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Economics of Microwave Plasma Dissociation of H_2S

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Abstract

The conventional treatment technology for hydrogen-sulfide is based on Claus chemistry; elemental sulfur is recovered but the hydrogen is lost as water although the fuel value of the hydrogen is recovered as heat. A new waste treatment technology, reported in the Soviet literature, has been validated in an experimental program at Argonne National Laboratory. The new technology uses microwave energy to dissociate hydrogen-sulfide and recovers both elemental sulfur and hydrogen. Recovery of the hydrogen provides for its reuse for its chemical value. A comparative economic analysis of the microwave technology and conventional sulfur recovery and tail-gas treatment technology such as Claus/SCOT is presented. The sensitivity of the comparative economics to process variables such as dissociation energy and conversion rate, and cost variables, such as the value of hydrogen and the cost-of-electricity is evaluated. Under the conditions of this analysis, the conclusion is that it is more cost-effective to recover the hydrogen for its chemical value via microwave dissociation rather than to accept its conversion to water and effective use as a fuel.

Introduction and Background

The current technology for treatment of H_2S is based on Claus chemistry. The sulfur is recovered as a saleable by-product but the hydrogen is converted to water and lost, although generally the heat that is released by the conversion of hydrogen to water is recovered for process use. In 1985, a novel H_2S treatment technology was reported in the Soviet scientific literature. [1,2] A microwave discharge was used to create a "cold," nonequilibrium plasma resulting in the dissociation of H_2S into elemental sulfur and hydrogen. The reported conversion rates ranged from 40% to 90% of the H_2S with energy consumptions of 26.0 to 60.8 kJ/mol (6.2 to 14.5 kcal/mol). The minimum theoretical energy consumption for dissociation of H_2S is 20 kJ/mol (4.77 kcal/mol) at standard conditions.

Over the past four years, the results reported in the Soviet literature have been validated in our laboratory. [3,4] Recently, the Soviet scientists who first reported on this new technology visited Argonne and collaborative efforts are being pursued.

As the technical feasibility of this technology has been confirmed, this paper examines the technology's economic feasibility relative to key process and cost variables. The comparative economics of the microwave technology vis-a-vis conventional H_2S treatment technology quantifies whether it is more cost-effective to recover hydrogen from a waste stream rather than to incur the cost of converting the waste stream into environmentally acceptable products and forego the use of the hydrogen as a chemical feedstock.

Basis of the Economic Comparison

One potential application for the microwave plasma dissociation technology is in the refining industry as an alternative to conventional sulfur recovery and tail-gas treatment (SR&TGT) technology such as Claus/SCOT. Typically, a hydrocarbon such as CH_4 is reformed to produce hydrogen which reacts with the sulfur of a "sour" feedstock to produce H_2S, Fig. 1.

The basis of the material and energy balances of Figure 1 is 170 x 10^3 kg/day (167.7 LTD) of H_2S which requires 10 x 10^3 kg/day (9.8 LTD) of H_2 from the reformer. The feedstock and fuel requirements of the reformer total 2.256 x 10^9 kJ/day (2138 million Btu/day). The H_2S and the feedstock are then separated in the purification unit which includes a condenser and an amine-stripper. The H_2S and small amounts of other acid gases such as CO_2

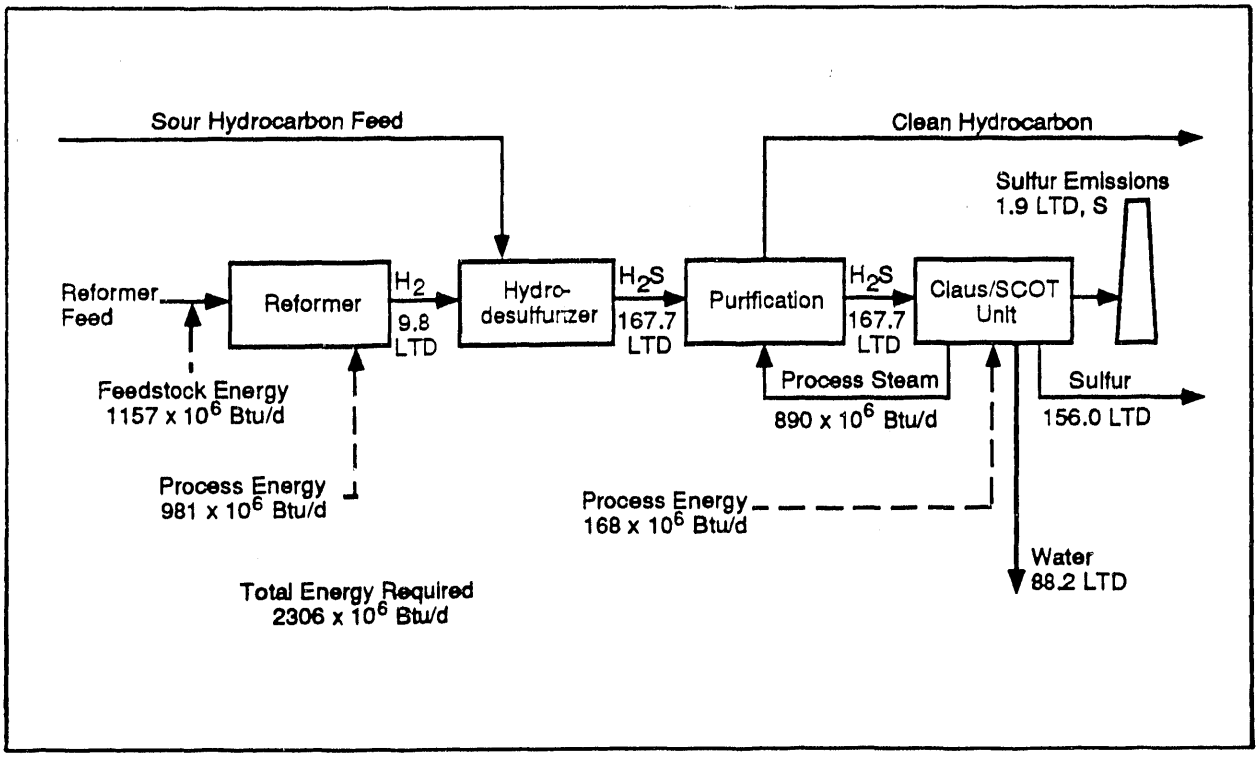

Figure 1. Energy and Material Balance for a Typical Hydrodesulfurization Train

are then processed in the SR&TGT section for recovery of elemental sulfur. The auxiliary power requirements and supplemental fuel requirements of the SR&TGT section contribute to a process energy demand of 177 x 10^6 kJ/day (168 million Btu/day). The total process energy for this system is 2.433 x 10^9 kJ/day (2306 million Btu/day). The SR&TGT section produces 939 x 10^6 kJ/day (890 million Btu/day) of recoverable heat which is typically used for regeneration of the amine-stripper in the purification unit of the system. The estimated capital cost of the SR&TGT section is $25 million.

Substitution of the microwave plasma technology for the conventional SR&TGT unit results in a reduction of process energy required for hydrodesulfurization of 568 x 10^6 kJ/day (538 million Btu/day), Fig. 2. Recovery and reuse of the hydrogen from the H2S is more efficient than production of the hydrogen from the steam reformer of the conventional system. The conversion of the H_2S is taken as 75% per pass. The dissociated H_2 and the H_2S are recycled back to the purification unit for separation by an absorber-stripper system. In this paper, an amine-stripper has been assumed, but any other commercially available physical/chemical sorption technology could be used. Depending on the compatibility of the species exiting the plasma reactor, the recycle loop may be blended with the gas stream entering the primary amine-stripper for separation. If the species are not compatible,

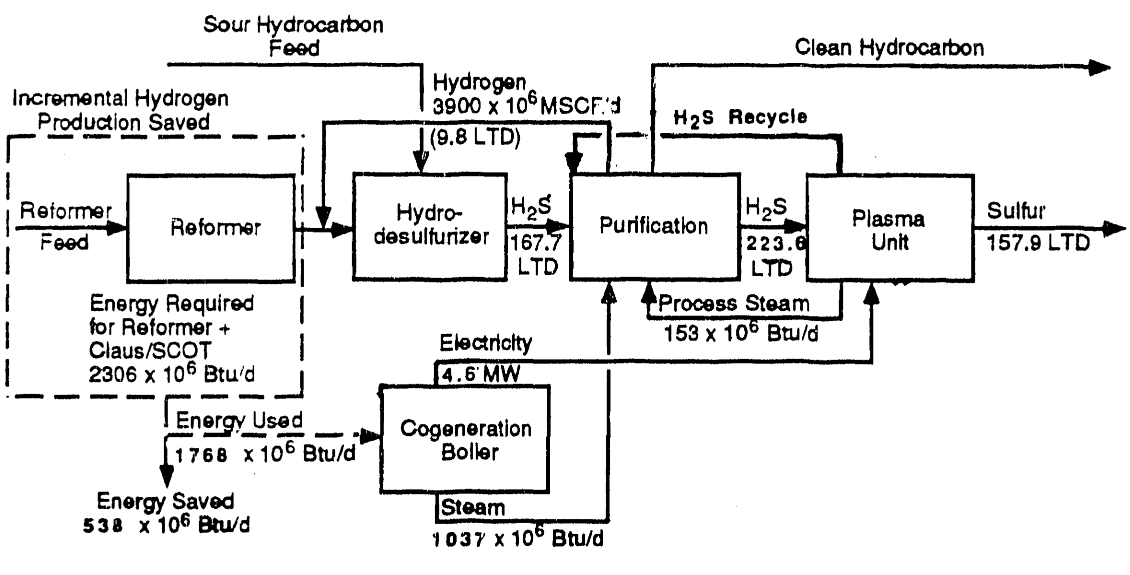

Figure 2. Energy and Material Balance for a Hydrodesulfurization Train With Microwave Plasma H_2S Treatment

the process would be modified to include a secondary stripper and regenerator. As the conversion rate of the H_2S in the plasma reactor decreases, the mass flow of the recycle loop increases and the cost of the amine-stripper for separating the H_2 and H_2S increases. In addition, the thermal requirements for regeneration of the amine-stripper increase as the loading of H_2S through the purification unit increases. At a 75% conversion of H_2S per pass in the plasma reactor, the effective cost and thermal requirements of the amine-stripper increase by 33% relative to a conventional system.

The recoverable heat from the plasma reactor is much less than that which is recoverable from a conventional SR&TGT unit. In the conventional system, the heat value of the hydrogen is available in addition to heat from process inefficiencies. In the plasma system, the only heat available is that which results from process inefficiencies. Further, the quality of the heat recovered from the plasma system is much lower than that from the conventional SR&TGT unit because the plasma system operates at a much lower temperature. The total heat required for regeneration of the amine system (both primary and secondary) is estimated at 1.249×10^9 kJ/day (1184 million Btu/day) of which 158×10^6 kJ/day (150 million Btu/day) can be supplied by recovery of heat from the plasma unit.

The dissociation energy of the plasma process is taken as 66.5 kJ/mol (15.9 kcal/mol) which is equivalent to 0.7 electron-volt per molecule of H_2S. Based on a bussbar to microwave power conversion efficiency of 80%, the power requirements for the microwave generator are 4.6 MW. In a typical refinery application, the power would be produced by an on-site cogeneration system with an estimated overall efficiency of about 80%. Thus, the energy requirements of the plasma technology could be met by a fuel consumption of 1.865×10^9 kJ/day (1768 million Btu/day), resulting in an energy savings relative to the conventional system of 0.568×10^9 kJ/day (1768 million Btu/day), as stated above.

Economic Analysis

As previously stated, the estimated capital cost of a conventional SR&TGT unit designed to handle process streams consistent with 170×10^3 kg/day (167.7 LTD) of H_2S is $25 million. Typically the tail-gas treating section has a capacity of 150% of design capacity.

The capital cost of a microwave plasma H_2S processing unit is estimated at $10 million at a capacity of 150% of design capacity, including contingencies, Table 1. The costs of the plasma section include the power supply, inverter, microwave generator, waveguide, and reactor. The capital costs of the H_2/H_2S separation unit are based on the incremental amine-stripper capacity required to handle the H_2/H_2S recycle loop. Contingencies include process and project contingencies of 15% and 20%, respectively.

Table 1. Estimated Installed Capital Cost of the Microwave Plasma H_2S Process

Basis: 75% H_2S conversion per pass @ 0.7 eV/molecule

Component	Cost, ($, million)
Recycle Compressor/Blowers	0.25
Microwave Generator and Reactor	6.35
Sulfur Knockout Drum	0.24
H_2/H_2S Separation	0.61
Subtotal	7.45
Contingencies (35% of Subtotal)	2.61
Total	10.05

Because the plasma section accounts for more than 60% of the total plasma system capital costs, the capital cost is more sensitive to the dissociation energy than it is to the conversion rate of the H_2S, Fig. 3. For example, if the dissociation energy is 104.5 kJ/mol (1.1 eV/molecule) instead of the 66.5 kJ/mol (0.7 eV/molecule) as in the base case, the system capital cost increases by almost 60%. A decrease in the conversion rate from 75% to 55% results in a modest increase in capital cost. However, the operating costs of the system would be expected to exhibit a greater sensitivity to the conversion rate since the regeneration heat requirements will increase as the conversion rate decreases.

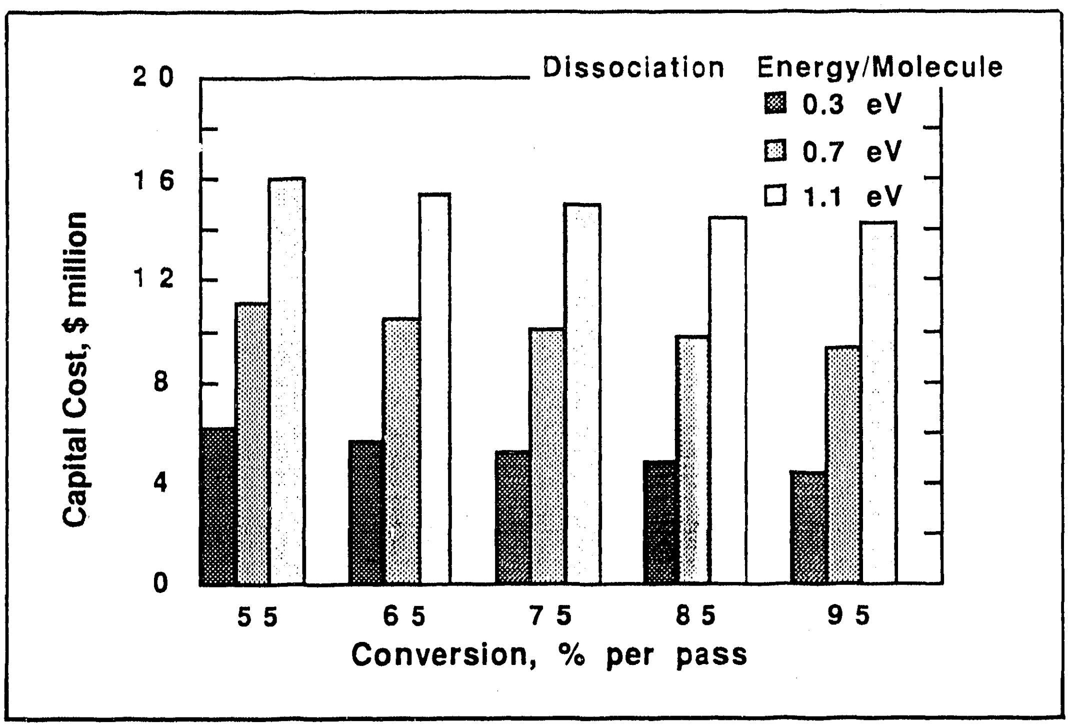

Figure 3. Microwave Plasma H_2S Process Capital Cost as a Function of H_2S Conversion Rate and Dissociation Energy

The total annual operating costs, including annual capital costs, for the conventional SR&TGT technology are estimated at $1.530 million per year compared to the microwave plasma technology which has estimated operating *profit* of $0.896 million per year, Table 2. The microwave plasma technology produces credits of about $2 million per year more than the conventional technology due primarily to the recovery of hydrogen. In the conventional system, a small amount of the sulfur would be lost as SO_2, such that the credit for sulfur recovered is slightly less than that expected for the microwave technology. Operating costs for the plasma process are about $1.8 million per year higher than the operating costs of the conventional technology. The two components of operating costs which attribute to this difference are: (1) fuel consumption required to provide the heat for regeneration of the amine-stripper in the plasma process whereas most of the heat for regeneration of the amine-stripper in the conventional system is recovered from the SR&TGT unit, and (2) the higher electricity consumption for the microwave generator. Nonetheless, the net credits for the plasma process exceed the net credits for the conventional process by about $200,000 per year. After taxes and consideration of capital costs, the total annual costs of the plasma process are about $2.4 million per year less than those of the conventional system.

Table 2. Cost Comparison of Conventional SR&TGT and Microwave Plasma H_2S Treatment

Plasma Process Basis: 75% H_2S conversion per pass @ 0.7 eV/molecule

Cost Component	Process: Conv. SR&TGT	Process: Plasma
	($, million)	
Credits		
Hydrogen, $5/million Btu	0.000	1.954
Sulfur, $120/ton	5.466	5.533
Subtotal	5.466	7.487
Operating Costs		
Fuel, $3/million Btu	0.034	1.078
Cat. & Chemicals	0.185	0.000
Electricity, $0.06/kWh	0.381	1.934
Maint./tax/ins. @ 4% of capital	1.000	0.402
Subtotal	1.600	3.414
Net Credits	3.866	4.073
Taxes, 40% of net credits	1.546	1.629
Annual Capital Costs, ^.154 FCR	3.850	1.548
Total Costs	1.530	-0.896

Clearly, under the conditions of this analysis, it is more cost-effective to recover the hydrogen from the waste H_2S stream for use as a chemical feedstock rather than converting the hydrogen to water and recovering its fuel value.

Sensitivity Analyses

Although the base case cost comparison indicates that the plasma process is more cost-effective than conventional SR&TGT technology, process uncertainties as well as economic assumptions will affect the viability of the process.

Process Uncertainties

With regard to process uncertainties, the two major process variables are conversion rate and the dissociation energy. In this analysis, we have treated these two variables as independent. Indeed, the experimental work at Argonne tends to indicate that they are independent. However, as the scale of the technology increases, we would expect a trade-off between these two variables. That is, to achieve very high conversion rates, we would expect a decrease in the dissociation energy efficiency. Determination of the relationship of these two process variables would allow for optimization of the process.

As the conversion rate decreases, there is a slight increase in the capital cost of the plasma process to handle the increased mass flows of H_2S in the recycle loop as previously discussed. In addition to the increased capital cost, operating costs also increase because the amount of heat required to regenerate the secondary amine-stripper will increase, Fig. 4.

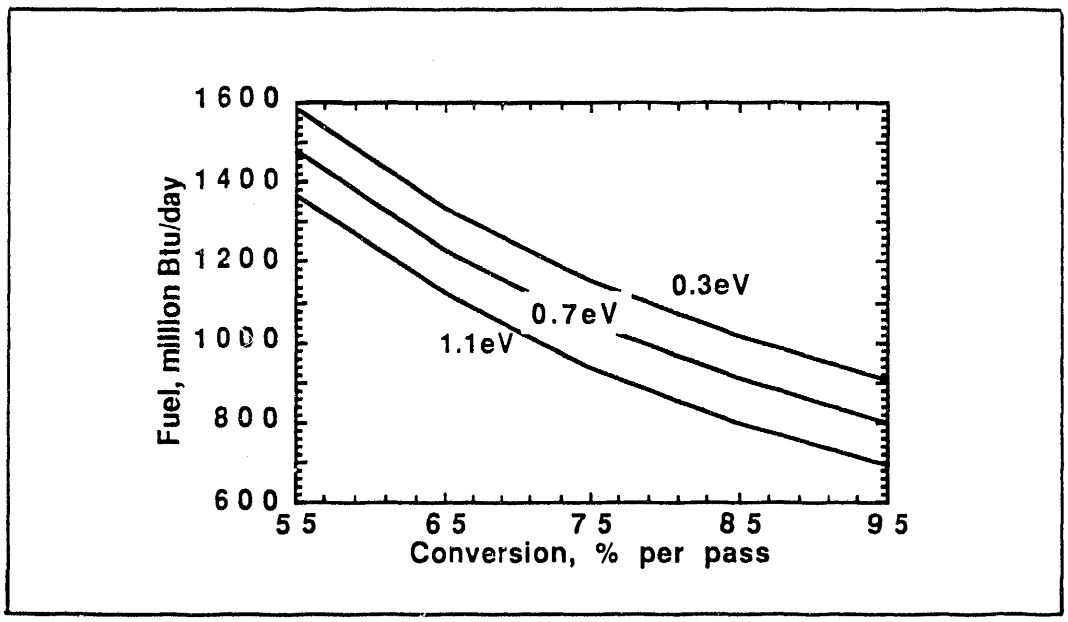

Figure 4. Net Process Heat Required as a Function of H_2S Conversion Rate and Dissociation Energy

The dissociation energy defines the amount of heat that can be recovered from the plasma process. That is, as the actual dissociation energy increases above the minimum theoretical dissociation energy, the amount of recoverable heat also increases. Consequently, the net process heat required for regeneration decreases with an increasing conversion rate (less total heat required) and increases with lower actual dissociation energy (less recoverable heat available).

Although less net process fuel is required at higher dissociation energies, this is not sufficient to overcome the major process cost factors which are (1) the capital cost of the plasma unit which, of course, increases with increasing dissociation energy and (2) the annual cost-of-electricity which also increases with increasing dissociation energies. Consequently, the total annual operating costs for the plasma process are lowest for low actual dissociation energies, and the operating costs are more sensitive to the dissociation energy than to the conversion rate. In essence, this simply states that the use of a plasma process as a source of process heat is not cost-effective, as we might well expect. However, in comparison to the conventional SR&TGT technology, the plasma process is cost-effective regardless of its achieved conversion rate or dissociation efficiency, Figure 5. This clearly indicates that it is more cost-effective to recover the hydrogen from the waste H_2S stream than to forego its chemical value for its heat value which is recovered in the conventional technology.

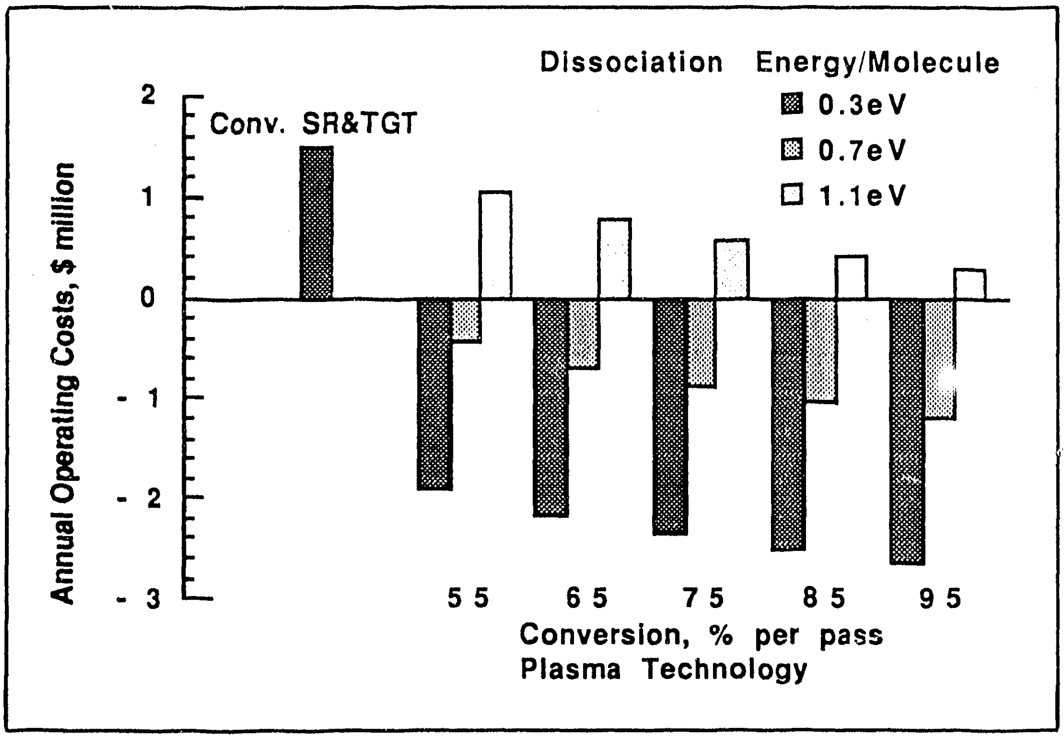

Figure 5. Annual Operating Costs of H_2S Treatment Technologies

Economic Variables

The three economic variables which are expected to exhibit the greatest influence over the relative costs of the plasma process are the value of hydrogen, the cost-of-electricity, and the plasma process capital cost. The breakeven cost of the plasma process as a function of the cost-of-electricity and the value of hydrogen is presented in Figure 6 for two capital cost cases. The plasma process is assumed to have an actual dissociation energy of 104.5 kJ/mol (1.1 eV/molecule) and a conversion rate of 75%; values which are clearly feasible based on the experimental data of the Argonne program and also consistent with the larger scale data indicated in our discussion with the Russian scientists.[5] At a conversion rate of 75% and a dissociation energy of 104.5 kJ/mol (1.1 eV/molecule), the estimated capital cost of the plasma process is $15 million. If the cost-of-electricity exceeds $0.09/kWh and the value of hydrogen is less than $4.74/kJ ($5.00/million Btu), the conventional SR&TGT technology is more cost-effective than the plasma technology, Fig. 6a. We would expect that for most applications the value of hydrogen and the cost-of-electricity are such that the plasma process is more cost-effective than the conventional SR&TGT technology.

In figure 6b, the breakeven curve is presented for the same conditions as in Figure 6a, except that the capital cost of the plasma process has been arbitrarily increased by 25%. Even with a 25% increase in process capital cost, the plasma process cost-effective regime is consistent with expected hydrogen values and costs-of-electricity in most applications.

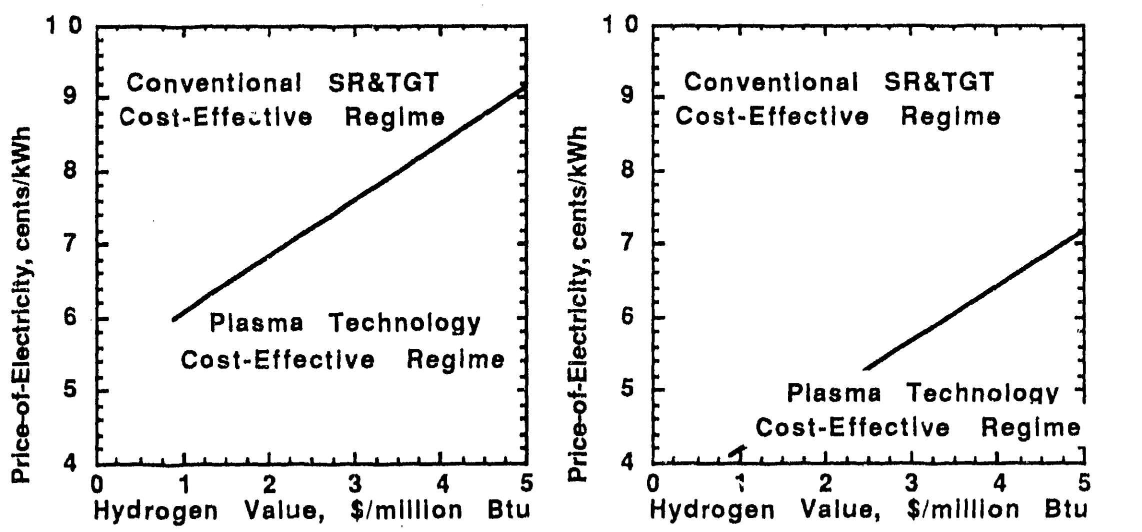

Figure 6a. Plasma Capital Cost=$15 million Figure 6b. 25% Increase in Plasma Capital Cost

Note: Plasma Technology: 75% Conversion @ 1.1 eV/molecule

Figure 6. Cost-Effective Regimes of H_2S Treatment Technologies

Conclusions

A novel H_2S waste treatment process which recovers both hydrogen and elemental sulfur appears to be cost-effective relative to conventional SR&TGT technology over the expected range of process conditions and process cost factors. The implication of the analysis is that the plasma process is expected to be cost-effective relative to conventional technology for most applications.

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