in a high-flux solar furnace. Natural gas is used as a reducing agent to process ZnO according to the following overall reaction:



The advantages of the PSI's SynMet process are: 1) methane is reformed in the absence of catalysts and the process can be optimized to produce syngas especially suited for methanol synthesis; 2) evolved gases are valuable commodities justifying their collection, eliminating emissions to the environment; and 3) co-production of zinc and syngas avoids CO₂ emissions in the traditional carbothermal reduction of ZnO.

The PSI process is in an advanced development stage. Results obtained, to date, indicate that co-production of zinc and synthetic gas from ZnO and natural gas upgrades the

calorific content of the initial reactants by as much as 39% while reducing CO₂ emissions by up to 78% in comparison to the traditional carbothermal ZnO reduction process. The main issue with the SynMet process is just that - it is not really a true water-splitting cycle, in that it utilizes a fossil fuel (*i.e.* methane/natural gas) and intended to produce synthetic gas for production of methanol (instead of hydrogen only). The essence of SynMet process has been to combine solar thermochemical hydrogen production and storage processes into one practice. SynMet process would be an ideal process for solar thermochemical hydrogen production if renewables-based methane were available at or near the plant site and direct methanol fuel cells (DMFCs) could be developed to full potential in time to utilize it. As it stands right now, DMFCs have serious problems with respect to power density that is an order of magnitude less than that of PEMFCs (this stems from the low current exchange within DMFC MEAs) that limits their use especially as vehicular power source. Moreover, there are several other technical issues needing resolution before SynMet process really becomes viable.

To mitigate the above-mentioned shortcomings, at the Florida Solar Energy Center (FSEC), we have conceived a new sulfur-ammonia cycle that is a better fit for use with the solar power source (see **Attachment 3** for complete Task III description). The sulfur dioxide solubility issues that hinder the application of the standard sulfur family cycles do not affect this cycle. FSEC's sulfur-ammonia cycle is depicted in Figure 2. A flowsheet of the cycle is given in Figure 3. Aqueous solution of ammonium sulfite is fed into a photocatalytic reactor via stream 10 where ammonium sulfite oxidizes to form ammonium sulfate and hydrogen by concurrent decomposition of water. Ammonium sulfate, stream 1, is then decomposed into ammonia gas and steam.

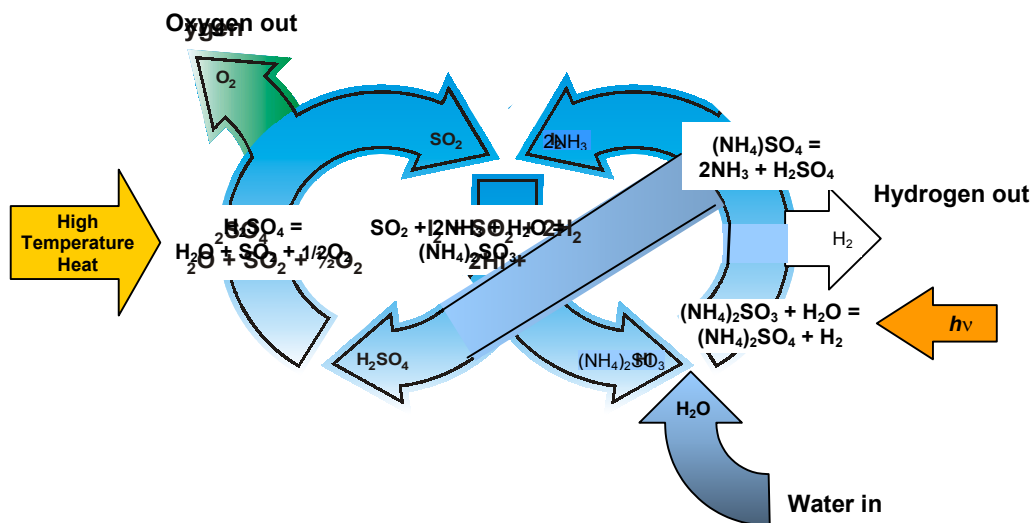


Figure 2. A schematic diagram of FSEC's sulfur-ammonia cycle.

Through decomposer, liquid sulfuric acid, stream 3, is fed into acid vaporizer that generates gaseous sulfur trioxide and water vapor. The sulfur trioxide is then converted to sulfur dioxide gas and oxygen, streams 4-6, within a decomposition reactor. Small amounts of sulfuric acid still remaining can be separated from the gaseous mixture

containing sulfur dioxide, oxygen and water using an acid scrubber. Sulfuric acid removed is then recycled, via stream 7, and sulfur dioxide and oxygen are mixed, *i.e.* streams 8 and 9, with ammonia and chemically adsorbed to regenerate ammonium sulfite to be recycled into the photocatalytic reactor and complete the cycle.

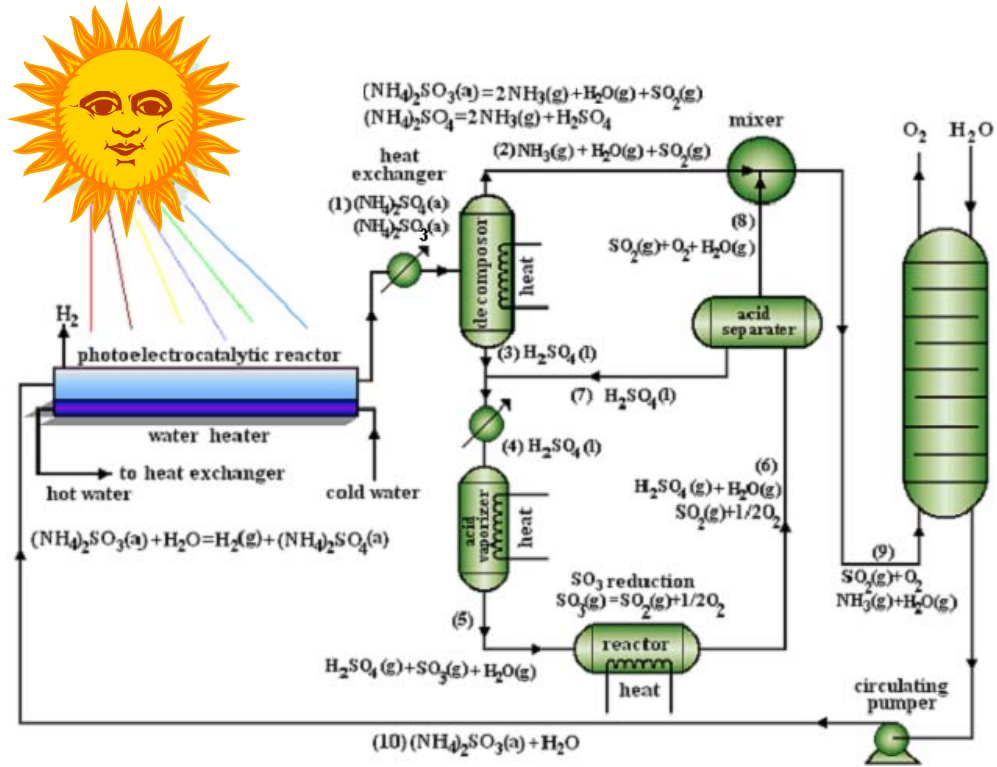
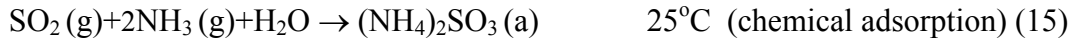
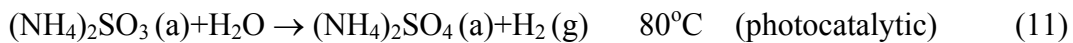


Figure 3. Flowsheet for FSEC's sulfur-ammonia cycle.

In the adsorption unit, oxygen is separated from the stream. Reactions involved in FSEC's sulfur-ammonia cycle are:



Among these reactions, reactions (11), (12) and (15) are unique to this new cycle. Reactions (13) and (14) are common to all sulfur family cycles.

This new, award-winning cycle (see **Attachment 4**) has the potential to achieve high overall efficiency utilizing only non-toxic and inexpensive chemicals. Solar energy is applied as a heat source and promotes the photocatalytic redox reaction. Experimental results on the photolytic oxidation of sulfite ions indicate that photolytic oxidation proceeds at acceptable rates and there are no indications of side reactions.

II. PUBLICATIONS/PRESENTATIONS

1. Huang, C., and A. T-Raissi "Systematic Analyses of Solar Hydrogen Production via Sulfur-Iodine Thermochemical Cycle Part II- Evaluation of Kinetic Models for the Decomposition of Sulfur Trioxide", for presentation at the 2005 *Solar World Congress* in Orlando and publication in *Solar Energy Journal*.
2. Huang, C. and A. T-Raissi, "Systematic Analyses of Sulfur-Iodine Thermochemical Cycle, Part II - Evaluation of Kinetic Models for the Decomposition of Sulfur Trioxide," submitted to *Solar Energy Journal*.
3. Huang, C. and A. T-Raissi, "Systematic Analyses of Sulfur-Iodine Thermochemical Cycle, Part I - Simulation of Purification and Decomposition of Sulfuric Acid," Special Issue of *Solar Energy Journal*, in press.
4. T-Raissi, A., and D.L. Block, "Hydrogen: Automotive Fuel of the Future," *IEEE Power & Energy Magazine*, 40-5, November/December, 2004.
5. Huang, C., and A. T-Raissi, "Analysis of New Solar Thermochemical Water-Splitting Cycles for Hydrogen Production," *Proc. of the 15th World Hydrogen Energy Conf.*, Yokohama, Japan, June 27- July 2, (2004).
6. Mohajeri N., and A. T-Raissi, "Hydrogen Storage in Ammonia-Borane Complexes," *Proc. of the 15th World Hydrogen Energy Conf.*, Yokohama, Japan, June 27- July 2, (2004).
7. Muradov, N.Z., A. T-Raissi, and T. Robertson, "Hydrogen Production via Catalytic Reforming of Low-quality Methane Containing Feedstocks," *Proc. of the Hydrogen Power Theoretical and Engineering Solutions International Symposium (HYPOTHESIS)*, Porte Conte, Italy, Sept. 7-10, 2003.
8. T-Raissi, A. "Hydrogen Storage in Ammonia and Aminoborane Complexes," Presentation at the Hydrogen Program Annual Review, Berkeley, CA, May 21, 2003.
9. T-Raissi, A. and C. Huang, "Technical Analysis of Hydrogen Production," A Semi-Annual Contract Report to U.S. DOE under DEFC3600GO10603, February 2003.
10. T-Raissi, A. "Chemical Storage - Overview," Keynote speech at the DOE Hydrogen Storage Workshop, Argonne National Laboratory, Argonne, IL, August 14, 2002.
11. T-Raissi, A. "Technoeconomic Analysis of Area II Hydrogen Production, Part II," *Proc. of the U.S. DOE Hydrogen Prog. Annual Review*, Golden, CO, May 7, 2002.
12. Linkous, C.A., C. Huang, J. Fowler, G. Scott, A. T-Raissi, N.Z. Muradov. "Closed Cycle Photochemical Methods for Deriving Hydrogen from Hydrogen Sulfide," *Proc. of the 14th World Hydrogen Energy Conf.*, Montreal, Canada, June 9-13, 2002.
13. A. T-Raissi, "Ammonia and Ammonia-Borane Complexes as Hydrogen Energy Storers for Fuel Cell Applications," at Session A2.8: Hydrides II, *14th World Hydrogen Energy Conf.*, Montreal, Canada, June 10, 2002.
14. T-Raissi, A. "Technoeconomic Analysis of Area II Hydrogen Production - Part I," *Proc. of the U.S. DOE Hydrogen Program Review*, Baltimore, MD, Apr. 17-19, 879-905, 2001.

III. SPECIAL RECOGNITIONS & AWARDS/PATENTS

1. T-Raissi, A., and C. Huang, "Innovative Technology Award," *15th World Hydrogen Energy Conf.*, Yokohama, Japan, June 27- July 2, (2004).

TECHNOECONOMIC ANALYSIS OF AREA II HYDROGEN PRODUCTION - PART 1[#]

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Abstract

The aim of this analysis is to assess the issues of cost, safety, performance, and environmental impact associated with the production of hydrogen by so called "Area II" technologies, not presently funded by the U.S. DOE Hydrogen Program. The hydrogen (H₂) rich feedstocks considered are: water, hydrogen sulfide (H₂S) rich sub-quality natural gas (SQNG), and ammonia (NH₃). Three technology areas to be evaluated are:

- 1) Thermochemical H₂S reformation of methane with and without solar interface,
- 2) Thermochemical water-splitting cycles suitable for solar power interface,
- 3) Catalyzed micro-reformers for decomposing ammonia.

This project is a two-year effort with following objectives:

- Analysis of the feasibility of the technology areas 1-3 from technical, economical and environmental viewpoints.
- Evaluation of the cost of hydrogen production by technology areas 1 & 2.
- Feasibility of the technology area 3 as a means of supplying H₂ to fuel cell power plants.

This paper provides the first account of our analysis pertaining to the technoeconomic aspects of H₂S-methane reformation, magnitude of the H₂S resource and other issues of interest.

[#] Proceedings of the U.S. DOE Hydrogen Program Annual Review, Baltimore, MD, April 18, 2001.

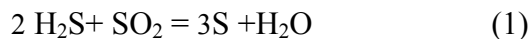
Thermochemical, CO_x-Free, H₂S Reformation of Methane

Background

Approximately one-third of the U.S. natural gas (NG) resource is low or sub-quality gas (SQNG) that does not meet market specifications for pipeline shipment (Hugman et al. 1993). Typical specifications call for gas with no more than 4 percent total carbon dioxide, nitrogen, and other inert gases; and 4 parts per million of hydrogen sulfide (H₂S) gas (Semrau et al. 1995). Some sub-quality gas can be blended with higher quality gas to meet market requirements. However, much of the sub-quality gas is too costly to upgrade and simply shut in.

Hydrogen sulfide concentration in NG varies from traces to 90% by volume. The Smackover zone and a deeper, contiguous zone called the Cotton Valley pinnacle reef in East Texas contain deposits wherein the subterranean gas composition at one location has been measured to contain as high as 87% by volume H₂S gas (Meyer 2000). Elsewhere, other examples of "ultra-sour" gas include: China's Zhaolanzhuang (60-90% H₂S), Canada's Caroline and Bearberry gas fields in West-Central Alberta (70-90% H₂S), Astrakhan gas field by Caspian sea (26% H₂S), and Lacq gas field in France (15% H₂S), to name just few (Kappauf 1985, Ullmann's 1989, Clark 1990).

In natural gas processing, H₂S is viewed as a pollutant requiring treatment and removal. Presently, H₂S is separated from hydrocarbon gases by amine adsorption and regeneration producing acid gas containing 10-90% by volume H₂S. When H₂S concentrations exceed 40%, gas is treated (or "sweetened") in the Claus plant (Cox et al. 1998). That is, a portion of the H₂S is burned to make SO₂, and then recombined with the main H₂S stream in a catalytic reactor to produce elemental sulfur and steam according to:



Elemental sulfur is sold as a feedstock for sulfuric acid manufacture. In Claus process, hydrogen in the H₂S is converted to water vapor. Furthermore, since Claus units do not convert all the H₂S to sulfur, tail gas cleanup units are needed to remove traces of SO₂ before the off-gases can be vented to atmosphere (Erekson 1996). It would be advantageous to perform H₂S conversion in a manner so that to recover and recycle its hydrogen content.

Finally, each year, U.S. refineries spend a quarter of billion dollars to produce hydrogen needed for hydrodesulfurization of refinery products (Doctor 1999). This hydrodesulfurization process generated more than 5.5 million tons of hydrogen sulfide waste gas in 1996 (Swain 1999). Furthermore, the review of the historical data on crude oil gravity and sulfur content indicates that generally lower quality crudes are being processed in the U.S. (Swain 2000). If one could recover the equivalent amount of H₂ from the refineries' waste H₂S stream, it would provide a significant fraction of the hydrogen now used for petroleum refining and upgrading.

Thus, the impetus for this study was to determine the potential for improving the overall economics of the H₂S reformation of natural gas (particularly CH₄) to hydrogen and carbon disulfide (CS₂, instead of CO₂, as in the SMR process). A viable process for H₂S reformation of methane should result in more SQNG to be made available for pipeline use as well as additional

onsite H₂ to become available for the refinery use. At this point, the main questions that need to be addressed are as follows:

1. What is the magnitude of the resource, *i.e.* how much H₂ can be recovered from H₂S present in the sub-quality natural gas and Claus-type H₂S?
2. Today, the benchmark process for hydrogen production is catalytic reforming of methane (CH₄) with steam. Is there a sulfur analog to steam methane-reforming (SMR) process? In other words, is it technically feasible to reform CH₄ with H₂S (instead of H₂O) yielding H₂ and CS₂ (instead of CO₂)? If so, is the technology available and what are the costs?
3. What are the potential markets and/or outlets for CS₂ product from H₂S/CH₄ reformation?
4. What are the environmental implications of H₂S reformation of natural gas with regard to reduction of greenhouse gases and potential use of solar thermal power?

In the following sections, we present results of our analysis and findings to questions above.

Magnitude of the H₂S Resource

A question is often asked as to the magnitude of H₂S resource. We note that the sub-quality natural gas containing unacceptable levels of H₂S comprises about 14% of the U.S. gas reserves (Dalrymple et al. 1994). Distribution of major H₂S regions in the lower-48 States has been compiled by Hugman et al. (1993). The report identifies about 20 Tcf of H₂S-contaminated sub-quality natural gas reserves. A summary of the more highly contaminated regions/plays is given in Tables 1&2. Based on the measured concentration of hydrogen sulfide (see Tables 1&2), an estimate of the magnitude of H₂S resource has been made and given in Table 3. We have also calculated and tabulated the higher heating value of hydrogen produced from H₂S (if all of it were converted to H₂ instead of Claus treatment) via CH₄ reformation. Furthermore, we have given the range of unexplored oil within Alaska's Arctic National Wildlife Refuge (ANWR). We assumed 46.2% yield of gasoline from one barrel of crude oil, see 1998 EIA data (Davis 2000).

The energy potential of the ANWR reserves that can be converted and used to produce gasoline is then calculated to lie between about 3.2 and 36 quads (actually, closer to 3.2 than 36) (King 2000). The data of Table 3 indicates that potentially comparable amount of energy can be had by efficient conversion of H₂S to clean CO_x-free hydrogen. Therefore, it is worthwhile not to burn H₂S in the process of upgrading the sub-quality natural gas reserves. Note that H₂S in the present SQNG reserves within the lower-48 States can yield hydrogen with energy content comparable to that from ANWR reserves. This resource can be made available where it is needed most (*i.e.*, the lower-48 States) without any threat to the pristine environment of the Alaska's ANWR.

Processes for H₂ Generation from Methane and Hydrogen Sulfide

Steam Methane Reforming (SMR)

The benchmark process for H₂ production is catalytic reforming of NG with steam according to:



Table 1. Range of H₂S content of discovered and undiscovered sub-quality natural gas in the lower-48 United States - *non-associated gas data*[#] (Hugman 1993).

Basin/Formation	H ₂ S (vol%)		Amount of NG (Bcf)			H ₂ S content (Bcf)		
	Mean	Max	a	b	c	a'	b'	c'
Mid Gulf Coast/Smackover	14.957	45.7	254	1289	2201	116.1	589	1006
Mid Gulf Coast/Norphlet	1.867	7.7	165	1844	4403	12.7	142.0	339
Michigan/Niagaran Salina	0.405	5.94	309	22	371	18.4	1.3	22.0
Michigan/Other	0.483	13	8	33	216	1.0	4.3	28.1
Arkla/Smackover	4e-3	0.1	98	864	2913	0.1	0.9	2.9
East Texas/Pettit	0.028	4	342	345	239	13.7	13.8	9.6
East Texas/Cotton Valley	0.187	11.954	2949	734	749	352.5	87.7	89.5
East Texas/Smackover	14.71	47.35	607	303	330	287.4	143.5	156.3
East Texas/Other	0.313	2.927	352	76	669	10.3	2.2	19.6
Louisiana Gulf Coast/Other	1e-3	0.2	5876	11156	19911	11.8	22.3	39.8
Texas Gulf Coast/Miocene	0.054	0.632	143	315	684	0.9	2.0	4.3
Texas Gulf Coast/Frio	4e-3	0.48	1622	3073	6677	7.8	14.8	32.0
Texas Gulf Coast/Vicksburg	0.013	0.1	1082	1851	4026	1.1	1.9	4.0
Texas Gulf Coast/Austin Chalk	0.228	2.194	50	160	348	1.1	3.5	7.6
Texas Gulf Coast/Edwards	1.347	8.222	315	949	2060	25.9	78.0	169.4
Texas Gulf Coast/Other	0.244	2.483	3780	12477	27119	93.9	309.8	673.4
Powder River/Other	1e-3	0.58	41	53	1309	0.2	0.3	7.6
Big Horn/Frontier	0.147	4	125	134	382	5.0	5.4	15.3
Wind River/Cody	4e-3	2.725	371	439	1048	10.1	12.0	28.6
Wind River/Frontier	3.624	4.458	262	360	1916	11.7	16.0	85.4
Wind River/Phosphoria	5.095	14	38	69	165	5.3	9.7	23.1
Wind River/Madison	11	11	0	0	2641	0.0	0.0	290.5
Green River/Frontier	3e-3	0.05	2310	392	4873	1.2	0.2	2.4
Green River/Phosphoria	13.4954	34.9	5	2	25	1.7	0.7	8.7
Green River/Weber	1.031	2.6	376	187	2734	9.8	4.9	71.1
Green River/Madison	2.778	4.6	368	634	8199	16.9	29.2	377.2
Paradox/Mississippian	0.93	1.178	15	9	535	0.2	0.1	6.3
San Juan/Mesaverde	0.016	0.317	6057	849	474	19.2	2.7	1.5
San Juan/Other	0.118	5.9	85	0	409	5.0	0.0	24.1
Overthrust/Weber	21.34	21.34	17	178	2376	3.6	38.0	507.0
Overthrust/Madison	14.838	14.838	782	5543	6311	116.0	822.5	936.4
Overthrust/Sun River	0.1	0.1	5	13	2970	5.0e-3	1.3e-2	3.0
Overthrust/Big Horn	3.858	6.783	54	275	4158	3.7	18.7	282.0
Anadarko/Chase	0.016	0.099	7777	2126	604	7.7	2.1	0.6
Anadarko/Marrow	2e-3	0.016	5124	5665	19183	0.8	0.9	3.1
Anadarko/Chester	1e-3	0.12	751	788	2674	0.9	0.9	3.2
Anadarko/Hunton	0.149	0.763	857	332	314	6.5	2.5	2.4
Anadarko/Other	5e-3	1.028	2868	3140	10630	29.5	32.3	109.3
Permian/Yates	6.7	11.497	168	67	197	19.3	7.7	22.6
Permian/Queen	0.402	4.992	183	67	197	9.1	3.3	9.8
Permian/Grayburg	0.585	1.233	14	58	81	0.2	0.7	1.0
Permian/Clear Fork	0.463	1.421	16	65	94	0.2	0.9	1.3
Permian/Tubb	0.478	1.358	14	44	61	0.2	0.6	0.8
Permian/Wichita Albany	0.458	0.786	53	181	256	0.4	1.4	2.0
Permian/Wolfcamp	0.182	0.652	735	1345	1903	4.8	8.8	12.4
Permian/McKnight	1.396	1.396	16	85	122	0.2	1.2	1.7
Permian/Cisco	0.172	0.485	32	113	158	0.2	0.5	0.8
Permian/Strawn	6e-3	0.434	445	1306	317	1.9	5.7	1.4
Permian/Atoka	7e-3	0.604	315	931	1317	1.9	5.6	8.0
Permian/Morrow	0.035	3.367	781	2345	3318	26.3	79.0	111.7
Permian/Pennsylvania	0.075	0.2	673	1881	2659	1.3	3.8	5.3
Permian/Devonian	0.304	12.5	1482	818	1741	185.3	102.3	217.6
Permian/Silurian	0.238	0.525	101	851	1203	0.5	4.5	6.3
Permian/Fusselman	0.461	1.229	221	204	554	2.7	2.5	6.8
Permian/Montoya	0.199	1.024	15	95	134	0.2	1.0	1.4
Permian/Ellenburger	0.019	0.365	1493	1635	3246	5.4	6.0	11.8
Permian/Other	0.403	3.842	390	1371	1939	15.0	52.7	74.5
Eastern Gulf of Mexico/Norphlet	5.23	5.73	3198	6795	25402	183.2	389.4	1455.5
Gulf of Mexico/Miocene	0	5.5	10329	29053	46797	568.1	1597.9	2573.8

[#] Notes: a,a') current proven reserves; b,b') reserve expected growth in existing fields; and c,c') anticipated new field potential.

Table 2. Range of H₂S content of discovered and undiscovered sub-quality gas in the lower-48 United States - associated & dissolved gas data (Hugman 1993).

Region/Depth (ft)	H ₂ S (vol%)		Current proven	H ₂ S content of the
	Mean	Max	Gas reserves (Bcf)	Associated gas (Bcf)
MAFLA Onshore/10,000-15,000	0.505	1.8	87	1.6
Midwest/5,000-10,000	0.07	7.232	231	16.7
Arkla, East Texas/0-5,000	2e-3	2.755	620	17.1
Arkla, East Texas /5,000-10,000	5e-3	3.8	741	28.2
Arkla, East Texas /10,000-15,000	0.015	5.23	50	2.6
South Texas/0-5,000	0.811	2.194	269	5.9
South Texas /5,000-10,000	0.227	7.091	1776	125.9
South Texas /10,000-15,000	1.079	2.132	74	1.6
Williston/unknown	2.298	11.96	88	10.5
Williston /0-5,000	1.839	3.8	76	2.9
Williston /5,000-10,000	10.608	29	220	63.8
Williston /10,000-15,000	3.006	12	212	25.4
Foreland/unknown	0.132	5	142	7.1
Foreland /0-5,000	2.131	15.976	216	34.5
Foreland /5,000-10,000	0.053	44	770	338.8
Foreland /10,000-15,000	0.368	20	165	33.0
Western Thrust Belt/5,000-10,000	8.337	10.749	113	12.1
Western Thrust Belt /10,000-15,000	0	0.22	315	0.7
Mid-continent/unknown	0.072	0.072	654	0.5
Mid-continent /5,000-10,000	1e-3	0.4	709	2.8
Permian Basin/unknown	0.491	1.36	319	4.3
Permian Basin /0-5,000	0.908	12.5	1592	199.0
Permian Basin /5,000-10,000	3.192	5.8	4135	239.8
Permian Basin /10,000-15,000	0.036	0.7	402	2.8

Table 3. Summary of the sub-quality gas data for combined non-associated and associated/dissolved gas in the lower-48 United States.

Resource	Current proven reserves	Expected growth in existing fields	Anticipated new field potential
Total SQNG, Tcf	80.9	106	238.5
H ₂ S content of SQNG, Tcf	3.4	4.7	9.9
H ₂ Equiv. H ₂ S of SQNG, Tcf	6.3	8.6	18.2
HHV of Equiv. H ₂ from H ₂ S, Quads	2.0	2.8	5.9
ANWR coastal plain, Bbbl/(Quads)	5.7-16/(3.2-36)		

The carbon monoxide (CO) formed during steam reforming reaction above reacts with excess steam, concurrently, to form CO₂ and more H₂ via the exothermic shift reaction:



The net chemical process for steam methane reforming is then given by:



Indirect heating provides the required overall endothermic heat of reaction for the SMR process. In autothermal (or secondary) reformers, the oxidation of methane supplies the necessary energy and carried out either simultaneously or in advance of the reforming reaction. The equilibrium of the methane steam reaction and the water-gas shift reaction determines the conditions for

optimum hydrogen yields. The optimum conditions for H₂ production require: high temperature at the exit of the reforming reactor (800-900°C), high excess of steam (molar steam-to-carbon ratio of S/C= 2.5-3) and relatively low pressures (below 30 atm). Most commercial plants employ supported nickel catalysts to perform SMR process (Ullmann's 1989).

The steam-methane reforming process described briefly above would be an ideal hydrogen production process if it was not for the fact that large quantities of natural gas (NG), a valuable resource in itself, are required as both feed gas and combustion fuel. For each mole of methane reformed, more than one mole of carbon dioxide is co-produced and discharged into the atmosphere. This is a major disadvantage as it results in the same amount of greenhouse gas emission as would be expected from direct combustion of NG or methane. In other words, production of H₂ as a clean burning fuel via steam reforming of methane and other fossil-based hydrocarbon fuels does not make sense, environmentally, if in the process, carbon oxide gases (CO_x) are generated and released into the atmosphere. Moreover, as the reforming process is not 100% efficient, some of the energy value of the hydrocarbon fuel is lost by conversion to hydrogen but with no tangible environmental benefit, *i.e.* reduction in emission of greenhouse gases. Despite that, the SMR process has the following advantages:

- Produces 4 moles of H₂ for each mole of CH₄ consumed.
- Feedstocks for the process (*i.e.* methane and H₂O) are readily available.
- Can use a wide range of hydrocarbon feedstocks besides methane.
- All process steps are well developed, *e.g.*, desulfurization, hydrocarbon reforming, etc.
- Can operate at temperatures in the range of 800-900°C.
- Operates at low pressures, less than 30 atm.
- Requires low excess steam: S/C ratio of 2.5-3.
- Low reforming input energy required (*i.e.* approximately 17% of the HHV of output H₂).
- Good process energetics, *i.e.* high input energy utilization (reaching 93%).
- Can use catalysts that are stable and resist poisoning.
- Good process kinetics.
- None of the process steps requires expensive materials and/or components.
- No problem with excessive soot formation or carbon lay down.
- No toxic chemicals produced or used.
- Has relatively low capital and operating costs.

Pyrolysis of Natural Gas and Methane

Since natural gas is readily available, relatively cheap resource and composed mainly of CH₄ (with small amounts of other mostly aliphatic hydrocarbons such as ethane, propane and butane), some thermocatalytic processes have sought to decompose NG hydrocarbons, directly (*e.g.* Dahl 2001, Arild 2000, Weimer et al. 2000, Uemura 1999, Muradov 1998, Wamnes 1997, Gaudernack 1996, and Steinberg 1987) according to:



One of the objectives in these processes is to fix the carbon content of the fuel, to be recovered in a form that is hopefully a salable product (*i.e.* activated carbon, carbon black or other non-graphitic varieties). By far, industrially, the most widely utilized type of carbon is carbon black or furnace black. Carbon black industry is well established and more than 100 years old. Although the list of applications for carbon black is long, about 90% of the production is used in a single application that is as a reinforcing agent and filler for rubber compounds employed in tires and automotive industry.

Carbon black constitutes 20-35% of the mass of automotive tires (Piskorz 1999). Paraffinic hydrocarbons are the best raw material for the production of carbon black. Other feedstocks such as olefins, diolefins, acetylene, and anthracene have also been used (Gallie 1946). There is a complex association between the tire, rubber, and carbon black industries. Markets for carbon black are tight and industry is squeezed between two giants: petroleum and coal industries on the supply side and auto industry on the demand side. In the past, this has historically depressed the price of carbon black. The changing trends in the rubber industry and the future of tire and carbon black producers are discussed by Lebel 1999.

If a hydrocarbon fuel such as NG (mostly methane) is to be used for H₂ production by direct decomposition, then the process that is optimized to yield H₂ may not be suitable for production of high quality carbon black by-product intended for the industrial rubber market. Moreover, based on the data available, to date, it appears that the carbon produced from high-temperature (at 850-950°C) direct thermal decomposition of methane is soot-like material with high tendency for the catalyst deactivation (*e.g.* Murata 1997). In other words, if the object of CH₄ decomposition is H₂ production, carbon by-product may not be marketable as high-quality carbon black for rubber and tire applications. Finally, the health and safety issues related to production and use of carbon black is still subject of on-going debate among the occupational and environmental health professionals (Nikula 2000, Brokmann 1998). In the light of the above, it is far from certain that large-scale by-product carbon generated from direct methane/NG decomposition for production of hydrogen fuel will find stable high-value commercial outlets. This is despite the forecasts that there are potentially new and emerging markets for carbon black use in the future (Rusinko 2000, Saraf 1997).

Pyrolysis of Hydrogen Sulfide

Production of hydrogen by direct decomposition of hydrogen sulfide has been studied extensively. There are several good reviews of the subject available (Luinstra 1996, Donini 1996, Zaman 1995, and Clark 1990). These reviews provide a detailed description of the H₂S decomposition processes including the use of microwave radiation, electric discharge methods, direct electrolysis, indirect electrolysis, thermal dissociation, thermochemical cycles, photocatalytic, and electron beam irradiation techniques.

Hydrogen sulfide decomposition is a highly endothermic process and equilibrium yields are poor (Clark 1995). At temperatures less than 1500°C, the thermodynamic equilibrium is unfavorable toward hydrogen formation. However, in the presence of catalysts such as platinum-cobalt (at 1000°C), disulfides of Mo or W at 800°C (*e.g.* Kotera 1976), or other transition metal sulfides supported on alumina (at 500-800°C), H₂S decomposition proceeds rapidly (Kiuchi 1982,

Bishara 1987, Al-Shamma 1989, Clark 1990, Megalofonos 1997). In the temperature range of about 800-1500°C, thermolysis of hydrogen sulfide can be treated simply in terms of reaction:



Where $x=2$. Outside this temperature range, multiple equilibria involving H_2S , S , HS , H , H_2 and polysulfur species (S_x , $x=1-8$), and H_2S_x ($x=2-9$) may be present depending on temperature, pressure, and relative abundance of hydrogen and sulfur (Clark 1990). Kinetics of both catalyzed and uncatalyzed H_2S thermolysis has been extensively investigated (Darwent 1953, Raymont 1975, Al-Shamma 1989, Kaloidas 1989, Shiina 1996, Harvey 1998, Karan 1999, Dowling 1999) and a good review of the subject is provided by Zaman 1995. Above approximately 1000°C, there is a limited advantage to using catalysts since the thermal reaction proceeds to equilibrium very rapidly (Raymont 1974, Noring 1982, Clark 1990). The hydrogen yield can be doubled by preferential removal of either H_2 or sulfur from the reaction environment, thereby shifting the equilibrium. The reaction products must be quenched quickly after leaving the reactor to prevent back reactions (Kappauf 1985, Diver 1985).

Since H_2S decomposition reactions run at relatively high temperatures, this process is a good candidate for interfacing to concentrated solar radiation (Harvey 1998). In fact, extensive work has been conducted over past twenty years or so to demonstrate the technical and economic viability of hydrogen production via solar thermal pyrolysis of hydrogen sulfide (Kappauf 1989, Lee 1995, Harvey 1998 and references therein).

According to Cox (1998), using an efficient $\text{H}_2/\text{H}_2\text{S}$ separation system, the thermal decomposition of H_2S is able to produce hydrogen at a cost approaching that of the conventional SMR process. The analysis of Cox et al. showed that the most economic route for hydrogen production by direct decomposition of H_2S is one in which CH_4 is burned to supply the decomposition heat and unconverted H_2S is recycled until extinction (see simplified flow diagram of Figure 1). This scheme would produce H_2 at a cost of about $\$4.50/10^6\text{BTU}$ (corrected to 1998 US dollars). This figure compares favorably with $\$4.75/10^6\text{BTU}$ (corrected to 1998 US dollars) for a Claus plant to treat the same amount of H_2S plus a conventional SMR plant to generate an equivalent amount of H_2 gas. In principal, this process can be integrated with a non-polluting heat source (for example, solar) to eliminate emission of greenhouse gases from the combustion furnace. Alternatively, part of the hydrogen gas produced in the process can be rerouted and burned in the furnace as fuel without any emission of greenhouse gases.

Finally, a review of U.S. patent literature revealed that several patents have granted that describe H_2S decomposition for the purpose of hydrogen production (*e.g.* Wang 1998, Bowman 1991, Elvin 1989, Daley 1984, Norman 1984, Chen 1978, Kotera 1976). These patents provide methods for H_2S splitting via direct thermolytic as well as indirect multi-step thermochemical cycles. Despite all that, no commercial process for the thermal dissociation of hydrogen sulfide exists. In summary, pyrolysis of methane and hydrogen sulfide has been thoroughly investigated. Direct thermal dissociation of methane and H_2S does not generate greenhouse gases. However, compared to SMR process, thermolysis of CH_4 and H_2S generates lesser amounts of hydrogen per mole of methane and hydrogen sulfide reacted. In fact, half as much hydrogen is produced in the case of methane dissociation and one quarter as much H_2 in the case of H_2S pyrolysis.

Unfortunately, SMR plants do emit undesirable greenhouse gases into the atmosphere. An alternative to SMR process that avoids release of greenhouse gases yet generates comparable amount of hydrogen is H₂S reformation of natural gas methane.

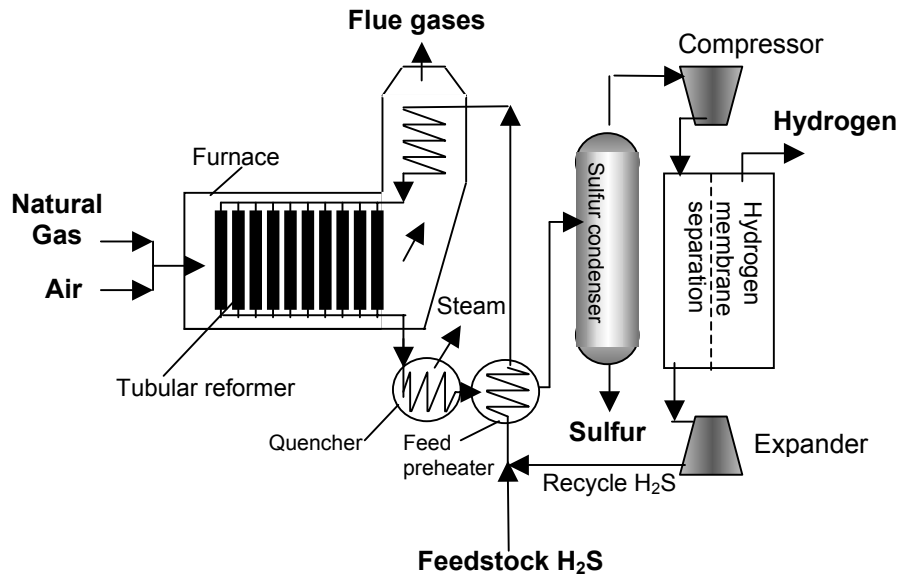


Figure 1- Simplified flow sheet for splitting hydrogen sulfide.

Hydrogen Sulfide Reformation of Natural Gas

The main idea here is to devise a process that combines the virtues of the three basic processes discussed above. They are: steam reforming of natural gas, direct thermolysis of methane and pyrolysis of hydrogen sulfide. Technically, the objective is to conceive a process capable of delivering at least four moles of hydrogen per mole of CH₄ reacted without production of greenhouse gases such as CO₂. The prospective process should be compatible with existing refinery and natural-gas-processing operations and be technically and economically feasible. Due to the availability of sub-quality/sour gas resources and the fact that hydrodesulfurization is a common process in all oil refineries, it made sense to investigate the possibility of H₂S reformation of natural gas. In a way, the reaction of H₂S with methane can be thought of as the sulfur analog of the SMR process. The reactions involved can be expressed in the following simplified forms:



The overall reaction for the H₂S methane reforming process may be written as follows:



The prospective process represented by the overall reaction above will produce carbon disulfide (CS_2) instead of elemental sulfur or carbon black. Unlike elemental sulfur and even carbon black, there are limited outlets for marketing CS_2 as is.

Carbon disulfide is used in the manufacture of xanthate for regenerated cellulosic products such as viscose rayon, cellophane, and non-woven fabrics. The viscose products represent about half of the market for CS_2 . The second major use for carbon disulfide is in the manufacture of carbon tetrachloride (CCl_4) that consumes about quarter of CS_2 production. Other applications include the use of CS_2 as ore floatation agents, rubber accelerators, chain transfer agents for polymerization, and agrochemicals such as fungicides, soil treatment agents, etc. (Ullmann's 1989). The potential market growth for CS_2 has been stymied due to declining rayon market since mid 1960s and phase out of the F-11 and F-12 halocarbons manufactured using CCl_4 .

Annual U.S. production of CS_2 in 1990 was about 114,000 tons (Erekson 1996). This amount of CS_2 required approximately 96,000 tons of elemental sulfur to produce. In 2000, elemental sulfur production in the U.S. was 9.4 million tons, of which 8.4 million tons or about 90% was recovered at the petroleum refineries, natural-gas-processing plants, and coking plants (Ober 2001). Clearly, established markets for CS_2 use in the U.S. do not provide an outlet for carbon disulfide produced from sulfur generated at the petroleum refineries and NG-processing plants. In fact, CS_2 production using elemental sulfur recovered at just one 200,000 barrel per day refinery would double current U.S. production of carbon disulfide (Erekson 1996).

A much larger outlet for CS_2 produced from recovered sulfur is for the production of sulfuric acid (H_2SO_4). Already, about 90% of the elemental sulfur produced in the U.S. is used for H_2SO_4 synthesis. In addition, approximately 26% of sulfur consumed in the U.S. in 2000 was provided by imported sulfur and sulfuric acid (Ober 2001). Clearly, huge outlets exist for the CS_2 produced from a prospective process that can convert H_2S from the hydrodesulfurization of petroleum products in refineries and/or sweetening of natural gas. In fact, CS_2 can be a more desirable feedstock for the sulfuric acid plants (Erekson 1996) than elemental sulfur used today. When combusted CS_2 provides more heat than elemental sulfur and CO_2 formed does not affect sulfuric acid solutions and thus would not present any handling problems for the H_2SO_4 plant.

The reaction between CH_4 and sulfur depicted above is the well-known methane process for production of CS_2 . Most commercial CH_4 -sulfur processes employ silica gel/aluminum catalyst for CS_2 production although it is possible for the process to proceed without a catalyst. The reaction of CH_4 with sulfur is thermodynamically favorable for CS_2 formation, and conversion is usually in the range of 90-95% with respect to methane (Ullmann's 1989). The industrial sulfur- CH_4 process operates in the temperature range of 500-650°C and pressure range of 4-7 atm. In the commercial plants, product H_2S is sent to the Claus unit and converted to steam and sulfur.

Conceptually, it should be possible to modify the existing methane-sulfur process and combine it with the H_2S decomposition according to Figure 1. This can be done by combining the product H_2S formed from the reaction of CH_4 with sulfur in the methane-sulfur process with that from the H_2S decomposition process. This approach is depicted in Figure 2. Ideally, both the methane-sulfur and H_2S dissociation reactions are carried out together in one reactor. In that case, the overall process is highly endothermic and requires about 116 kJ/mol of H_2S reacted.

With reference to Figure 2, we note that the reaction furnace can be heated by electric power, solar energy or combustion of a portion of the H_2 generated. Harvey (1998) and co-workers have suggested that solar reactors are especially suited to couple to highly endothermic processes such as H_2S splitting because they provide a large energy absorption venue. In fact, several other researchers have also studied the thermochemical decomposition of H_2S using concentrated solar radiation (*e.g.* Bishara 1987, Kappauf 1985). Likewise, solar pyrolysis of methane has also been under investigation (Dahl 2001, Weimer 2000). Notably, H_2S reformation of methane is energetically more endothermic than either H_2S or CH_4 thermolysis. Thus, H_2S reformation of methane should provide an even better process for solar power interface. As far as we know, no experimental work has been carried out to study H_2 production via H_2S reformation of CH_4 under solar-thermal conditions.

The feed stream, a mixture of CH_4 and H_2S represented by stream "a" in Figure 2, is compressed and combined with the recycle H_2S stream "o." The combined stream enters the feed heater (FH) at a pressure of 1.5 atm and $25^\circ C$. Stream temperature at the feed heater exit is $552^\circ C$. The reforming reactor runs at a pressure of 1.35 atm and a temperature of about $1227^\circ C$. The exit stream "d" is rapidly quenched in the waste heat boiler (WHB) to $875^\circ C$ followed by further cool down (for elemental sulfur collection) to about $390^\circ C$.

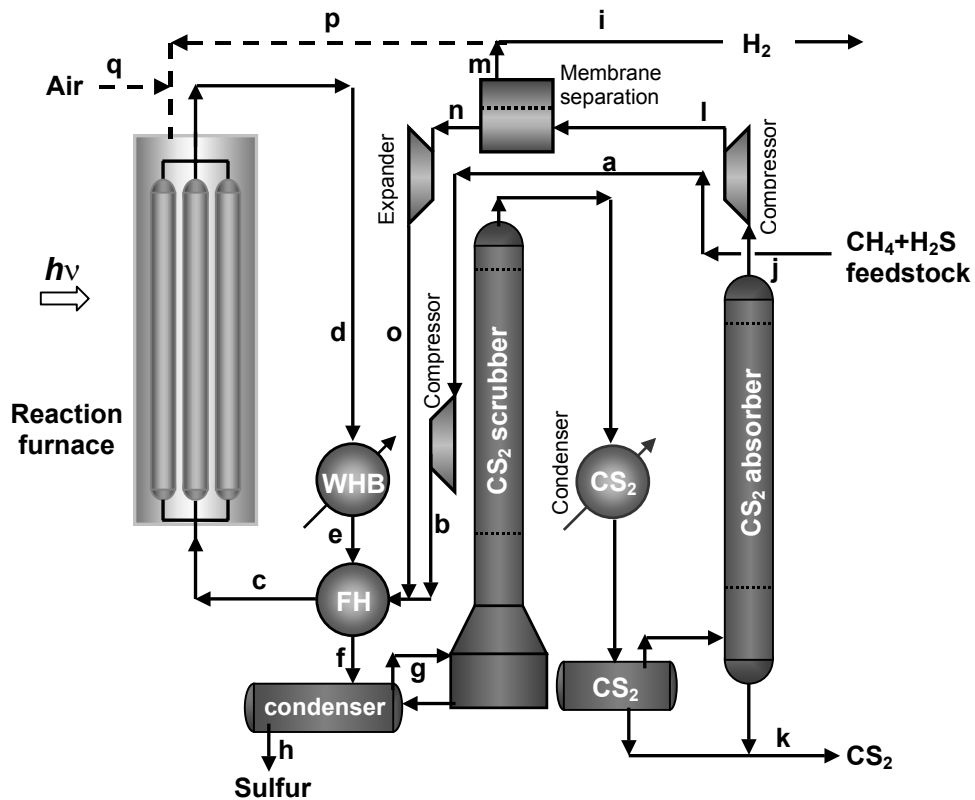


Figure 2- Process for hydrogen and CS_2 production.

Most of the residual sulfur is removed at this stage before entering CS₂ scrubber/condenser/absorber train. Finally, a mixture of hydrogen, recycle H₂S and unconverted CH₄ enter membrane hydrogen separation unit at a temperature of about 25°C and a pressure of 10 atm. Typical membrane H₂ separation efficiency of 90% can be assumed. A portion of the recovered H₂ is directed, as necessary, to the reaction furnace and combusted with air to furnish the energy requirement of the reforming reactions during the night or reduced light periods. During the daylight periods, solar energy provides the bulk of the power required for driving the endothermic reforming reactions. In this way, once the reformer reaches steady-state operating condition, its temperature is not affected by the irradiance fluctuations resulting from varying or intermittent solar radiation. The reformer always kept at optimum and stable temperature and operating state regardless of the changes in the climatic or solar condition.

Chemical Equilibrium Considerations

Calculations involving minimization of the Gibbs free energy were carried out using the F*A*C*T equilibrium code EQUILIB-Web (Pelton 1990) and GASEQ (Morley 2000). We calculated the equilibrium concentration of H₂S-CH₄ reaction products at various temperatures and pressures, and initial H₂S to CH₄ molar concentrations (x). Figures 3 & 4 depict typical results obtained for x values equal to 2, 4 and 6 at 1 atm pressure and reaction temperatures in the range of 500-2000 K. Additional information are given in Figures 5-7.

Several key findings emerge from investigating these results as follows:

- 1- The reaction between sulfur and methane (reaction 7) is the primary CH₄ consuming reaction resulting in the formation of CS₂.
- 2- The hydrogen sulfide decomposition reaction (6) does not take effect until about 1000-1100 K (depending upon the H₂S to CH₄ molar feed ratio, x). Generally, the yield of soot/carbon lay-down increases with temperature up to about 1100 K. Above that the yields decrease. Reaction (6) plays a key role in the production of hydrogen and CS₂ from H₂S and CH₄ by providing the required sulfur feedstock for reaction (7) to occur.
- 3- Hydrogen, CS₂ and S₂ are thermodynamically favored products of H₂S-CH₄ reaction at high temperatures.
- 4- CS and SH are minor by-products that are thermodynamically favored only at temperatures higher than about 1600 K.
- 5- The temperature span for carbon lay-down for the H₂S-CH₄ reaction system depends primarily on the H₂S to CH₄ molar feed ratio, x . At any given pressure and temperature, there is a specific H₂S to CH₄ molar feed ratio ($x = x_{\text{pinch}}$) for which equilibrium concentration of C(s) = 0, *i.e.* no soot formation is possible. This is shown in Figure 5 that depicts the equilibrium products of H₂S-CH₄ reaction system as a function of H₂S to CH₄ molar feed ratios, x , at 1350 K and 1 atm. At $x = x_{\text{pinch}} \approx 6.9$ (about 0.87 on horizontal axes, Figure 5), the combined yield of product carbon and elemental sulfur dips to a minimum. This effect can also be seen in the graphs of Figure 4 that correspond to x values equal to twice and three times the stoichiometric H₂S to CH₄ molar feed ratio of $x_{\text{stoichiometric}} = 2$, respectively. Figure 6 is a plot of $x_{\text{pinch}} / (1 + x_{\text{pinch}})$, vs. temperature depicting the soot-free domain for the H₂S-CH₄ reaction equilibria.

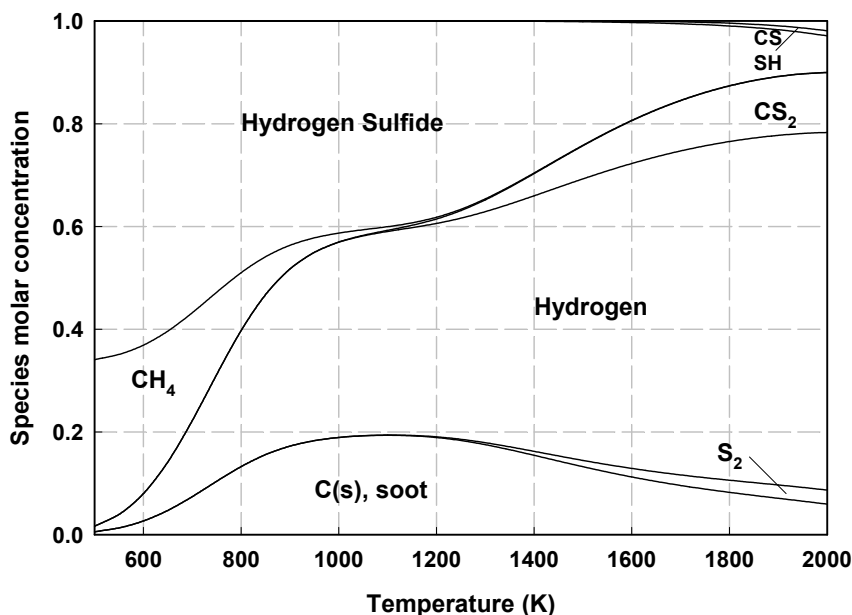


Figure 3- Equilibrium concentration of reaction products of $\text{CH}_4 + 2 \text{H}_2\text{S}$ at 1 atm.

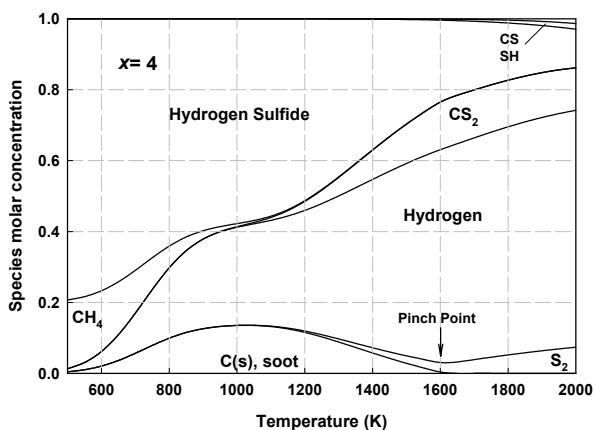


Figure 4- Equilibrium concentration of $\text{CH}_4 + x \text{H}_2\text{S}$ reaction products at twice and three times $x_{\text{stoichiometric}} = 2$.

- 6- The equilibrium yield of the major H_2S - CH_4 reaction by-products are given in Figure 7 for a range of temperatures and H_2S to CH_4 molar feed ratios, x . An examination of these results indicate that, in general, the yield of CS_2 increases with temperature up to a maximum yield that is a function of H_2S to CH_4 molar feed ratio, x . The temperature at which maximum CS_2 yield is obtained corresponds to the no soot formation condition. This temperature is a function of the H_2S to CH_4 molar feed ratio and lies in the range of about $1100\text{-}1300^\circ\text{C}$, corresponding to x values in the range of approximately 4-6. From thermodynamics point of view, this range of $x \approx 4\text{-}6$ and $T \approx 1100\text{-}1300^\circ\text{C}$ seems to provide the optimum conditions

needed for performing $\text{H}_2\text{S}-\text{CH}_4$ reformation reactions. This is so because the reaction between H_2S and CH_4 can be conducted at a reasonable temperature range, does not require excessive H_2S recycle, soot formation is nil and production of elemental sulfur by-product can be kept to a minimum.

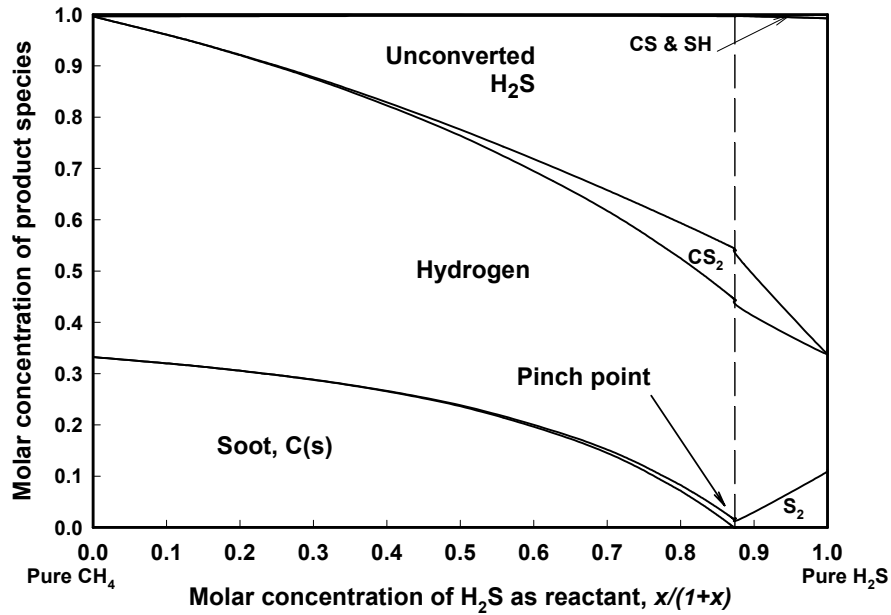


Figure 5- Product slate for reaction $\text{CH}_4 + x \text{H}_2\text{S}$ at 1350 K and 1 atm.

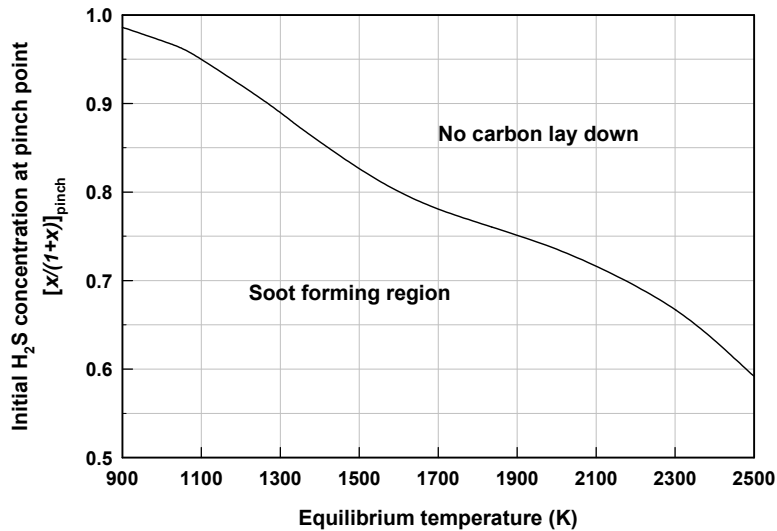


Figure 6- Soot forming region for $\text{CH}_4 + x \text{H}_2\text{S}$ reaction at 1 atm.

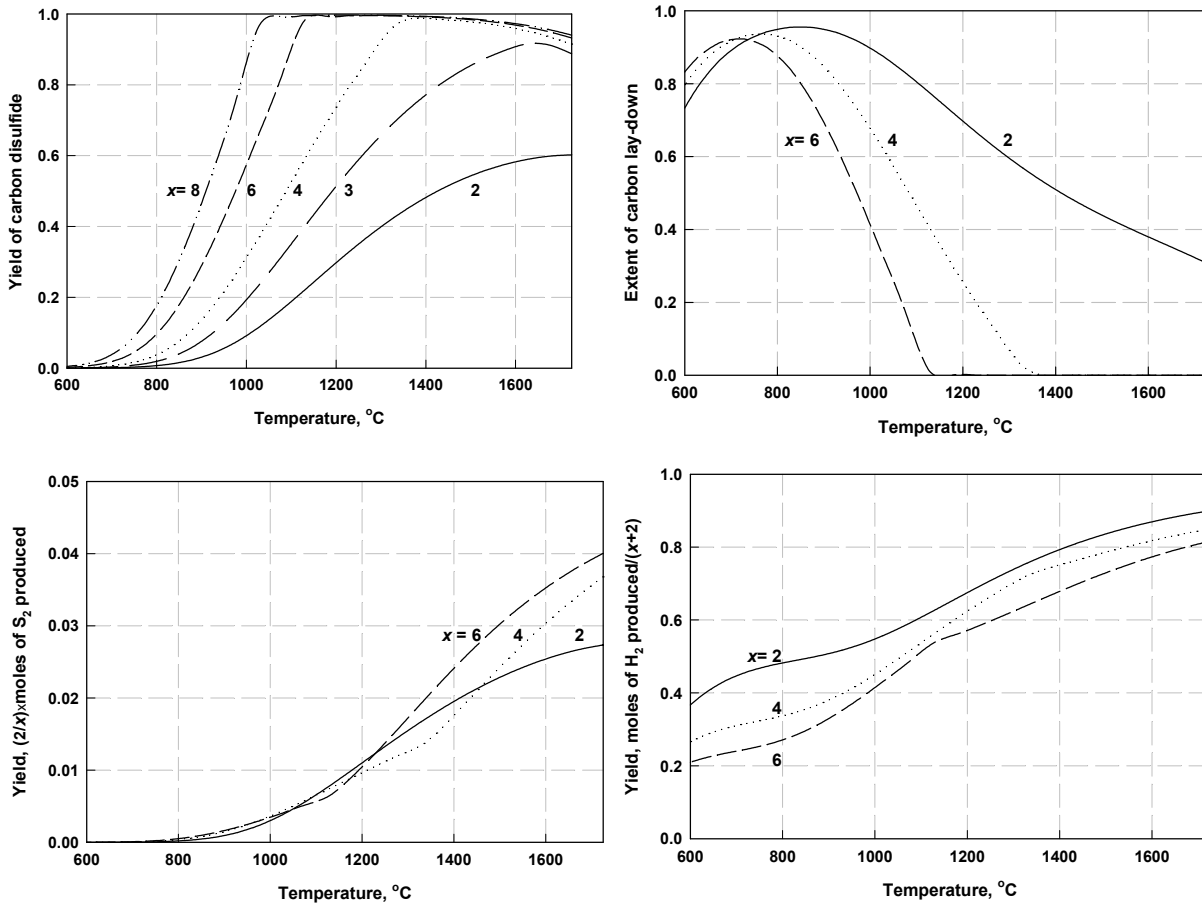


Figure 7- Equilibrium yields of major H₂S-CH₄ reaction products at various H₂S to CH₄ molar feed ratios, x, and 1 atm.

In addition, we calculated the equilibrium concentration of species formed and stream compositions for the H₂S-CH₄ reformation scheme of Figure 2. Results are presented in Table 4 for a H₂ membrane separation efficiency of $\eta_m = 91\%$, reformer temperature of 1350 K and H₂S to CH₄ molar feed ratio of 2.323. In Table 4, if $y = 0$ is allowed (*i.e.* "p" stream in Figure 2 is cut-off and no H₂ gas flows to the burner/reformer), then for every mole of CH₄ reacted, 4.316 moles of hydrogen is produced. In addition, the amount of heat transfer to the reformer is calculated as $\Delta H_{cd} \approx 518.6$ kJ per mole of CH₄ consumed. In the case $y = 0$, ΔH_{cd} must be supplied from an external source such as solar or electric power. ΔH_{cd} is a function of, among others; reformer temperature, pressure and the extent of H₂ recycle. The extent of hydrogen recycle is a function of the membrane efficiency η_m . Table 5 presents ΔH_{cd} values as a function of reformer temperature T_c for the case for which hydrogen recycle is 10%, $T_d = 552^\circ\text{C}$, reformer pressure $P_1 = 1.35$ atm and no carbon lay-down.

The process conditions can be optimized so that the least amount of energy is required for deriving reforming reactions. In general, for CO_x-free operation, ΔH_{cd} can be supplied by one of three methods. One technique is to combust a portion of the H₂ produced (*i.e.* letting $y \neq 0$ in Table 4). In that case, $y_{max} = 518.6/241.84 \approx 2.14$. In other words, approximately 2.14 moles of

hydrogen are required (for each mole of CH₄ consumed) to operate the reformer autothermally. Under these conditions, 100*(2.14/4.316) or about 50% of the hydrogen produced must be burned to derive H₂S-CH₄ reformation reaction (8).

Table 4- Stream compositions for the process scheme of Fig. 2.

Stream No.	T (K)	P (atm)	[CH ₄] (moles)	[H ₂ S] (moles)	[H ₂] (moles)	[CS ₂] (moles)	[S ₂] (moles)	[HS+CS] (moles)	ΔH (kJ/mol)	ΔG ⁰ (kJ/mol)
a	298	1.00	0.98944	2.29853	0	0	0	0	-36.875	-97.91
b	298	1.50	1.0	5.0	0.42235	0	0	0	-27.63	-87.17
c	825	1.45	1.0	5.0	0.42235	0	0	0	-6.785	-204.3
d	1500	1.35	0.01056	2.70147	4.69278	0.98753	0.15382	0.015782	54.84	-295.6
e	875	1.20	0.01056	2.70147	4.69278	0.98753	0.15382	0.015782	29.873	-156.66
f	390	1.10	0.01056	2.70147	4.69278	0.98753	0	0.015782	nc*	nc
g	390	1.09	0.01056	2.70147	4.69278	0.98753	0	0.015782	nc	nc
h	380	1.00	0	0	0	0	0.15382	0.015782	nc	nc
i	298	1.00	0	0	4.27043-y	0	0	0	-1.883E-3	-38.914
j	300	1.00	0.01056	2.70147	4.69278	0	0	0	-7.528	-56.664
k	300	1.00	0	0	0	0.98753	0	0	nc	nc
l	300	10.0	0.01056	2.70147	4.69278	0	0	0	-7.528	-50.92
m	300	1.05	0	0	4.27043	0	0	0	55.865E-3	-39.054
n	300	10.0	0.01056	2.70147	0.42235	0	0	0	-17.861	-71.8613
o	298	1.50	0.01056	2.70147	0.42235	0	0	0	-17.9273	-76.2014
p	298	1.05	0	0	y	0	0	0	nc	nc
q	298	1.00	0	0	0	0	0	0	nc	nc

* Not calculated.

Table 5- Input energy requirement as a function of the reformer temperature.

T _c (°C)	850	950	1050	1160	1227	1727
Input concentration of [H ₂ S] _a (vol%)	69.5	69.4	70.1	70.4	70.6	71.7
ΔH _{cd} (kJ/mol of CH ₄)	663	619.3	589.8	573.65	573.53	649.6

The second method is to use electric heating, if available. The third option may be the use of a concentrating solar furnace. The fact that reaction (6) is highly endothermic makes this option especially attractive. In addition, results of Figures 3-7 indicate the advantages of running H₂S-CH₄ decomposition reaction at high temperatures readily achievable from a typical concentrating solar furnace. We note that solar-only furnaces cannot operate continuously. This has a profound effect on the economics and practicality of solar-only process for providing input power to the H₂S-CH₄ reformation plant. Depending on the particular situation, one, a combination of two, or

all three options combined may prove to be the most economical. Plausible scenarios include: solar-only, combined solar-electric, electric-only, H₂ burning furnace, combined solar and hydrogen combustion furnace, combined electric and H₂ combustion furnace, and combination solar-electric-H₂ combustion furnace. The economics of each approach is affected by the price of natural gas feedstock and electric power used as well as the value of hydrogen and carbon disulfide produced in the process.

Hydrogen and Carbon Disulfide Pricing and Marketing Considerations

As for the value of H₂ produced, no matter what type of process or energy input option is chosen, the H₂S-methane reformation won't be commercially viable unless H₂ production cost is comparable to that from SMR plants. A recent survey of the economics of hydrogen production technologies including SMR process is given by Padro (1999). For large SMR facilities, *i.e.* 50-1000 million SCF per day, the hydrogen prices vary between \$5.75 and \$7.90 (1998 US dollars). For a small facility having a hydrogen production capacity of 9.5 million SCF per day, a hydrogen price of about \$11.80 was given. On average, the price of natural gas feedstock constituted about 60% of the total cost for large SMR plants and approximately 40% for small ones. For these estimates, a natural gas price of \$3.12 per million BTU was assumed.

According to Cox (1998), the supply costs of hydrogen are approximately \$4.20 and \$5.32 (corrected to 1998 US dollars) per million BTU for SMR plant H₂ output of 20 and 5 million SCF per day, respectively. Cox (1998) used a natural gas price of \$1.75 (corrected to 1998 US dollars) per million BTU hydrogen. After correcting for the differences in the feedstock costs, the hydrogen prices from Cox's estimate becomes \$5.72 and \$7.36 per million BTU for H₂ output of 20 and 5 million SCF per day, respectively. This is in general agreement with the figures reported by Padro (1999). We note that at the time of writing this document, the futures contract for natural gas prices (per million BTU) at the New York Mercantile Exchange (NYMEX) for the month of May 2001 varied between \$4.69 and \$3.99.

As for the sulfur recovery part of the H₂S-methane reformation, the by-product credit for CS₂ would lie between the price of recovered sulfur and that commanded by CS₂ in conventional markets (Erekson 1996). The rationale for this is that refineries are already selling the sulfur from Claus operation to the sulfuric acid plants. As noted before, the large outlet for CS₂ is in the production of H₂SO₄. The price of recovered sulfur ranged from \$0.02 to \$0.15/lb depending on purity (Chemical Market Reporter 2000). The price of sulfur corresponds to the lower limit of by-product credit for CS₂. The maximum price that carbon disulfide produced by the H₂S-methane reformation process can fetch is set by its value in the conventional markets that is about \$0.24/lb (Chemical Market Reporter 2000). In short, the by-product CS₂ from H₂S-methane reformation process should command a value in the range of approximately \$0.02 to \$0.20/lb of CS₂ (after correcting for the difference in molar mass between CS₂ and S₂).

Finally, the capital and operating costs of the prospective H₂S-methane reformation plant should be comparable to that of a baseline Claus process that it aims to replace. For example, the capital cost of a modified Claus plant that produces about 600 ton per day (tpd) sulfur is approximately 30 million US dollars (Cox 1998). While, the total installed cost of a 163 tpd air based Claus sulfur plant including the tail gas cleanup unit (TGCU) is approximately \$18-20 million (Schendel 1993). We note that TGCUs typically cost as much as the Claus plant itself. A detailed

discussion of the Claus plants, other sulfur recovery and tail gas cleanup processes is given by Leppin (1997). For the large-scale modified Claus units with TGCU, typical, rough, order of magnitude treatment costs is about \$100 per ton of elemental sulfur recovered (Leppin 1997).

Gas Separation and Purification Considerations

As we briefly discussed before, various methods have been devised for the equilibrium displacement and separation of hydrogen from H_2S in hot gas streams. A review of the available techniques has been given by Clark (1990). Examples include the use of polymeric, metallic and ceramic oxide membranes, pressure-swing adsorption (Bandermann 1982) and thermal diffusion through Vycor-type glass or microporous alumina membranes at temperatures as high as 1000°C (Kameyama 1981, Ohashi 1998, Fan 1999, Fan 2000). A good discussion of $\text{H}_2\text{S}/\text{H}_2$ separation membranes of especial interest to this work is given by Cox (1998). A packaged polyimide membrane system can be used to affect hydrogen- H_2S separation if the concentration of H_2S in the mixture does not exceed 10%. Ceramic membranes are not limited by the H_2S concentration, but they yield poor separation factors, typically 2 or lower (Cox 1998). If the separation mechanism is due to Knudsen diffusion as it is for most porous membranes, then the maximum separation factor achieved is 4.1, the square root of the ratio of the molar masses for H_2S and H_2 . According to Cox (1998), new membrane separation technologies under development at the Air Products and Chemicals, Inc. (APCI) is poised to change all that. It has been shown that the APCI membrane is not limited by the separation factor 4.1 imposed by Knudsen diffusion separation mechanism.

Catalyst and Kinetics Considerations

One of the main objectives of this effort was to search for processes and catalysts that facilitate the reaction between methane and hydrogen sulfide (reaction 8) to form carbon disulfide and hydrogen. If a suitable catalyst(s) and process can be found, the prospective $\text{H}_2\text{S}-\text{CH}_4$ reformation process will be able to:

- Eliminate the need for steam-methane reformer for hydrogen production.
- Eliminate the need for Claus plant for treating sulfurous/sour feedstock.
- Yield more than four moles of H_2 for each mole of CH_4 reacted.
- Utilize common feedstocks (*i.e.* CH_4 and H_2S contained in NG and refinery gases).
- Use a range of H_2S to methane molar feed ratios.
- Employ a process with most steps proven at full-scale.
- Operate at a temperature range of $1100-1300^\circ\text{C}$, ideal for solar interface.
- Operate at low pressures, less than 10 atm.
- Operate with relatively low recycle H_2S , *i.e.*, $\text{H}_2\text{S}/\text{CH}_4$ ratio of about 4-6.
- Operate with a low dark reforming enthalpy (about half of the output H_2 energy content).
- Function under no soot formation or carbon lay-down condition.
- Simultaneously convert both H_2S and methane to hydrogen gas.
- Operate with no CO_x , acid or greenhouse gases generated or released into the atmosphere.
- Simultaneously fix both C and sulfur in the form of a valuable reagent, *i.e.* CS_2 .

As noted before, the H₂S decomposition reaction (6) is an important step in the H₂S-CH₄ conversion process. In addition, we note that effective catalysts such as platinum-cobalt and disulfides of Mo or W supported on alumina are known to considerably hasten H₂S dissociation. On the other hand, reaction (7) is a well-known methane conversion reaction used commercially to produce CS₂. There are also commercial catalysts such as silica gel/aluminum used for CS₂ synthesis reaction (7). Now, the main issue is whether bi-functional catalyst(s) can be found that affect(s) H₂S decomposition reaction (6) while holding activity and stability toward reaction (7). Such catalyst(s) will be able to render the H₂S-CH₄ reformation more efficient and potentially cost effective. The search for such catalysts and processes has been conducted by the Institute of Gas Technology (now Gas Technology Institute, GTI) researchers (Miao 1998, Erekson 1996) and earlier by Schuman (1968). The objective of the work conducted by Miao and Erekson was to develop a two-step thermochemical process. In the first step, a group of catalysts was sought for the direct conversion of methane and hydrogen sulfide to carbon disulfide. In their second step, the CS₂ hydrogenation to be carried out for the production of gasoline-range hydrocarbon liquids. The first developmental step of their effort has more direct relevance to our own analysis and is summarized briefly below:

1. In a search to find bi-functional catalysts capable of H₂S dissociation while holding activity and stability toward reaction of sulfur and methane, nine catalysts were tested. Experiments were conducted at five different reaction temperatures (*i.e.* 700, 800, 900, 1000, 1100°C), two different residence times (*i.e.* 1 and 5 s), and three distinct H₂S to CH₄ molar feed ratios (*i.e.* $x = 2, 4$ and 8).
2. It was found that the H₂S to CH₄ molar feed ratio, x , had a strong effect on the yield of carbon disulfide. The $x = 2$ (*i.e.* the stoichiometric ratio) did not give the highest CS₂ yield, but the highest yields, >95%, were achieved at $x = 4$ (*i.e.* twice the stoichiometric ratio of 2). In other words, the yields of CS₂ are not as great as when an excess of hydrogen sulfide is in the feed (consistent with the results of Figure 7). This may be at temperatures above 1000°C (1273 K); the conversion of methane nearly reaches completion. At these temperatures dehydrogenated CH₄ or carbon precursors on the surface would be in greater abundance, and with the excess H₂S in the gas phase, CS₂ yield is increased.
3. In general, the CS₂ yield increased with temperature up to 1100°C. Above that the yields decreased - again, consistent with the equilibrium calculations, Figure 7. The highest yields were for catalysts IGT-MS-103 and IGT-MS-105. The designations IGT-MS-103 and IGT-MS-105 refer to Cr₂S₃ and Ce₂S₃ catalysts, respectively.
4. IGT catalysts were tested to determine their propensity and activity toward methane decomposition and surface accumulated carbon regeneration. These tests showed that two catalysts that had most activity for inhibiting carbon formation, as well as for the regeneration after carbon deposition were IGT-MS-103 (Cr₂S₃) and IGT-MS-105 (selenium sulfide) catalysts.
5. Both IGT-MS-103 (Cr₂S₃) and IGT-MS-105 (selenium sulfide) catalysts were active in dissociating H₂S, an essential reaction in the H₂S-CH₄ reformation reaction pathway. In addition, these catalysts were stable above 1000°C (1273 K) and do retain most of their original surface area (2-5 m²/g). These catalysts were also the most effective in promoting the reaction of H₂S and the carbon deposits on their surfaces.

In summary, certain transition metal sulfides such as Cr_2S_3 and Ce_2S_3 can work as bi-functional catalysts that are active in dissociating H_2S yet stable at temperatures above 1000°C (1273 K) to allow H_2S reaction with the carbon precursors formed on their surfaces. In general, these catalyst powders are prepared by sulfide conversion, drying, reduction and calcination. In the IGT method, the metal sulfides are precipitated from an aqueous solution of the metal using ammonium hydrosulfide (Miao 1998). There are also commercially prepared metal sulfide catalysts (e.g. Cerac 2000). Additional information pertaining to transition metal sulfides, their preparation and properties are given elsewhere (Lacroix 1991, Chivers 1980).

Cost Considerations

As noted above, the highest activity (>95% at 1100°C toward CS_2 formation) and selectivity amongst all catalysts tested by IGT belonged to two transition metal sulfide catalysts, particularly Cr_2S_3 . The high yields of CS_2 (and H_2) from the Cr_2S_3 -catalyzed H_2S - CH_4 reformation process were encouraging. A preliminary economic analysis was carried out by IGT to determine the viability of the H_2S - CH_4 process for refinery applications (Erekson 1996). It was assumed that H_2S was available from an acid gas removal unit, H_2S conversion was 100% and hydrogen production was 13 million SCF per day. With these assumptions, the capital and operating costs were estimated without taking credit for elimination of the Claus unit and its associated TGPU. The cost of H_2 was calculated based on a range of by-product credit for CS_2 that was varied from \$0.04 to \$0.23/lb (1995 US\$). The lower limit of the CS_2 price range corresponds to the price of recovered sulfur (\$0.04 to \$0.15/lb depending on purity, 1995 estimate). The upper limit corresponds to the price of CS_2 in the conventional markets. Results of IGT analysis are depicted in Figure 8. Figure 8 shows that as the market value of CS_2 increases, the cost of hydrogen decreases, accordingly. For CS_2 prices higher than about \$0.10/lb, hydrogen cost is negative. In other words, at CS_2 prices above approximately \$0.10/lb, the revenue generated by selling CS_2 would be more than enough to pay for the cost of hydrogen production.

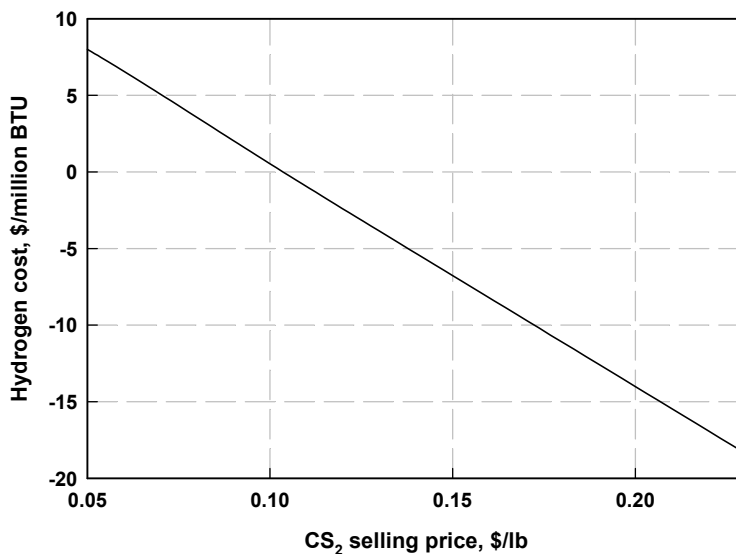


Figure 8- Comparison of CS_2 Selling Price and H_2 Cost (Erekson 1996).

Conclusions and Recommendations

- The concept of H₂S-methane reformation to produce H₂ and CS₂ was evaluated. In addition, the concept was assessed for its potential for cost effective production of hydrogen for the refinery and other applications.
- An assessment of the magnitude of H₂S resource that can be recovered (in the lower 48 US) from the sub-quality natural gas (SQNG) sweetening and refinery type (hydrodesulfurization) operations was made. It was found that the energy value of the hydrogen extracted from the H₂S-rich feedstocks using H₂S-methane reformation process exceeds 10 quads. The energy potential of the Alaska's Arctic National Wildlife Refuge (ANWR) reserves that can be converted and used to produce gasoline is estimated to lie between about 3.2 and 36 quads. Considering the added energy value of the sweetened SQNG made available by the H₂S-methane process, it appears that an order of magnitude larger untapped energy resource is available within the lower 48 US than there is in the Alaska's ANWR.
- With the state-of-the-technology today, the H₂S-methane reformation process discussed here is technically doable and can be economically viable as well.
- All of the reaction steps for the H₂S-methane reformation process are well developed and some are already practiced commercially, for many years.
- Viable bi-functional catalysts have been identified and well developed for the sole purpose of performing H₂S-methane reformation process, efficiently. Among them are several catalysts identified by a recent IGT study aimed at the production of hydrogen and CS₂ from H₂S and CH₄. Cr₂S₃ and Ce₂S₃ catalysts are found to be active in dissociating H₂S and stable at temperatures above 1000°C (1273 K) to allow H₂S reaction with the carbon precursors that reside on their surfaces. All transition metal sulfide catalysts are available commercially.
- A preliminary economic analysis of the H₂S-methane reformation process for H₂ and CS₂ production indicates that the process is a potential replacement for the present day Claus plants and associated Tail Gas Cleanup Units (TGCU). The cost of hydrogen produced depends on the price of the co-produced CS₂ and can conceivably be zero dollars, *i.e.* free.
- Efforts are underway to develop solar-thermal direct decomposition of the methane and H₂S for production of hydrogen. However, despite its potential benefits, no work has been done to show the viability of a solar driven H₂S-methane reformation process. Considering that close to 50% of the US refinery capacity and considerable SQNG reserves are located within two States with also considerable solar resource, *i.e.* Oklahoma and Texas, it is worthwhile to begin the development of the solar-driven thermochemical H₂S-methane reformation process

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TECHNOECONOMIC ANALYSIS OF AREA II HYDROGEN PRODUCTION - PART II Hydrogen from Ammonia and Ammonia-Borane Complex for Fuel Cell Applications

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Abstract

The aim of this analysis is to assess the issues of cost, safety, performance, and environmental impact associated with the production of hydrogen by so called "Area II" technologies, not presently funded by the U.S. DOE Hydrogen Program. The hydrogen (H_2) rich feedstocks considered are: water, hydrogen sulfide (H_2S) rich sub-quality natural gas (SQNG), and ammonia (NH_3). Three technology areas to be evaluated are:

- 1) Thermochemical H_2S reformation of methane with and without solar interface,
- 2) Thermochemical water-splitting cycles suitable for solar power interface,
- 3) Ammonia and ammonia adducts as hydrogen energy storers for fuel cell applications.

This project is a multi-year effort with following objectives:

- Analysis of the feasibility of the technology areas 1-3 from technical, economical and environmental viewpoints.
- Evaluation of the cost of hydrogen production by technology areas 1 & 2.
- Feasibility of the technology area 3 as a means of supplying H_2 to fuel cell power plants.

This paper provides the second in a series of analysis focusing on the prospects of ammonia and ammonia-borane compounds for use as hydrogen carriers for fuel cell applications. Due to extreme toxicity of ammonia, it is difficult to envision its widespread use as the future transportation fuel. This is despite the fact that ammonia is a low cost, readily available, environmentally clean and very high-density hydrogen energy storer. One approach to mitigate this problem is to complex ammonia with a suitable hydride so that the resulting material is neither toxic nor cryogenic. A class of compounds known as amine-boranes and their certain derivatives meet this requirement. The simplest known stable compound in this group is ammonia-borane, H_3BNH_3 (or borazane). Borazane is a white crystalline solid that upon heating reacts to release hydrogen in a sequence of reactions that occur at distinct temperature ranges. Ammonia-borane contains about 20 wt% hydrogen and is stable in water and ambient air.

Introduction

The use of ammonia as chemical hydrogen storage compound that can be easily dissociated and used in the fuel cells and power plants is not new and has been ongoing for more than 40 years [1-58]. In the early 1970s when the concept of "Hydrogen Energy Economy" was widely debated, it was envisioned that ammonia (NH_3) would provide a perfect storage medium for hydrogen produced by the ocean thermal energy conversion (OTEC) plantships [16,32]. In the early 1980s, Strickland at the Brookhaven National Laboratory (BNL) conducted a systems study to determine the economic prospects of using anhydrous liquid ammonia, produced by OTEC, as a hydrogen carrier for annual H_2 demand of 10-100 million standard cubic feet [28,31]. BNL study showed that OTEC NH_3 was competitive with H_2 made at the point of use via water electrolysis, steam reforming of natural gas, or OTEC liquid hydrogen (LH_2), in the upper fifth of the use range. In another BNL study, three alternative transportation fuels (ATFs) were compared with respect to the input energy required for their production from NG, their H_2 storage capacity and cost per unit of energy contained (\$/million BTU)[26]. The ATFs chosen were LH_2 , hydrogen produced by steam reformation of methanol (MeOH), and H_2 generated via thermocatalytic dissociation of anhydrous liquid ammonia. The BNL results showed that anhydrous liquid ammonia had considerable advantage over MeOH and LH_2 , coming very close to matching gasoline performance as a motor fuel.

The work of Strickland at BNL was supported by the efforts at the Lawrence Berkeley National Laboratory (LBNL) [27,29]. In the early 1980s, Ross conducted a detailed experimental and analytical study on the use of indirect NH_3 -air alkaline fuel cells (AFCs) for vehicular applications [27]. The impetus for his work was the belief that ammonia provided a feasible storage medium for H_2 produced from non-fossil sources, e.g. by the off-land OTEC or remote solar-thermal facilities. According to Ross, anhydrous liquid ammonia provides an excellent medium for H_2 storage, even though energy is required to evaporate and dissociate NH_3 resulting in somewhat lower efficiencies. LBNL results showed the advantages of AFCs relative to acidic electrolyte fuel cells, that is 2-3 times higher power densities and a factor of two lower component costs, resulting in 4-6 times lower total power plant costs. In addition, the ammonia dissociation reaction and power characteristics of an alkaline fuel cell operating on cracked NH_3 and air was determined. For a single cell unit, results obtained by Ross indicated that thermal efficiencies in the range of 34-44% at power densities of 1-2.2 kW/m^2 (using 1980s electrode technology) were achievable.

As the 1980s drew to close and with the demise of non-fossil hydrogen production technologies as a near-term reality, ammonia disappeared as a viable hydrogen storage medium from the U.S. DOE programs [57]. The commonly held view was that OTEC would be roughly twice as expensive as the conventional energy forms due to the high capital cost of OTEC plants made under existing designs at that time. It is often stated that a \$40/barrel oil cost would be necessary to spur investors into seriously considering OTEC technology [58]. The total energy efficiency is lower with ammonia as the H_2 carrier compared to methanol. Therefore, if methane is used as the primary fuel, then methanol will likely be the liquid fuel of choice for fuel cells, especially PEMFCs. Presently, the DOE fuel cell for transportation program appears to be focused on the use of fossil fuels and for that reason ammonia is not generally considered as a viable H_2 carrier. The ammonia scenario was unique to the OTEC project, where the electrical energy would be generated at a remote location and it was not feasible to install either power lines or a hydrogen pipeline to the shore. Hydrogen production and subsequent conversion to NH_3 for shipment to the shore seemed to be the most attractive way to store and transport OTEC hydrogen. Using ammonia directly in the fuel cells then appeared to be the most plausible approach. In other words, in the case of solar/renewable hydrogen production,

ammonia can still be viewed as a viable chemical storage medium for supplying hydrogen to fuel cells, especially AFCs.

Karl Kordesch was one of the early advocates of the AFCs and the use of ammonia as a high density H₂ carrier for automotive fuel cell applications [10]. According to Kordesch and co-workers, using readily available, off-the-shelf materials, an ammonia cracker can be fabricated providing on demand H₂ on-board fuel cell vehicles [50,51,53,54]. In addition, ammonia is a more desirable source of hydrogen for AFCs, as the small amounts of unconverted NH₃ that may remain in the dissociated gas would not harm the fuel cell function. In other words, there is no need for complete removal of trace impurities in the output stream of an ammonia reformer connected to an AFC power plant. Traditionally, the main issue with the AFC technology has been the perceived problem with the fuel (*i.e.* hydrogen) storage. In acid fuel cells, hydrogen can be stored as methanol. Required hydrogen for operation of the acid fuel cell can be delivered by steam reformation of methanol employing an onboard MeOH reformer. The carbon dioxide generated during this process does not present a serious problem to the acid fuel cell electrolyte function. In the case of an alkaline fuel cell, the electrolyte would react with the carbon oxides, forming problematic insoluble carbonate [53].

Much effort has been expended to develop steam reformation of methanol as a process for generating hydrogen for use in fuel cells. Nonetheless, a comparison of the economics of H₂ production via ammonia decomposition for alkaline fuel cells versus methanol reformation for acid fuel cells has shown that ammonia decomposition is economically more favorable [40,41,55]. Commercial ammonia is prepared at 99.5% purity (the impurity is mainly water which is harmless), whereas the higher alcohol impurities present in commercial methanol can result in production of contaminants during reforming that can lead to poisoning of the catalyst. Thus, the decomposition of ammonia appears to be an excellent choice for production of hydrogen for alkaline fuel cells as well as acid fuel cells if the unreacted NH₃ in the hydrogen stream is removed to below the admissible level [59].

Problems with the formation of insoluble carbonate in the electrolyte of an AFC can be expected if air is used (without CO₂ scrubbing) instead of pure oxygen (as is the case with the space-bound AFCs) at its cathode. AFCs employed in the U.S. Space Program on-board space vehicles use the porous solid matrices soaked with potassium hydroxide (KOH) electrolyte. The main reason for using matrix-type electrolyte in the space-bound vehicles is to improve system reliability by employing only passive devices that do not contain any moving parts. The use of matrix-type electrolyte in space AFCs is not problematic because high purity hydrogen and oxygen are available on-board the spacecraft. However, in terrestrial applications, air is used and therefore the use of matrix-type electrolyte will not be practical. According to Kordesch, for terrestrial AFCs, it is more advantageous to use a circulating type electrolyte. The exchangeability of circulating KOH solution allows the operation of AFC using air with less than complete CO₂ removal [53].

The system analysis studies conducted by Avery at the Johns Hopkins University and MacKenzie of the World Resources Institute in the late 1980s and throughout 1990s indicate that ammonia can play a key role in the future H₂-based transportation systems [42]. More recently, in a 1995 study by Miller at the Colorado School of Mines, ammonia has been shown to readily convert to a mixture of H₂ and N₂ by recycling the heat generated by an alkaline fuel cell, which operates in the temperature range of 70-150 °F [60]. As recently as 1999, ammonia economy has been advocated again as a way to address concerns with global warming, smog, and acid rain coupled with the slow pace of the progress and problems in the production and storage of practical commercial hydrogen-fueled and battery powered vehicles [49].

Benefits of Ammonia Use

Ammonia is the second largest synthetic, commodity product of the chemical industry with world production capacity exceeding 140 million metric tons. According to the mineral commodity data compiled by the U.S. Geological Survey, in 2000, the U.S. domestic ammonia production was about 15.8 million metric tons. During the same year, the total ammonia consumed in the U.S. exceeded 20 million metric tons, of which about 88% was for agricultural use as fertilizer [61]. Furthermore, anhydrous ammonia costs about \$150 per short ton (f.o.b. U.S. Gulf Coast) or less than \$6.25 per million BTU of hydrogen contained [62]. Besides the large volume of production and use, and relatively low cost, ammonia has many other advantages as a hydrogen- rich fuel for fuel cell applications. They are as follows [26,27,31,42,49,59,63]:

- Anhydrous ammonia contains 17.8 percent by weight hydrogen.
- Technology for transportation, distribution, storage and utilization of ammonia is well established and widely available.
- Ammonia can be stored under moderate pressure (about 370 psig) and its physical properties mimic those of liquid propane.
- Anhydrous liquid NH_3 stores 30% more energy per unit volume than LH_2 (after taking into account the energy required for both evaporation and decomposition of liquid NH_3).
- Explosion span for ammonia-air (at 0°C and 1 atm) is much narrower than that for hydrogen-air mixtures (*i.e.* 16 – 27 vol % NH_3 vs. 18.3 – 59 vol % H_2).
- Autoignition temperature for ammonia vapor is much higher than that for hydrogen (*i.e.* 651°C for ammonia vs. 585°C for hydrogen).
- Using ammonia in fuel cell power plants does not generate CO_x or NO_x emission.
- Only 16% of the energy stored in ammonia is needed to break gaseous ammonia into nitrogen and hydrogen gases.
- Ammonia as fuel for AFCs requires no shift converter, selective oxidizer or co-reactants such as water as in other hydrocarbon or alcohol fuel cell power devices.
- Hydrogen produced from ammonia can be utilized in AFCs that are amongst the most efficient and least costly fuel cell power plants.
- No final hydrogen purification stage is needed. Since nitrogen is an inert gas in the fuel cell and simply passes through as a diluent.

Ammonia can be readily converted to hydrogen and nitrogen gas by thermocatalytic decomposition. NH_3 decomposition reaction is well studied and can be accomplished in a simple reactor using variety of catalysts including transition metals and alloys [64]. Among metal catalysts, ruthenium and iridium are the most active for NH_3 dissociation under mild conditions [55,65]. Other compounds that exhibit high activity for NH_3 cracking include alloys such as Fe-Al-K, Fe-Cr, La-Ni (-Pt) and La-Co (-Pt). In general, catalysts containing noble metals are not used in the commercial processes due to high cost. The widely used supported Ni catalyst requires very high temperatures (in excess of 1000°C). Transition metal nitrides and carbides, such as Mo_2N , VN, and VC_x , have also been tested for NH_3 decomposition. Catalytic action of nitrides and carbides is similar to those of noble metals with respect to the reactions involving H_2 [66]. It has also been shown that the nitrated MoN_x and NiMoN_x on $\alpha\text{-Al}_2\text{O}_3$ are both very active for NH_3 dissociation. For example, the ammonia conversion for $\text{NiMoN}_x/\alpha\text{-Al}_2\text{O}_3$ exceeds 99% even at 650°C, and reaches a maximum of 99.8% when the atomic ratio of Ni/(Ni + Mo) is close to 0.60 [66]. This temperature is much lower than the operating temperatures of the commercial catalysts such as the ICI's 10%-wt Ni on alumina (catalyst 47-1), Haldor Topsøe's triply promoted iron-cobalt (catalyst DNK-2R) or SÜD-Chemie 27-2, nickel oxide (NO) on alumina catalyst [67,68].

Conventional large-scale ammonia crackers (in the power ranges of up to 1200 kW) are used in metallurgical industry for metal nitriding (69). Newer, highly efficient and fully integrated ammonia dissociators are being developed for smaller and more specialized applications. One example is the system developed by the Boston-based Analytic Power Corporation (now Dais Analytic Corp.) that provides hydrogen source for small (150 W) fuel cell power supplies (45).

Another example involves the MesoSystems Technology, Inc. (MTI). MTI has developed a compact system for ammonia storage, reforming, H₂ generation and purification utilizing the microchannel reaction technology. MTI's objective was to produce a 50W power supply to deliver one kW-hr equivalent hydrogen from a 1-kilogram hydrogen source. The weight includes the microchannel cracker, ammonia precursor, and all the necessary scrubbers to purify the resulting hydrogen/ammonia stream [70,71]. MTI estimates costs of about \$300 for the H₂ generator (for orders of 10,000 systems or more) and about \$10-\$20 for each NH₃ fuel canister delivering about 60g of H₂ (net), for orders of 100,000 units or more [72].

Somewhat larger ammonia crackers than those developed at Dais Analytic and MTI are needed for vehicular fuel cell applications. The Apollo Energy Systems, Inc. of Fort Lauderdale, Florida and researchers at the Technical University (TU) of Graz, Austria have jointly developed an 11.5 kW ammonia cracker [73]. TU team's approach was to improve the commercially available NH₃ pyrolysis catalysts such as the SÜD-Chemie 27-2 and NO on alumina by modification with noble metals (e.g. 0.3 wt% ruthenium on nickel oxide catalyst). Apollo Energy Systems (AES) plans to market 10-kW alkaline fuel cells that can use liquid ammonia as a base fuel that is converted to H₂ in their proprietary autothermal ammonia cracker [74]. To date, no cost data are available on any of the AES crackers. Autothermal NH₃ reformers are described in the next section. For the time being it suffices to say that for larger multi-kW ammonia crackers such as those developed by Kordesch and co-workers for AES, the overall efficiency of the system can reach as high as 85% [75]. For smaller NH₃ crackers for PEM fuel cell applications, the efficiency values of about 60% have been reported by Yang and Bloomfield [76], with as much as 40% of the product H₂ burned to supply dissociation energy needed for their autothermal reformer and also compensate for the heat losses.

Apparently, both AES and Analytic Power ammonia reformers described above are based on a system design first developed by Ross, Jr. at LBNL [77,78]. Although the NH₃ reformer used by Bloomfield and co-workers in a 1998 demonstration by Analytic Power [76] utilized Ross' design, it is not clear why their reported H₂ efficiency (*i.e.* only ca. 60%) was so much lower than the 80% or so obtained in the Ross' laboratory unit [78]. One explanation for this may be the attempt by the Analytic Power to reduce the size of the reformer by using higher temperatures (1050°C versus 450°C in Ross' lab unit). The theoretical (adiabatic) efficiency is 85%.

Autothermal Reformation of Ammonia

As noted above, a more direct method for supplying the required energy to drive the dissociation reaction while minimizing the heat losses is by autothermal ammonia reformation. Autothermal ammonia decomposition provides an especially effective way to supply H₂ for use in the proton exchange membrane (PEM) fuel cell systems. This technique combines endothermic heterogeneous NH₃ decomposition reaction (into H₂ and N₂ on a supported catalyst) with the exothermic homogenous oxidation of ammonia (into N₂ and water) in the gas phase [79]. This direct coupling of ammonia dissociation and oxidation within the same reactor greatly improves heat transfer and process energetics. For optimum performance, ammonia reformer must approach adiabatic operation and allow cooling of the reactor effluent via feed gas preheat in a suitable heat exchanger.

There are other advantages of autothermal ammonia reformation. Ammonia conversions exceeding 99% with H₂ selectivities above 65% have been reported at space velocities as high as 10⁶ hr⁻¹ [80]. We used Thermfact's chemical equilibrium program FactSage 5.0 to minimize the Gibbs free energy and determine species concentration during autothermal reformation of ammonia. Results are depicted in Figure 1 for autothermal adiabatic reaction of ammonia with air (consisting of nitrogen, oxygen and carbon dioxide gases). It was further assumed that the feed gas entering the reformer is heated to the same temperature as the reactor effluent (that is equal to the reformer temperature). The reformate mole fractions are calculated for a range of temperatures and initial NH₃ to oxygen molar ratios (x_{NH_3}). Figure 1 depicts calculation results obtained for x_{NH_3} values in the range of 1.33 to 49.2. Results of Figure 1 indicate that autothermal NH₃ reformation can be carried out over a wide range of x_{NH_3} values. Lower ratios lead to higher ammonia conversions but lower H₂ selectivities as more hydrogen is converted into water.

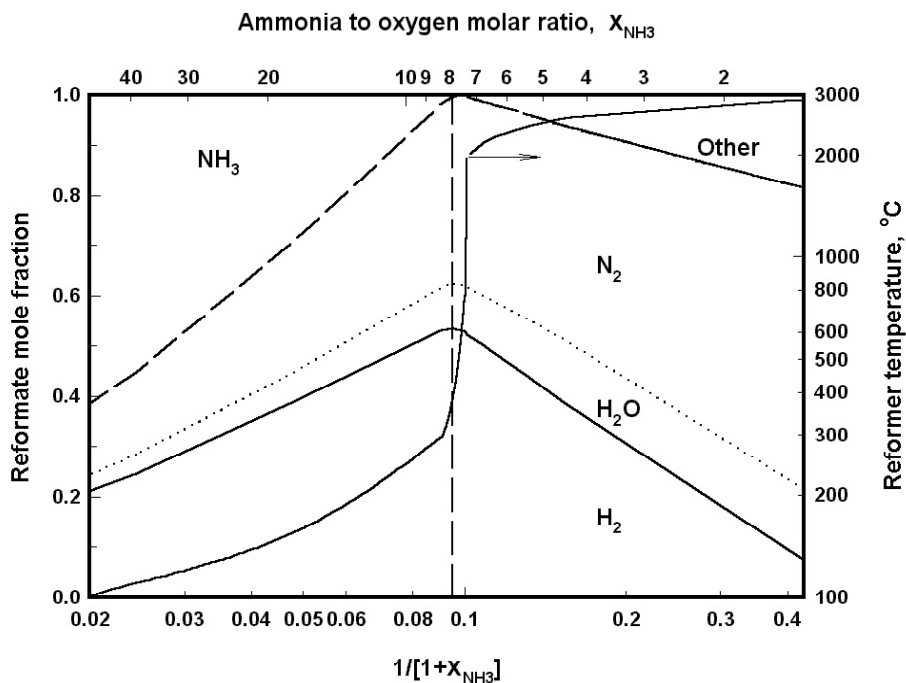


Figure 1. Autothermal reformation of ammonia in air,
 $[O_2+3.76N_2+0.002CO_2+x_{NH_3}NH_3]_{in}$.

Figure 2 depicts the effect of reformation temperature on the reformate mole fractions for the same process conditions as that in Figure 1. It can be seen that autothermal ammonia reformation is accomplished over a wide range of reformer temperatures. Furthermore, no NO_x or any other undesirable species such as unreacted oxygen is detected in the reformer effluent for x_{NH_3} values in the range of 7 to 8 and reforming temperatures from about 400°C to 1500°C.

These results are in general agreement with the experimental data of Goetsch and Schmit given in Table 1 for ammonia decomposition on ruthenium catalyst in coaxial autothermal reformer with feed gas preheating [80].

The main disadvantage of autothermal reforming of ammonia is that the effluent stream needs to be cooled down to a temperature compatible with PEM fuel cell operation. In addition, the

dilution of H₂ with N₂ from air may be undesirable in some applications. The scrubbing of the residual NH₃ (at ppmv levels) in the effluent stream may also be necessary.

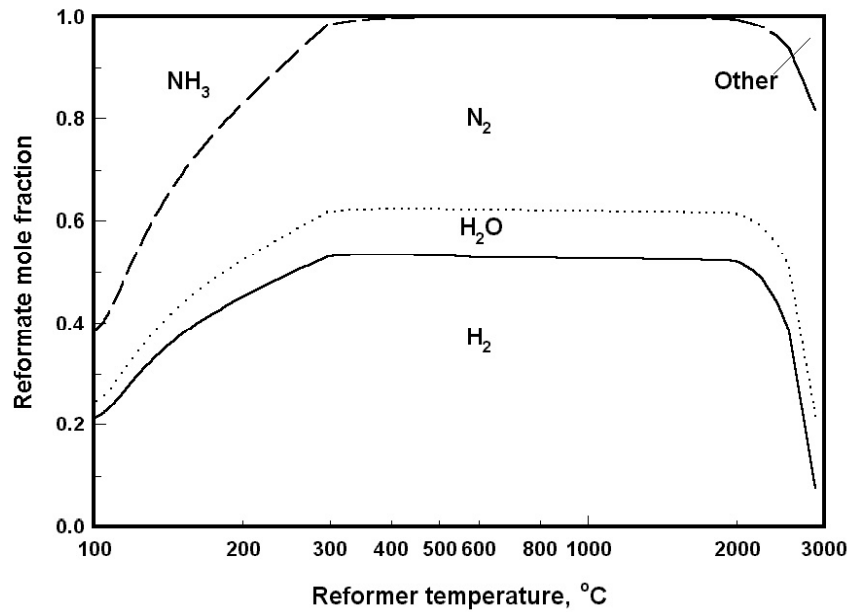


Figure 2. Effect of temperature on reformat concentration for autothermal reaction of ammonia with air.

Table 1. Autothermal reformation of NH₃ in a coaxial reactor on monolithic Ru catalyst [80].

x_{NH_3}	NH ₃ conversion	N ₂ yield	H ₂ yield	H ₂ selectivity	H ₂ O yield	H ₂ O selectivity
3	0.989	0.989	0.634	0.641	0.355	0.359
4	0.976	0.976	0.707	0.725	0.268	0.275
5	0.926	0.926	0.702	0.758	0.224	0.242
6	0.826	0.826	0.607	0.735	0.219	0.265
7	0.754	0.754	0.541	0.718	0.213	0.282
8	0.645	0.645	0.445	0.689	0.201	0.311
9	0.596	0.596	0.390	0.654	0.206	0.346

Drawbacks to Ammonia Use

For vehicular fuel cell applications and for economic and performance related reasons, it is necessary to reduce the size and lower the operating temperature and cost of ammonia dissociator. Special consideration has to be also given to the safety and environmental factors resulting from the direct involvement of the public.

One major drawback to ammonia as a fuel and chemical carrier for hydrogen, especially in vehicular applications, is its extreme toxicity and adverse health effects. Permissible levels of exposure to toxic gases are defined by their time-weighted average (TWA), short-term exposure limit (STEL) and concentration immediately dangerous to life or health (IDLH). Anhydrous NH₃ has a TWA of 25 ppm, an STEL of 35 ppm and an IDLH of 500 ppm [81]. Although injury from

NH_3 is most commonly the result of inhalation, it may also follow direct contact with eyes and skin or ingestion. The EPA has identified NH_3 as one of 366 extremely hazardous substances subject to community right-to-know provisions of the Superfund Act and emergency planning provisions of the Clean Air Act [82]. There are also other less obvious drawbacks to the widespread use of ammonia as vehicular fuel. For example, anhydrous ammonia is used, extensively, in the manufacture of illicit drug methamphetamine. Anhydrous NH_3 is used in the so-called "Nazi method" to spur methamphetamine production [83]. This method does not require extensive knowledge of chemistry, uses no heat, and is much simpler technique than the ephedrine-pseudoephedrine reduction or "Red P" method that is also used for producing methamphetamine.

Due to these and other considerations, it appears unlikely that NH_3 will find widespread use as a high-density chemical carrier for H_2 in the future transportation applications. This is despite the fact that ammonia is a superb fuel for power plants, in general, and fuel cells, in particular. Furthermore, due to economic and energy efficiency considerations, it will be advantageous if a method could be found that completely eliminated the need for or greatly simplified the function of the on-board NH_3 reformer. One approach to mitigate ammonia's shortcomings is to complex NH_3 with other hydrides so that the resulting compound is stable but not toxic or cryogenic. The prospective process must produce a compound that contains H_2 at gravimetric and volumetric densities comparable to that of anhydrous ammonia. A class of compounds (with generalized formula $\text{B}_x\text{N}_x\text{H}_y$) known as amine-boranes and some of their derivatives satisfy this requirement.

Hydrogen from Pyrolysis of Amine-Boranes

Review of literature prior to 1980 reveals that several methods have been investigated as a means of high capacity hydrogen storer compounds. The compounds that have been considered are primarily based on complex borohydrides, or aluminohydrides, and ammonium salts. These hydrides have an upper theoretical H_2 yield limited to about 8.5% by weight. Improvements in H_2 weight yield will not result from solid reactants based upon the interaction of metal borohydrides, or aluminohydrides, and ammonium salts, or from catalytic decomposition of the active hydride compounds. This is so because for $\text{NaBH}_4/\text{NH}_4^+$ salt systems the generation of hydrogen is the result of reaction between NH_4^+ cation and the BH_4^- anion [84]. Therefore, the counter ions only serve to stabilize these reactive species, resulting in a lower hydrogen yield because of their added weight. Thus, in order to achieve higher hydrogen yields, it is advantageous to consider those compounds that have, on a molecular basis, only moieties that react to form hydrogen. Amongst the compounds that contain only B, N, and H (both positive and negative ions), representative examples include: amine-boranes, boron hydride ammoniates, hydrazine boron complexes, and ammonium octahydrotriborates or tetrahydroborates. Of those, amine-boranes (and especially ammonia-borane) have been extensively investigated as H_2 carriers [84-91].

During 1970's and 80's, the U.S. Army and Navy funded efforts aimed at developing H_2 /deuterium gas-generating compounds for use in the HF/DF and HCl chemical lasers, and gas dynamic lasers [85-91]. Earlier H_2 gas-generating formulations were prepared using amine-boranes (or their derivatives), mixed and ball milled together with a reactive heat-generating compound, such as LiAlH_4 or a mixture, such as NaBH_4 and Fe_2O_3 , until a uniform mixture was obtained [90]. Upon ignition, the heat-generating compound in the mixture reacts and the energy released pyrolyzes the amine-borane(s) forming boron nitride (BN) and hydrogen gas. A nichrome heating wire is used to initiate a self-sustaining reaction within these gas-generating compounds. Ammonia-borane or borazane (H_3BNH_3) is the simplest stable amine-borane used

in these gas-generators. Another stable amine-borane used in the gas-generators is diborane diammoniate, $H_2B(NH_3)_2BH_4$ [92].

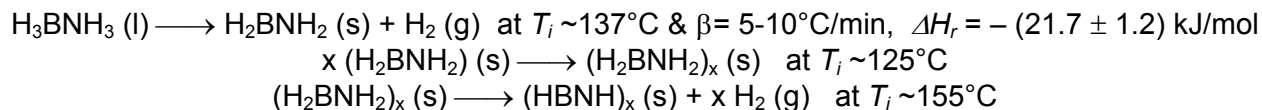
Ammonia-borane and diborane diammoniate both pyrolyze upon heating, releasing H_2 gas. Reaction products, besides H_2 , include a polymeric solid residue of poly(aminoborane) $(BH_2NH_2)_x$. With further heating, more hydrogen is released and borazine ($B_3N_3H_6$) forms, a compound that is structurally analogous to benzene. Borazine can react further releasing additional H_2 to produce boron nitride, BN. Techniques for preparation of an all amine-borane formulation consisting of hydrazine (bis)borane, $N_2H_4 \cdot 2 BH_3$ and diborane diammoniate, in the form of a compacted solid fuel is given by Grant and Flanagan [92].

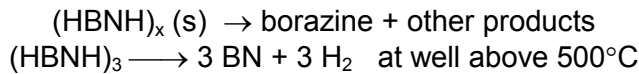
In addition to the gas generating compounds discussed above that provide hydrogen yields in the range of 16 wt% and better than 99% H_2 purity, other formulations that were based on the magnesium borohydride diammoniate (MBDA), $Mg(BH_4)_2$ have also been prepared and tested [93]. Formulations based on MBDA are generally more stable and better suited for the field applications. MBDA-based compounds contain an oxidizer selected from $LiNO_3$ and KNO_3 and polytetrafluoroethylene (PTFE) as the binder. For example, a blend of 85 wt% MBDA, 7.5 wt% $LiNO_3$, and 7.5 wt% PTFE provides a H_2 yield of about 12.5 wt% with excellent pellet thermal stability (up to $75^\circ C$) and physical properties [93].

Physiochemical Properties and Synthesis of Ammonia-Borane Complex

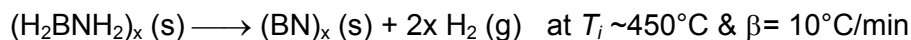
Ammonia-borane is a white crystalline solid at normal conditions that contains about 20-wt% hydrogen. Pyrolysis of ammonia-borane is a complex process and the products of the decomposition reaction markedly depend on the conditions employed. Furthermore, the initial process is a solid-state reaction for which the onset of decomposition (T_i) is a function of heating rate of the substrate (β). In one study based on TG-FTIR and TG-DSC analysis, heating a borazane sample to $90^\circ C$ at a rate of $\beta = 0.5^\circ C/min$ and then holding it at that temperature for 200 min resulted in a loss of about 10.2% of initial sample mass [94]. FTIR analysis of the evolved gases shown approximately one mol of H_2 forming per mol of BH_3NH_3 reacted. Reaction products, in addition to hydrogen, include monomeric aminoborane BH_2NH_2 and a small amount of volatile borazine ($B_3N_3H_6$) [94]. The monomeric aminoborane is unstable at room temperature oligomerizing to form a non-volatile white solid residue of poly(aminoboranes) $(BH_2NH_2)_x$ [95-99]. The inorganic analog of polyethylene, polymeric $(NH_2BH_2)_x$ is still not fully characterized [98]. Crystalline cyclic oligomers, $(NH_2BH_2)_n$ (where, $n = 2, 3, 4, 5$) have been prepared in the past [100] and an amorphous $(NH_2BH_2)_x$ consisting of solvated linear chains with $x = 3-5$ has also been produced by gas-phase pyrolysis of ammonia-borane [101].

Unlike aminoborane oligomers, borazine (isoelectronic with benzene) is a volatile colorless liquid that boils at $55^\circ C$ [94]. Based on the TG and DSC analysis of Geanangel and co-workers [97], pyrolysis of ammonia-borane begins with a sharp endothermic peak that appears just above the melting point of BH_3NH_3 ($112-114^\circ C$ depending on the sample heating rate β) [94,96]. Near $117^\circ C$, a steep exothermic peak was observed, reaching a maximum at about $130^\circ C$ with rapid evolution of gas. A final broad exotherm was observed to occur near $150^\circ C$. Although processes other than step-wise decomposition and hydrogen loss are involved to some degree in H_3BNH_3 and its intermediate compounds, nonetheless the following sequence of events also occur [94,96-98]:





and,



Due to the large amount of evolved H₂ and the exothermicity of the process, ammonia-borane appears to be a more effective chemical storer of H₂ than anhydrous NH₃ [94,102]. Other physicochemical properties of ammonia-borane complex are given in Table 2 below.

Table 2. Selected physicochemical properties of ammonia-borane complex.

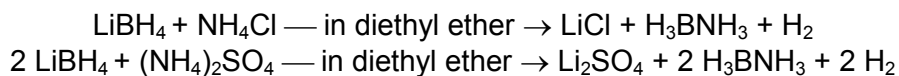
Property	Description	Reference
Formula	NH ₃ BH ₃	-
Molecular weight	30.86	-
X-ray structure	C _{4v} symmetry; unit cell is tetragonal	[103,104]
Odor	Ammonia-like	-
Density, g/mL	0.74	[103-105]
Melting point	112-114°C, slow decomposition at approx. 70°C	[94,96]
Heat of formation	ΔH _f ^o = -178 ± 6 kJ/mol	[106]
Heat of combustion	ΔH _c ^o = -1350 ± 3 kJ/mol	[106]
Water stability	10% solution stored at ambient temperatures:	[107]
	<u>Dormancy</u>	<u>% hydrogen loss</u>
	4 days	1.8
	11 days	3.6
	1 month	48
	2.5 months	93
	18 months	45.0

Another important factor is interaction with water and other solvents. Unlike ionic hydrides, NH₃BH₃ does not react violently with water. Table 3 depicts the solubilities of borazane in water and a number of organic solvents. More information is available in reference [108].

Table 3. Solubilities of ammonia-borane complex in various solvents [107].

Solvent	Wt%	Temperature, °C	Density of saturated solution, g/mL
Water	26	23	0.89
Methanol	23	23	0.78
Ethyl Ether	0.80	24	0.71
Hexane	0.003	25	0.56
Benzene	0.03	25	0.87
Methylene Chloride	0.08	21	1.32

Borazane can be prepared through several indirect procedures [109-114] including the reaction with lithium borohydride, LiBH₄, in diethyl ether by either of the following two methods:



Alternatively, H₃BNH₃ is prepared directly from the gases by reacting diborane with ammonia in polar organic solvents (e.g. ether and dioxan) and in aqueous media [105,114]:



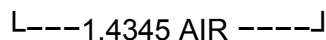
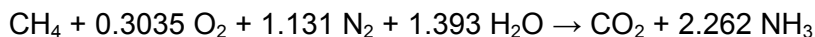
A comprehensive survey of synthetic procedures applicable to most of the known boron-nitrogen compounds (except boron nitrides) including amine-boranes and their physical properties can be found in the reference [114].

For vehicular fuel cell applications, the main drawback to the use of amine-boranes, in general, and H_3BNH_3 , in particular, is the present high cost of these compounds and lack of a suitable reformer design for the on demand generation of hydrogen. No data could be found for the large-scale production costs of ammonia-borane. However, the Callery Chemical Co manufactures large quantities of dimethylamine borane (DMAB), which has significant use in the electroless plating industry. Depending on the volume, the price of DMAB is in the range of about \$75-100/lb [115]. It can be expected that the large volume price of ammonia-borane to be also in this range. The issue of the cost of ammonia-borane can be highlighted by comparing its price to the bulk material prices for other chemical hydrides under consideration as hydrogen storer compounds. The feasibility of using various ionic hydrides as potential hydrogen storer compounds for alkaline fuel cell (AFC) applications has been investigated by Kong et al. [116]. Their application required a hydrogen storage system capable of supplying hydrogen to an AFC generator producing 1 kW of electrical power for 8 hours. The fuel cell was assumed to operate at 57% efficiency (0.7 V) requiring 231 mol of H_2 (assuming 100% utilization) to meet the target duty. Table 4 depicts the cost of several hydrogen storer compounds including H_3BNH_3 .

Table 4. Required mass, volume and cost of chemical hydrides for specified targeted duty.

Storer	Mass, kg	Volume, L	Cost, US\$	Reference
LiH	1.7	3.7	109	[116]
CaH ₂	4.5	4.0	104	[116]
NaBH ₄ (35 wt% aqueous)	6.21	6.21	102	[116,117]
H_3BNH_3	2.38	3.21	390-525	This study

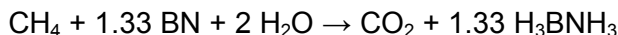
New chemical synthesis techniques and/or processes are needed to reduce the H_3BNH_3 production costs. Some work is already underway in this area. The U.S. Army has funded Venture Scientific International to investigate new methods for the synthesis of H_3BNH_3 and its pyrolytic decomposition to hydrogen, as well as packaging this compound into a compact, high output portable power source [118]. In addition to the cost issues, new processes must also be developed to allow recycling of the by-products of ammonia-borane decomposition on-board fuel cell powered vehicles. For example, if an on-board ammonia-borane based hydrogen storage system is to be developed for maximum H_2 delivery, then it will be desirable, if not necessary, to be able to retrieve and recycle the boron nitride residue. Here, the challenge is to develop a chemical route for activating boron-nitrogen bond in a manner analogous to dinitrogen bond activation in the Haber-Bosch process for ammonia synthesis. In the modern ammonia plants, steam reformation of natural gas is used as the primary source of hydrogen. Based on pure methane, let's formulate a simple stoichiometric equation for ammonia production by steam methane reformation (SMR) as follows [63]:



In real processes, a high degree of irreversibility exists and considerable amount of energy is needed to produce ammonia from methane, air and water. The stoichiometric quantity of

methane required in the equation above is about 583 m³ per ton of ammonia produced. Energetically, this corresponds to approximately 20.9 GJ per ton of NH₃ (LHV). It can be argued that this is the minimum amount of energy needed per ton of ammonia produced using SMR process. It is interesting to note that the best energy figure reported for commercial ammonia production is about 27 GJ/t NH₃ [63]. This figure corresponds to a rather high efficiency of around 75% with respect to the theoretical minimum of 20.9 GJ/t NH₃, calculated as stoichiometric methane demand discussed above.

In a like manner, an idealized process for ammonia-borane synthesis from recycled BN (or borazine) may be written as:



Or,



If similar processes could be developed at energy conversion efficiency levels that are comparable to the present day SMR-based ammonia synthesis plants, it is then possible to realize a major reduction in the production costs of ammonia-borane complex that is useful for the vehicular fuel cell applications. We note that a concept similar to that discussed above has been developed for a new nitric acid synthesis process based on boron nitride analogous to the Haber-Bosch route for HNO₃ production from ammonia [119]. In another recent report, nano-structured hexagonal boron nitride (h-BN) was prepared by mechanical milling under hydrogen atmosphere [120]. Hydrogen uptake in the mechanically activated h-BN reached 2.6% by mass of the material after milling for 80 h. Mechanical milling may be one approach to facilitating hydrogenation and reformation of boron nitride to amine-boranes. Finally, recent results have shown that unusual parallel behavior exists between hydrocarbons and their corresponding B-N analogues [121]. Thus, hydrogenation of benzene to cyclohexane may provide a model for the reformation of borazine to other amine-boranes.

Conclusions

There are many advantages to the use of NH₃ as hydrogen source for vehicular FC applications. However, a major drawback is ammonia's extreme toxicity and adverse health effects. By complexing NH₃ with diborane, a stable, non-toxic and non-cryogenic material (H₃BNH₃) can be prepared. This ammonia-borane complex is stable in water and ambient air and when heated liberates H₂ in a sequence of reactions between 137°C and 400°C that reaches about 20% of the initial mass of H₃BNH₃. Successful implementation of ammonia-borane as a potential future transportation fuel, however, requires new chemical techniques and/or processes for its synthesis that promise substantial reduction in its production costs.

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Analysis of a New Solar Thermochemical Water-Splitting Cycle for Hydrogen Production

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Abstract

High efficiency thermochemical water splitting cycles (TCWSCs) require a high-temperature heat source that can be either nuclear or solar power based. In the hybrid Bowman-Westinghouse TCWSC, an electrolytic process is combined with thermal decomposition of sulfuric acid to co-produce hydrogen and oxygen. The main drawback of the Bowman-Westinghouse cycle is that the electrolysis step requires low concentration of sulfuric acid leading to higher energy consumption in the acid concentration and separation step. A new sulfur-ammonia TCWSC has been proposed for decomposing water into hydrogen and oxygen that consists of three steps: 1) photocatalytic oxidation of ammonium sulfite to generate ammonium sulfate with simultaneous reduction of water to hydrogen. This process utilizes both thermal and ultraviolet portion of the solar spectrum; 2) ammonium sulfate decomposition into ammonia and sulfuric acid, with the later undergoing the same reduction process as that in the sulfur family cycles; and 3) chemical co-adsorption of ammonia and sulfur dioxide to produce ammonium sulfite which is then recycled to produce hydrogen and ammonium sulfate. The new cycle has the potential for higher overall efficiency by using readily available and inexpensive chemicals. Solar energy is used as a heat source and UV portion is utilized for a photocatalytic redox reaction. Prior experimental results indicate that photolytic and/or photocatalytic oxidation of sulfite ions occurs at acceptable rates with no occurrence of side reactions.

Keywords: thermochemical, water splitting cycles, sulfur family cycles, hydrogen production, ammonia, ammonium sulfite, ammonium sulfate, solar, ultraviolet light.

1. Introduction

In the course of past several decades, many thermochemical cycles have been devised for production of hydrogen (H_2) from water. It has been shown that TCWSCs have the potential to deliver overall system efficiencies in excess of 40%. Among the most studied TCWSCs are sulfur-halogen cycles. Figure 1 is a simple schematic diagram depicting the sulfur-halogen TCWSCs. At present, there are two potential high temperature heat sources available for use with TCWSCs. They are solar thermal concentrator and central receiver systems, and nuclear reactors (*i.e.* high temperature gas-cooled reactors, HTGR). U.S. DOE under Nuclear Energy Research Initiative (NERI) Program has funded several efforts aimed at hydrogen production using nuclear power.

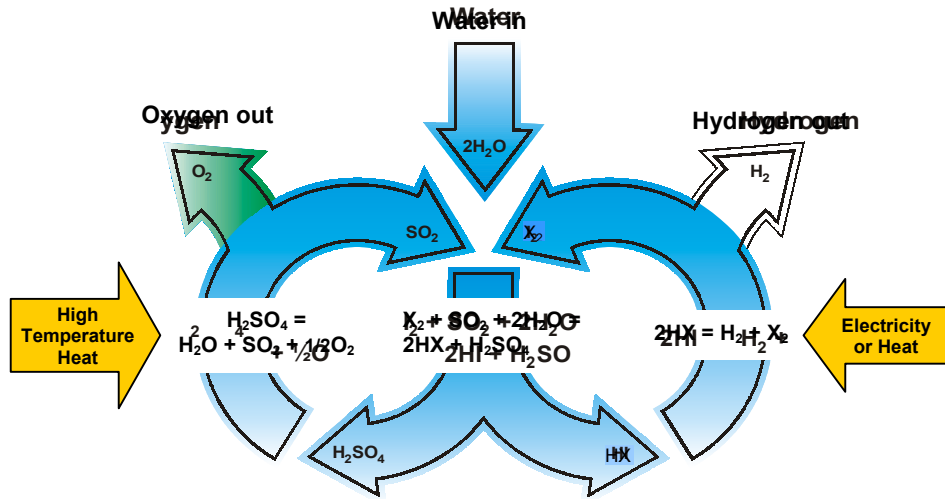


Figure 1. A schematic diagram of the sulfur-halogen TCWSCs (X= iodine or bromine)

One major program has been underway at the General Atomics (GA) Corp., in collaboration with the University of Kentucky (UK) and Sandia National Laboratories (SNL). The objective of the GA/UK/SNL study was to assess the technoeconomics of hydrogen production using HTGR. GA/UK/SNL reports provided a starting point for the evaluation of TCWSCs suitable for solar interface and capable of providing efficient and cost-effective means of H₂ production from water. After analyzing more than 100 different TCWSCs, the GA/UK/SNL study narrowed the prospective cycles to two; namely, the UT-3 cycle developed at the University of Tokyo and GA's Sulfur-Iodine (S-I) cycle. Another process not considered by the GA/UK/SNL group but of value to solar-driven processes is the SynMet process developed at the Paul Scherrer Institute (PSI), Switzerland. In the following sections, these systems are briefly reviewed:

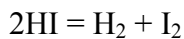
2. Leading Thermochemical Hydrogen Production Systems

2.1 Bunsen reaction involving iodine and thermal decomposition of HI

As depicted in Figure 1, in addition to sulfuric acid decomposition step, the following reactions are employed:

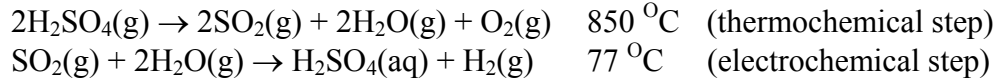


Followed by thermal decomposition of hydroiodic acid:



This is the General Atomic (GA) process with the revised cycle having improved energetics and an overall efficiency of about 50%. A variation of this TCWSC is the so-called Bowman-Westinghouse cycle [1-4] that employs a reaction involving bromine (instead of iodine) and electrolysis of hydrobromic acid (in lieu of thermal decomposition

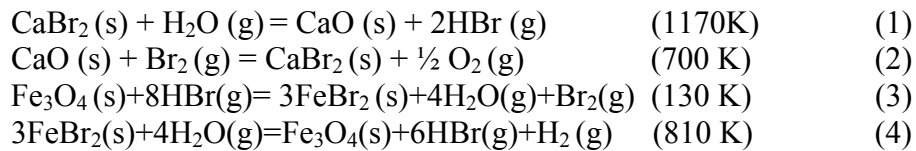
of HI). The electrolytic decomposition of HBr requires a cell voltage of about 0.80 V (for acid concentration of 75 wt%). The Bowman-Westinghouse cycle consists of two reactions:



One problem with the Bowman-Westinghouse cycle involves the pH effects during electrolysis of sulfur dioxide in aqueous solution. At low solution pH, sulfur forms instead of hydrogen. To avoid sulfur formation, one has to maintain high solution pH that requires a reduction in acid concentration in the solution. Low acid flow rates translate into low hydrogen evolution rate. In summary, we note that hydrogen production rate depends on the solution pH, while pH is depended on sulfur dioxide concentration. To avoid sulfur formation, the electrolytic process has to maintain low acid concentration levels to keep pH levels high. This in turn leads to a decrease in H₂ production rate. Low sulfuric acid concentration in the outlet of an electrochemical reactor will also require more intensive and costly acid separation and concentration step reducing the efficiency of H₂SO₄ decomposition to sulfur dioxide and oxygen (see Figure 1) because acid decomposition step consumes a major portion of the input energy to the cycle.

2.2 UT-3 thermochemical cycle

This TCWSC has been developed by Kameyama and Yoshida (at the University of Tokyo). The UT-3 process is one of the most studied thermochemical hydrogen production cycles in the world. It should be noted that the UT-3 process is being developed for coupling to nuclear power reactors. The reported cycle efficiency is in the range of 40 to 50%. The cycle involves the following four gas-solid reactions:



Reaction (1) has been the slowest step, kinetically, amongst the four reactions, thus, being the rate limiting for the whole cycle. Since it is necessary that all of the reactions proceed at a same rate for continuous operation of the cycle, the slow rate of hydrolysis of calcium bromide adversely affects the whole process efficiency. Another undesirable feature of UT-3 cycle is that it is a gas-solid type process consisting of a pair of hydrolysis (endothermic) and Br reduction (exothermic) reactions that occur in four series reactors. In order to conduct these processes as in fixed bed reactors, the gaseous must alternatively flow in opposite directions. In other words, a given reactor must run an endothermic reaction in one direction for about two hours and then an exothermic one in the opposite direction for the next two hours, and so forth.

The UT-3 cycle has been investigated extensively for almost 25 years since it was first proposed in 1978. It has also been fully flow sheeted and many issues related to the reaction chemistry and kinetics of individual processes as well as the process separation

issues has been studied in detail. The overall efficiency of the improved adiabatic UT-3 process has been reported as 40% to 50%. However, difficulties remain with UT-3 cycle requiring further improvements. Examples include: 1) heat-transfer and temperature control - reactions 1 and 4 are hydrolytic reactions, which require energy input while reactions 2 and 3 are exothermic requiring heat removal from the reactors; 2) steady-state operation - circulation time period for the UT-3 cycle has been reported to be two hours; 3) separation issues - to cool down exothermic reactors and sweep the reaction products out of reaction zones, excess steam is needed; 4) packed reactor design; 5) process lifetime issues; etc.

2.3 Zn/ZnO process

This is so-called "SynMet" process developed at PSI. The process combines ZnO-reduction and CH₄-reforming within a solar reactor. It consists of a gas-particle vortex flow confined to a solar cavity-receiver that is exposed to concentrated solar irradiation. A 5-kW reactor has been built at PSI and subjected to tests in a high-flux solar furnace. Natural gas is used as a reducing agent to process ZnO according to the following overall reaction:



The process reforms methane in the absence of catalysts and is being optimized to produce syngas especially suited for methanol synthesis, and co-production of Zn and syngas avoids CO₂ emissions in the traditional carbothermal reduction of ZnO. Even though the PSI process is the only system developed for direct solar interface, it is not, however, a typical TCWSC, per se.

In this paper, we describe a new solar driven process - "sulfur ammonia cycle," for co-production of hydrogen and oxygen from water, as follows:

3. New Sulfur Ammonia Cycle

3.1 Flow sheet and reactions of sulfur-ammonia TCWSC

In an attempt to mitigate above-mentioned shortcomings, a new sulfur-ammonia cycle has been conceived that is a better fit to solar power source and is not affected by sulfur dioxide solubility issues. This cycle is depicted in Figure 2. A flowsheet of the cycle is given in Figure 3. Ammonium sulfite is fed into a photocatalytic reactor from Stream (10) where sulfite ions are oxidized into sulfate ions while water is reduced to hydrogen gas. Ammonium sulfate, stream (1), is then decomposed into ammonia gas and steam. Through decomposer, liquid sulfuric acid, stream (3), is introduced into acid vaporizer to generate gaseous sulfur trioxide and water. The product sulfuric trioxide is then reduced to produce sulfur dioxide gas and oxygen, streams (4) to (6), in a reduction reactor. Small amounts of sulfuric acid that remains can be separated from the gaseous mixture containing sulfur dioxide, oxygen and water with an acid scrubber. Sulfuric acid removed is then recycled; stream (7), and sulfur dioxide and oxygen are mixed, *i.e.* streams (8) to (9), with ammonia and chemically adsorbed to produce ammonium sulfite, which is then fed into the photocatalytic reactor to start the cycle anew.

In the adsorption unit, oxygen is separated from the stream. The chemical reactions involved in the proposed sulfur-ammonia cycle are as follows:

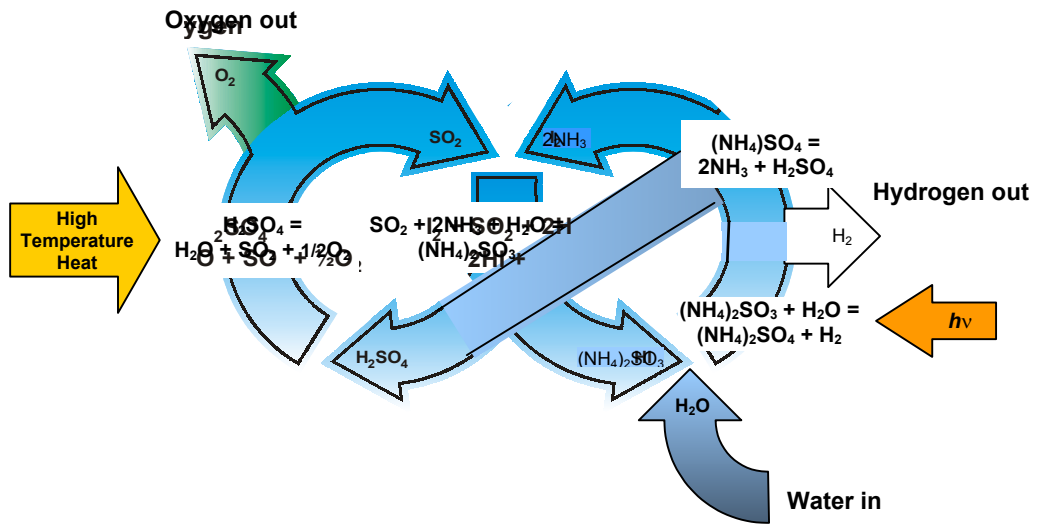


Figure 2. A schematic diagram of sulfur-ammonia TCWSC.

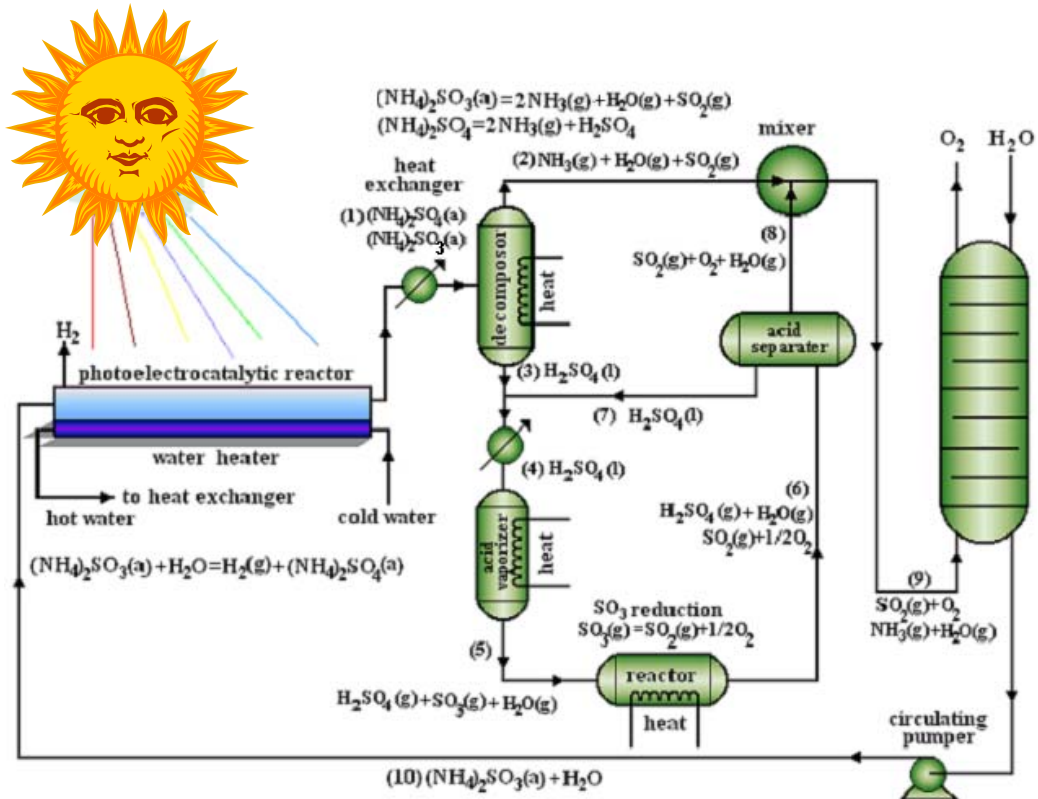
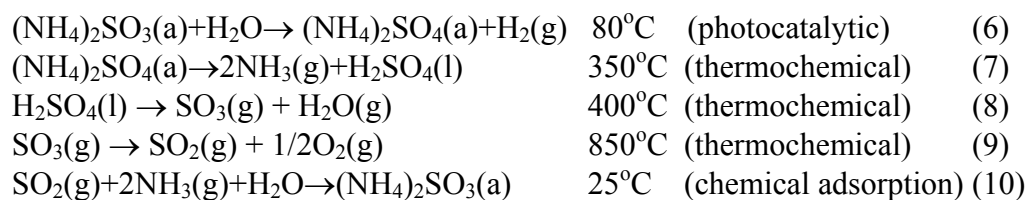


Figure 3. Flowsheet for the proposed sulfur-ammonia TCWSC.



Among these reactions, reactions (6), (7) and (10) are unique to this new cycle. Reactions (8) and (9) are common to all sulfur family cycles.

3.2 Solubility of ammonium sulfate and ammonium sulfite

If reaction (6) is carried out at a temperature of 80 ~ 90°C, the concentration of ammonium sulfate is about 50 wt% (assuming complete conversion of sulfite to sulfate ions). This concentration is six times higher than that in the Bowman-Westinghouse cycle. Since pH in ammonium sulfate (or ammonium sulfite) solution, is higher than that of pure sulfuric or sulfurous acid at the same concentration of anions, sulfite ion oxidation can be conducted in a higher concentration solution without elemental sulfur repercussion. Furthermore, higher sulfuric acid concentration will ease acid separation and concentration as well as improve the process energetics. Moreover, increased acid concentration will increase the sulfite ion oxidation rate. Interestingly, the solubilities of sulfite and sulfate ions are comparable at 30°C. However, at temperatures higher than 30°C, ammonium sulfite has higher solubility in water than ammonium sulfate. If reaction (6) is carried out at 80°C, the concentration of sulfite ions becomes higher than sulfate ions, thus increasing the rate of oxidation. The solubility of ammonium sulfate and ammonium sulfite in aqueous solution is listed in Table 1. The energy required to separate the products of reaction (7), *i.e.* ammonia and sulfuric acid, can be partially supplied by reaction (10) to reduce the net energy input required. This is not, however, the case with the S-I cycle, as it requires energy input for HI decomposition.

Table 1. Solubility of ammonium sulfate and ammonium sulfite in aqueous solution [5].

Temperature (°C)	0	10	20	30	40	60	80	100
ammonium sulfate (NH₄)₂SO₄								
solubility (g/100 g H ₂ O)	70.6	73	75.4	78.0	81	88	95	103
weight percentage (wt.%)	41.4	42.2	43.0	43.8	44.8	46.8	48.7	50.7
molar conc.(mol/100 g H ₂ O)	0.527	0.545	0.563	0.582	0.604	0.657	0.709	0.769
ammonium sulfite (NH₄)₂SO₃								
solubility (g/100 g H ₂ O)	47.9	54.0	60.8	68.8	78.4	104	144	153
weight percentage (wt.%)	32.4	35.1	37.8	40.8	43.9	51	59	60.5
molar conc.(mol/100 g H ₂ O)	0.406	0.458	0.515	0.583	0.664	0.881	1.220	1.297

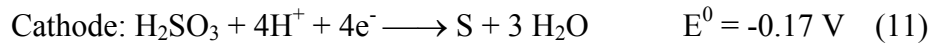
The solubility of sulfur dioxide in water at temperatures of 0 °C and 30 °C and 1 atm ranges from 22.83 g to 7.80 g per 100 grams of water, respectively. The solubility of ammonia at the same temperature and pressure range is 89.5 g to 41.0 g per 100 grams of water, respectively - four times higher than that of sulfur dioxide. More importantly, with ammonia dissolved in the water, sulfur dioxide reacts with the ammonia to form a

highly soluble compound, *i.e.* ammonium sulfite (see Table 1). Thus, ammonia and sulfur dioxide co-dissolved in water is a thermodynamically more favorable solution for separating oxygen from the gas mixture, eliminating the need for sulfur dioxide compression and liquefaction, as in the Bowman-Westinghouse process. The absorption process carried out at room temperature and one atmosphere can minimize operational costs for the entire process.

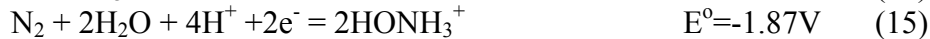
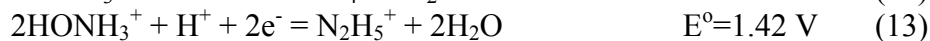
3.3 Side reaction in photoelectrochemical oxidation of sulfite ions

The S-NH₃ cycle is well suited to solar input as the heat source and UV light. The UV part of solar spectrum is of great value for the photolytic and/or photocatalytic redox reactions. In the photocatalytic reactor, sulfite ions are oxidized to sulfate ions and hydrogen is released. The photoreactor consists of two segments. First layer absorbs UV light promoting a redox reaction. Because neither sulfite nor sulfate can absorb visible light, a second under-layer can be used to absorb concentrated long wavelength light heating and decomposing sulfur trioxide to sulfur dioxide.

It is known that sulfite ions can be electrolytically (or photochemically) oxidized into sulfate ions [6-8]. The activity of the oxidation depends on reaction temperature, pH and concentration of sulfite ions. In general, higher the temperature and concentration of sulfite ions, higher the rate of oxidation is. However, pH dependency is relatively complicated because bisulfite ions (HSO₃⁻) have a higher oxidation activity than sulfite ions, and low pH favors bisulfite ion oxidation. Therefore, the criterion for pH selection is to keep the solution pH as low as possible, but not so low, that sulfur is produced in accordance with the following cathodic reaction (11).



The question that arises is that if introduction of ammonium ions will affect hydrogen production from cathode reaction. Several possible cathode NH₄⁺ reactions are listed below [9]:



Because no nitrogen gas is involved in the cycle, reactions (15) to (17) will not affect hydrogen production. Unlike reaction $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$ ($E^0 = 0.0 \text{ V}$), reactions (12) to (14) are not likely because the overpotentials are far higher than that of protonic reduction to hydrogen. Based on the potential sequence, it can be concluded that cathode reactions in terms of ammonium compounds will be involved in the oxidation process. Therefore, the hydrogen produced based on sulfide ion oxidation can be of a very high purity.

4. Conclusions

TCWSCs employing solar energy as the heat source can be attractive due to their relatively higher efficiency. Sulfur family thermochemical water splitting cycles studied in the past (e.g. Bowman-Westinghouse cycle) involve an electrolysis step that requires low concentration of sulfuric acid leading to higher energy consumption in the acid concentration and separation process. A new sulfur-ammonia thermochemical cycle has been proposed for decomposing water into hydrogen and oxygen. The proposed cycle has the potential for achieving high overall energy efficiency by using readily available and inexpensive chemicals. Solar energy is used as the source of heat input. In addition, UV light is utilized for a photocatalytic redox step. Prior experimental results obtained at the Florida Solar Energy Center indicate that photolytic and/or photocatalytic oxidation of sulfite ions occurs at acceptable rates with no occurrence of side reactions.

5. Acknowledgments

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ATTACHMENT 4

The attachment posted in the next page refers to an "Innovative Technology Award," given to Drs. Huang and Raissi for the conceptualization of a new sulfur-ammonia cycle for hydrogen production via solar thermochemical water splitting at the *15th World Hydrogen Energy Conference* held in Yokohama, Japan, June 27- July 2, (2004).

The complete story can be found at the following URL:

<http://www.hydrogenresearch.org/WHEC%20Innovative%20Technology%20Award.pdf>

Also, for the poster, see: <http://www.hydrogenresearch.org/Poster%20Award.pdf>



Innovative Technology Award

Drs. C. HUANG & Ali T-RAISSI

On behalf of
the organizing committee of
the 15th World Hydrogen Energy Conference,
I take great pleasure in thanking you
for invaluable poster entitled

**Analysis of a New Solar Thermochemical Water-Splitting
Cycle for Hydrogen Production**

Presented at 15th World Hydrogen Energy Conference,
which was held from June 27-July 2, in Yokohama Japan.

Hideo Kanayama

Hideo Kanayama, Dr.
Chairperson, Scientific Committee of
the 15th World Hydrogen Energy Conference