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 (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) 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 H_2 to fuel cell power plants.

This paper provides the first account of our analysis pertaining to the technoeconomic aspects of H_2S-methane reformation, magnitude of the H_2S resource and other issues of interest.

Thermochemical, CO$_X$-Free, H$_2$S 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 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 (H$_2$S) gas (Semrau 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 H$_2$S gas (Meyer 2000). Elsewhere, other examples of "ultra-sour" gas include: China's Zhaolanzhuang (60-90% H$_2$S), Canada's Caroline and Bearberry gas fields in West-Central Alberta (70-90% H$_2$S), Astrakhan gas field by Caspian sea (26% H$_2$S), and Lacq gas field in France (15% H$_2$S), to name just few (Kappauf 1985, Ullmann's 1989, Clark 1990).

In natural gas processing, H$_2$S is viewed as a pollutant requiring treatment and removal. Presently, H$_2$S is separated from hydrocarbon gases by amine adsorption and regeneration producing acid gas containing 10-90% by volume H$_2$S. When H$_2$S concentrations exceed 40%, gas is treated (or "sweetened") in the Claus plant (Cox 1998). That is, a portion of the H$_2$S is burned to make SO$_2$, and then recombined with the main H$_2$S stream in a catalytic reactor to produce elemental sulfur and steam according to:

$$2\ H_2S + SO_2 = 3S + H_2O \qquad (1)$$

Elemental sulfur is sold as a feedstock for sulfuric acid manufacture. In Claus process, hydrogen in the H$_2$S is converted to water vapor. Furthermore, since Claus units do not convert all the H$_2$S to sulfur, tail gas cleanup units are needed to remove traces of SO$_2$ before the off-gases can be vented to atmosphere (Erekson 1996). It would be advantageous to perform H$_2$S 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 H$_2$ from the refineries' waste H$_2$S 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 H$_2$S reformation of natural gas (particularly CH$_4$) to hydrogen and carbon disulfide (CS$_2$, instead of CO$_2$, as in the SMR process). A viable process for H$_2$S reformation of methane should result in more SQNG to be made available for pipeline use as well as additional

onsite H_2 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 H_2 can be recovered from H_2S present in the sub-quality natural gas and Claus-type H_2S?
2. Today, the benchmark process for hydrogen production is catalytic reforming of methane (CH_4) with steam. Is there a sulfur analog to steam methane-reforming (SMR) process? In other words, is it technically feasible to reform CH_4 with H_2S (instead of H_2O) yielding H_2 and CS_2 (instead of CO_2)? If so, is the technology available and what are the costs?
3. What are the potential markets and/or outlets for CS_2 product from H_2S/CH_4 reformation?
4. What are the environmental implications of H_2S 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 H_2S Resource

A question is often asked as to the magnitude of H_2S resource. We note that the sub-quality natural gas containing unacceptable levels of H_2S comprises about 14% of the U.S. gas reserves (Dalrymple 1994). Distribution of major H_2S regions in the lower-48 States has been compiled by Hugman (1993). The report identifies about 20 Tcf of H_2S-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 H_2S resource has been made and given in Table 3. We have also calculated and tabulated the higher heating value of hydrogen produced from H_2S (if all of it were converted to H_2 instead of Claus treatment) via CH_4 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 H_2S to clean CO_X-free hydrogen. Therefore, it is worthwhile not to burn H_2S in the process of upgrading the sub-quality natural gas reserves. Note that H_2S 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 H_2 Generation from Methane and Hydrogen Sulfide

Steam Methane Reforming (SMR)

The benchmark process for H_2 production is catalytic reforming of NG with steam according to:

$$CH_4 + H_2O = CO + 3H_2 \qquad \Delta H_{298K} = +206.36 \text{ kJ/mol} \qquad (2)$$

Table 1. Range of H_2S content of discovered and undiscovered sub-quality natural gas in the lower-48 United States - *non-associated gas data*[#] (Hugman 1993).

Basin/Formation	H_2S (vol%) Mean	Max	Amount of NG (Bcf) a	b	c	H_2S content (Bcf) 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)	H₂S (vol%) Mean	Max	Current proven Gas reserves (Bcf)	H₂S content of the 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
H₂S content of SQNG, Tcf	3.4	4.7	9.9
H₂ Equiv. H₂S of SQNG, Tcf	6.3	8.6	18.2
HHV of Equiv. H₂ from H₂S, 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 CO_2 and more H_2 via the exothermic shift reaction:

$$CO + H_2O = CO_2 + H_2 \qquad \Delta H_{298K} = -41.16 \text{ kJ/mol} \qquad (3)$$

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

$$CH_4 + 2H_2O = CO_2 + 4H_2 \qquad \Delta H_{298K} = +165.2 \text{ kJ/mol} \qquad (4)$$

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 H_2 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 H_2 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 H_2 for each mole of CH_4 consumed.
- Feedstocks for the process (*i.e.* methane and H_2O) 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 H_2).
- 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 CH_4 (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 2000, Uemura 1999, Muradov 1998, Wamrnes 1997, Gaudernack 1996, and Steinberg 1987) according to:

$$C_nH_m = nC + (m/2)H_2 \qquad\qquad (5)$$

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 H_2 production by direct decomposition, then the process that is optimized to yield H_2 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 CH_4 decomposition is H_2 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 H_2S 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), H_2S 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:

$$H_2S = H_2 + 1/xS_x \qquad\qquad \Delta H_{298K} = +79.9 \text{ kJ/mol} \qquad (6)$$

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 H_2/H_2S 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 $4.50/10^6$BTU (corrected to 1998 US dollars). This figure compares favorably with $4.75/10^6$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 H_2S reformation of natural gas methane.
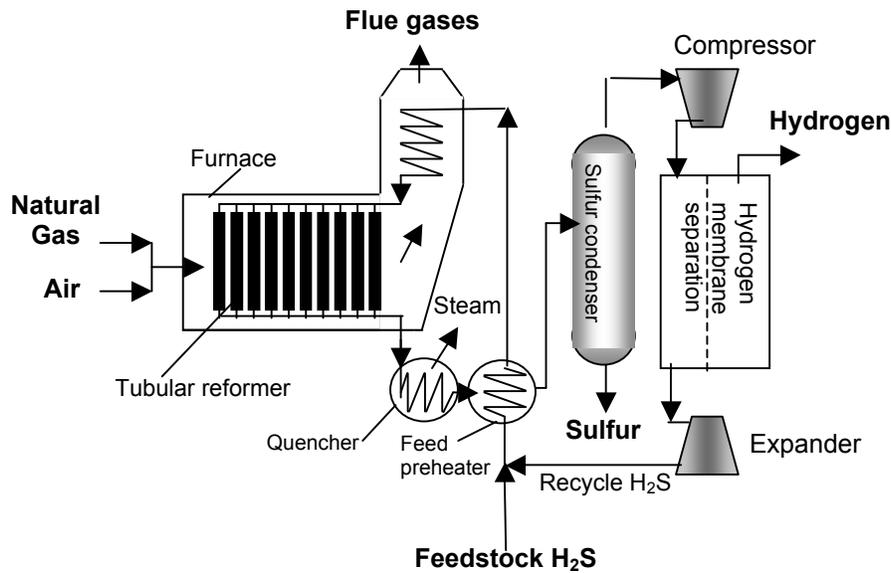
Figure 1- Simplified flow sheet for splitting hydrogen sulfide.

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 CH_4 reacted without production of greenhouse gases such as CO_2. 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 H_2S reformation of natural gas. In a way, the reaction of H_2S 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:

$$H_2S = H_2 + 1/2S_2 \qquad \Delta H_{298K} = +79.9 \text{ kJ/mol} \qquad (6)$$
$$CH_4 + 2S_2 = CS_2 + 2H_2S \qquad \Delta H_{298K} = -107 \text{ kJ/mol} \qquad (7)$$

The overall reaction for the H_2S methane reforming process may be written as follows:

$$CH_4 + 2\,H_2S = CS_2 + 4H_2 \qquad \Delta H_{298} = +232.4 \text{ kJ/mol} \qquad (8)$$

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°C. Stream temperature at the feed heater exit is 552°C. The reforming reactor runs at a pressure of 1.35 atm and a temperature of about 1227°C. The exit stream "d" is rapidly quenched in the waste heat boiler (WHB) to 875°C followed by further cool down (for elemental sulfur collection) to about 390°C.
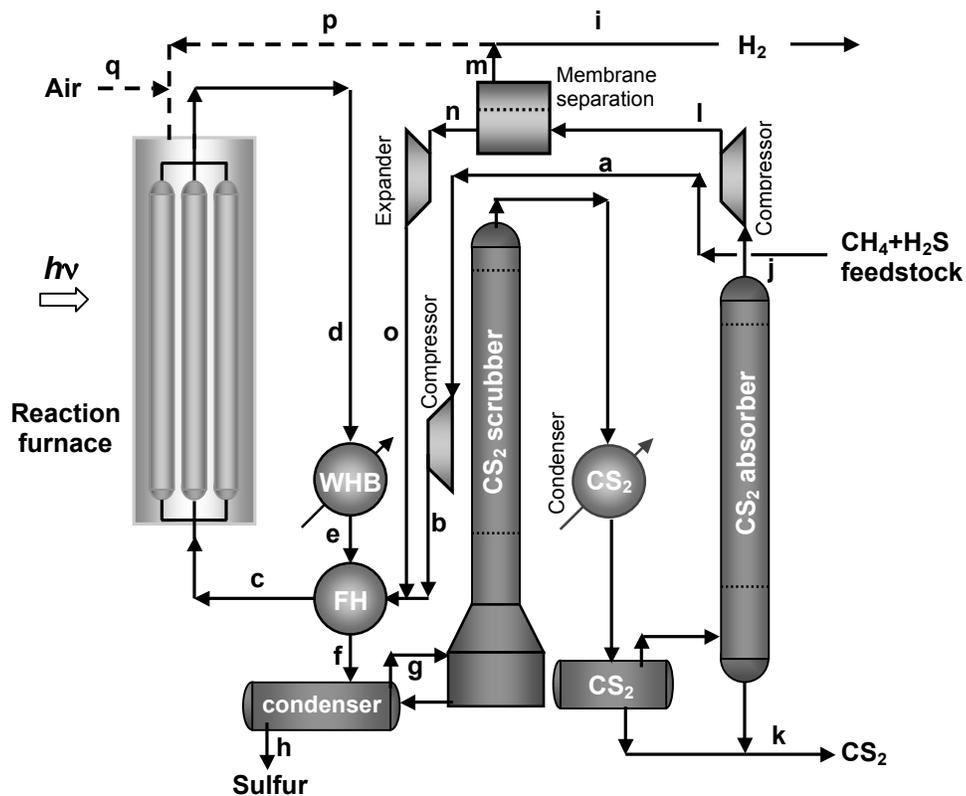
Figure 2- Process for hydrogen and CS$_2$ production.

Most of the residual sulfur is removed at this stage before entering CS_2 scrubber/condenser/ absorber train. Finally, a mixture of hydrogen, recycle H_2S and unconverted CH_4 enter membrane hydrogen separation unit at a temperature of about 25°C and a pressure of 10 atm. Typical membrane H_2 separation efficiency of 90% can be assumed. A portion of the recovered H_2 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 H_2S-CH_4 reaction products at various temperatures and pressures, and H_2S to CH_4 molar feed ratios (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 CH_4 consuming reaction resulting in the formation of CS_2.

2- The hydrogen sulfide decomposition reaction (6) does not take effect until about 1000-1100 K (depending upon the H_2S to CH_4 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 CS_2 from H_2S and CH_4 by providing the required sulfur feedstock for reaction (7) to occur.

3- Hydrogen, CS_2 and S_2 are thermodynamically favored products of H_2S-CH_4 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 H_2S-CH_4 reaction system depends primarily on the H_2S to CH_4 molar feed ratio, x. At any given pressure and temperature, there is a specific H_2S to CH_4 molar feed ratio ($x = x_{pinch}$) 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 H_2S-CH_4 reaction system as a function of H_2S to CH_4 molar feed ratios, x, at 1350 K and 1 atm. At $x = x_{pinch} \approx 6.9$ (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 H_2S to CH_4 molar feed ratio of $x_{stoichiometric} = 2$, respectively. Figure 6 is a plot of $x_{pinch}/(1 + x_{pinch})$, vs. temperature depicting the soot-free domain for the H_2S-CH_4 reaction equilibria.
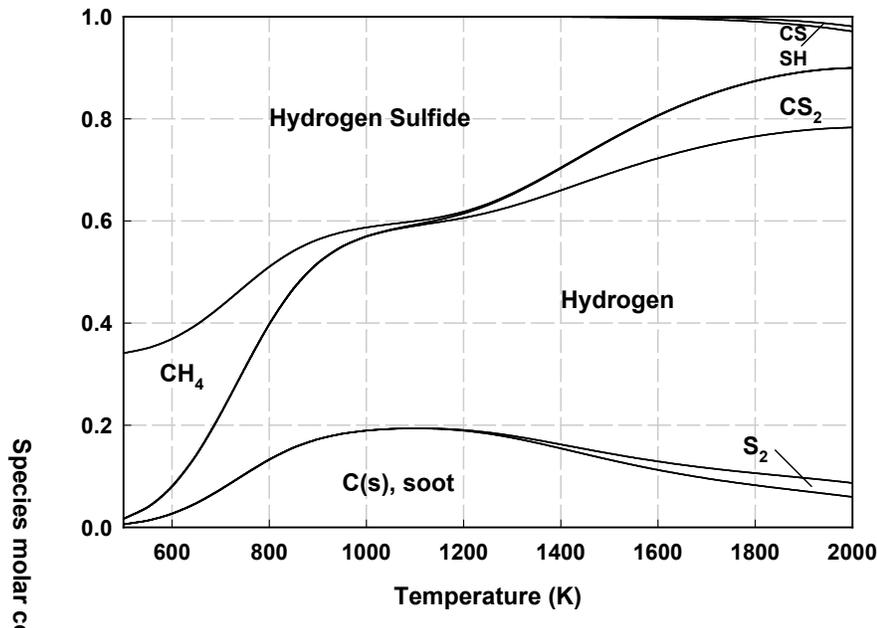
Figure 3- Equilibrium concentration of reaction products of $CH_4 + 2 H_2S$ at 1 atm.
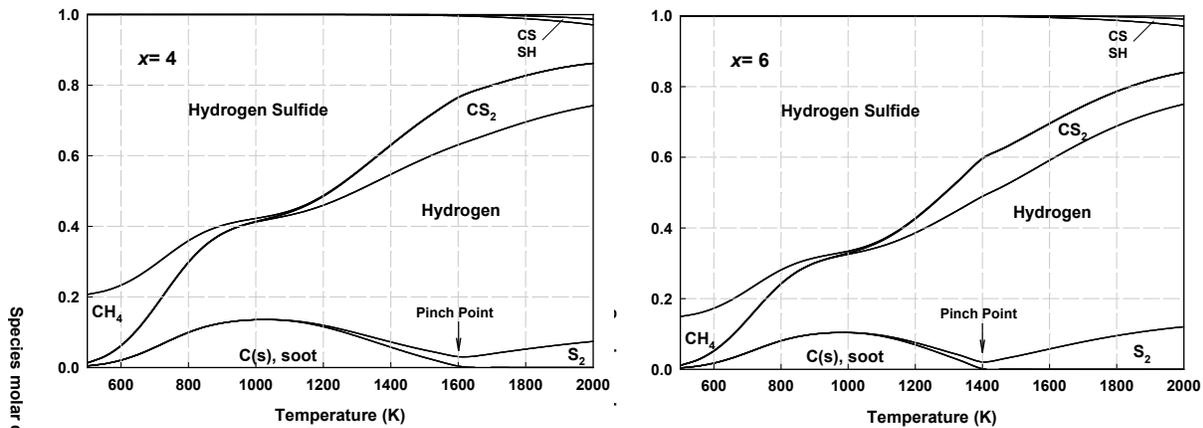
Figure 4- Equilibrium concentration of $CH_4 + x H_2S$ reaction products at twice and three times $x_{stoichiometric}= 2$.

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 1100-1300°C, corresponding to x values in the range of approximately 4-6. From thermodynamics point of view, this range of $x \approx 4$-6 and T $\approx$ 1100-1300°C seems to provide the optimum conditions

needed for performing H_2S-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.
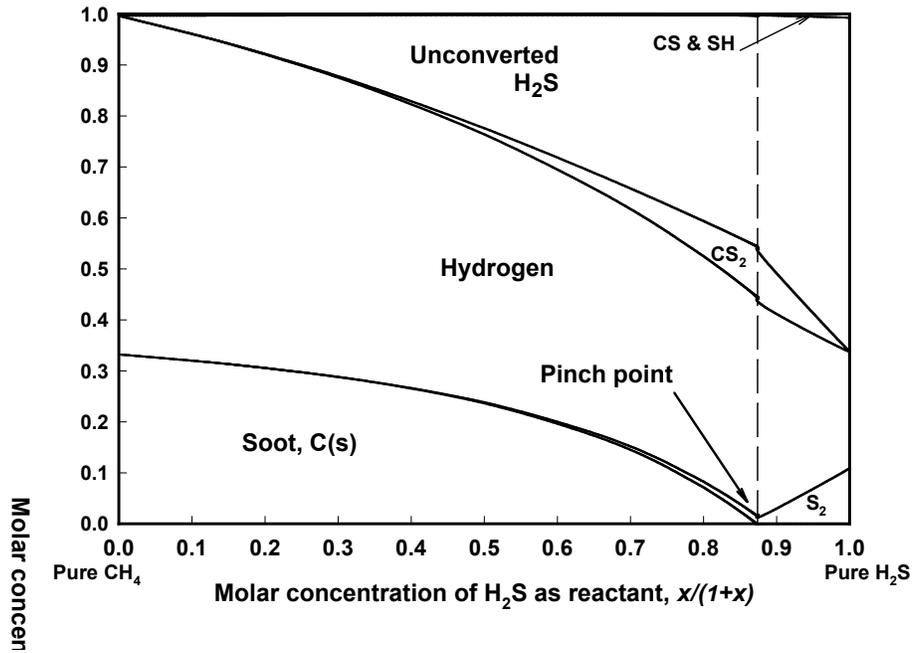
Figure 5- Product slate for reaction CH_4 + x H_2S at 1350 K and 1 atm.
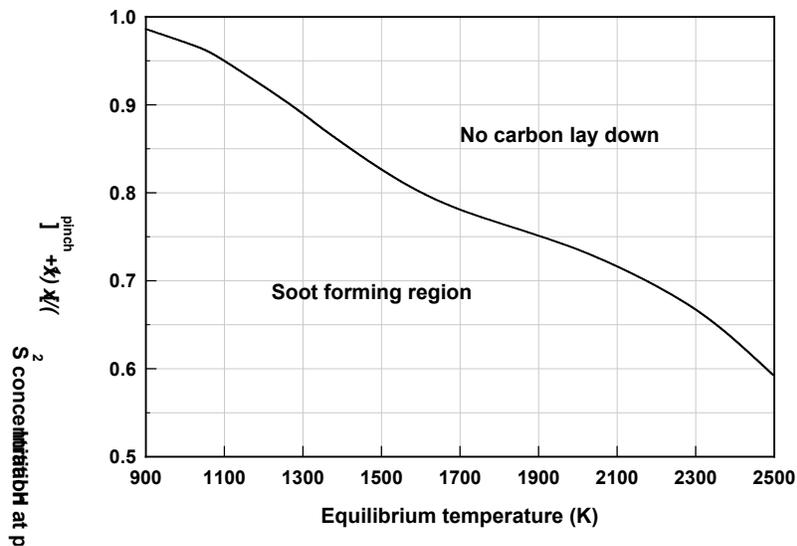
Figure 6- Soot forming region for CH_4 + x H_2S reaction at 1 atm.
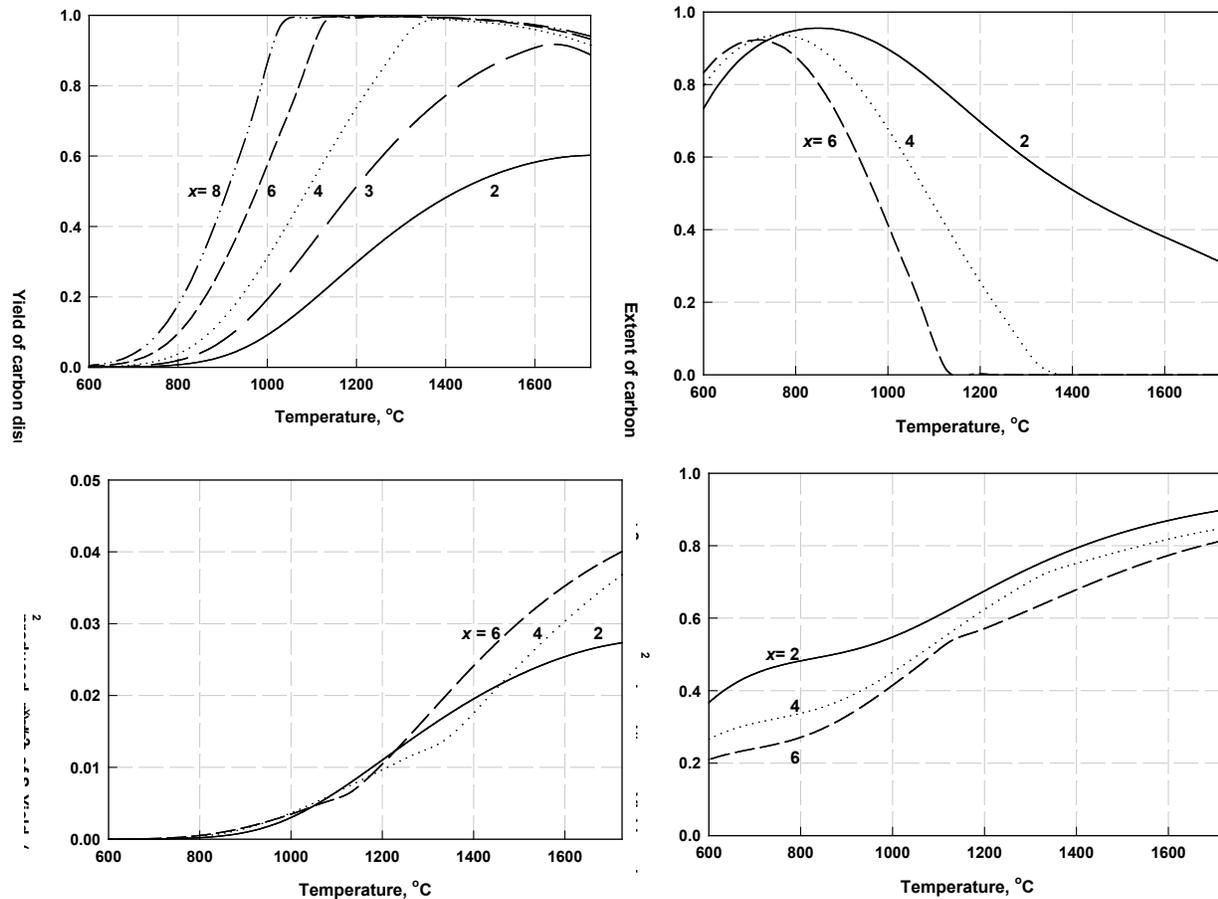
Figure 7- Equilibrium yields of major H₂S-CH₄ reaction products at various H₂S to CH₄ molar feed ratios, *x*, and 1 atm.

In addition, we calculated the equilibrium concentration of species formed and stream compositions for the H_2S-CH_4 reformation scheme of Figure 2. Results are presented in Table 4 for a H_2 membrane separation efficiency of η_m= 91%, reformer temperature of 1350 K and H_2S to CH_4 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 H_2 gas flows to the burner/reformer), then for every mole of CH_4 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 CH_4 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 H_2 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°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 H_2 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 CH_4 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 H_2S-CH_4 reformation reaction (8).

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

Stream	T	P	[CH₄]	[H₂S]	[H₂]	[CS₂]	[S₂]	[HS+CS]	ΔH	ΔG⁰
No.	(K)	(atm)	(moles)	(moles)	(moles)	(moles)	(moles)	(moles)	(kJ/mol)	(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 [H₂S]ₐ (vol%)	69.5	69.4	70.1	70.4	70.6	71.7
ΔH_{cd} (kJ/mol of CH₄)	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 H_2S-CH_4 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 H_2S-CH_4 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, H_2 burning furnace, combined solar and

hydrogen combustion furnace, combined electric and H_2 combustion furnace, and combination solar-electric-H_2 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 H_2 produced, no matter what type of process or energy input option is chosen, the H_2S-methane reformation won't be commercially viable unless H_2 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 H_2 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 H_2 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 H_2S-methane reformation, the by-product credit for CS_2 would lie between the price of recovered sulfur and that commanded by CS_2 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 CS_2 is in the production of H_2SO_4. 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 CS_2. The maximum price that carbon disulfide produced by the H_2S-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 CS_2 from H_2S-methane reformation process should command a value in the range of approximately $0.02 to $0.20/lb of CS_2 (after correcting for the difference in molar mass between CS_2 and S_2).

Finally, the capital and operating costs of the prospective H_2S-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 H_2S/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 H_2S-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°C, ideal for solar interface.
- Operate at low pressures, less than 10 atm.
- Operate with relatively low recycle H_2S, *i.e.*, H_2S/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 H_2S decomposition reaction (6) is an important step in the H_2S-CH_4 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 H_2S dissociation. On the other hand, reaction (7) is a well-known methane conversion reaction used commercially to produce CS_2. There are also commercial catalysts such as silica gel/aluminum used for CS_2 synthesis reaction (7). Now, the main issue is whether bi-functional catalyst(s) can be found that affect(s) H_2S decomposition reaction (6) while holding activity and stability toward reaction (7). Such catalyst(s) will be able to render the H_2S-CH_4 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 CS_2 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 H_2S 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, 1100ºC), two different residence times (*i.e.* 1 and 5 s), and three distinct H_2S to CH_4 molar feed ratios (*i.e.* $x = 2$, 4 and 8).

2. It was found that the H_2S to CH_4 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 CS_2 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 CS_2 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 1000ºC (1273 K); the conversion of methane nearly reaches completion. At these temperatures dehydrogenated CH_4 or carbon precursors on the surface would be in greater abundance, and with the excess H_2S in the gas phase, CS_2 yield is increased.

3. In general, the CS_2 yield increased with temperature up to 1100ºC. 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 Cr_2S_3 and Ce_2S_3 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 (Cr_2S_3) and IGT-MS-105 (selenium sulfide) catalysts.

5. Both IGT-MS-103 (Cr_2S_3) and IGT-MS-105 (selenium sulfide) catalysts were active in dissociating H_2S, an essential reaction in the H_2S-CH_4 reformation reaction pathway. In addition, these catalysts were stable above 1000ºC (1273 K) and do retain most of their original surface area (2-5 m^2/g). These catalysts were also the most effective in promoting the reaction of H_2S 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 TGCU. 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.
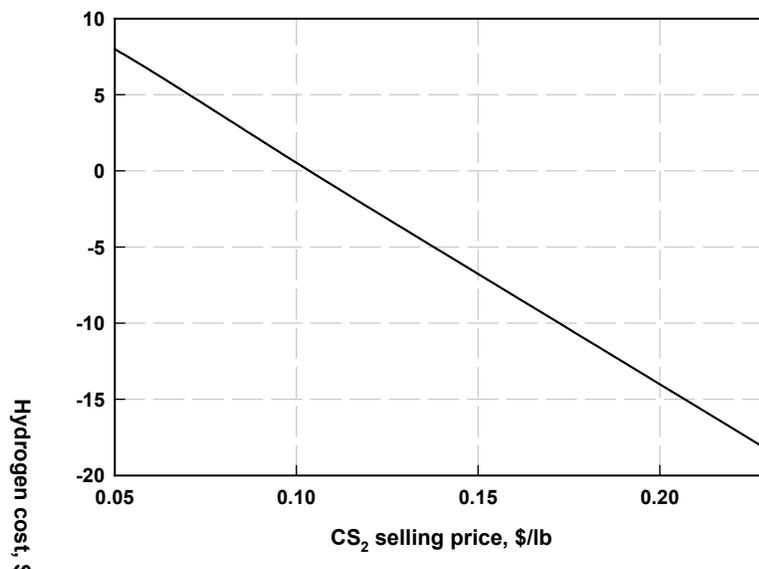
Figure 8- Comparison of CS_2 Selling Price and H_2 Cost (Erekson 1996).

Conclusions and Recommendations

- The concept of H_2S-methane reformation to produce H_2 and CS_2 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 H_2S 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 H_2S-rich feedstocks using H_2S-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 H_2S-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 H_2S-methane reformation process discussed here is technically doable and can be economically viable as well.

- All of the reaction steps for the H_2S-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 H_2S-methane reformation process, efficiently. Among them are several catalysts identified by a recent IGT study aimed at the production of hydrogen and CS_2 from H_2S and CH_4. Cr_2S_3 and Ce_2S_3 catalysts are found to be active in dissociating H_2S and stable at temperatures above 1000ºC (1273 K) to allow H_2S reaction with the carbon precursors that reside on their surfaces. All transition metal sulfide catalysts are available commercially.

- A preliminary economic analysis of the H_2S-methane reformation process for H_2 and CS_2 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 CS_2 and can conceivably be zero dollars, *i.e.* free.

- Efforts are underway to develop solar-thermal direct decomposition of the methane and H_2S for production of hydrogen. However, despite its potential benefits, no work has been done to show the viability of a solar driven H_2S-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 H_2S-methane reformation process.

Acknowledgments

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