DRAFT TECHNICAL ANNUAL REPORT

DOE/GO/10049--T1

Production of Hydrobromic Acid From Bromine, Methane and Steam for Hydrogen Production

Cooperative Agreement: DE-FC36-95GO10049

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1997 Annual Report
Covering the Period
Dec. 15, 1996 – Jan. 31, 1998

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17 July, 1998

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ABSTRACT

This document is report on the 1997 effort under the cooperative agreement (DE-FC36-95GO10049) between Solar Reactor Technologies, Inc. (SRT) and the U.S. Department of Energy. It covers the period December 15, 1996 through January 31, 1998.

The 1997 effort was a success. A new apparatus for studying the reaction was assembled. It consisted of a quartz tube reactor, bromine delivery system, steam generator, and sampling glassware. Initial experiments showed that bromine reacted readily with methane and steam to produce high concentrations of HBr. Reaction temperatures ranged between 650 and 900 °C. Gas exiting the sample capture tube was analyzed for CO and CO_2 with a GC. Small amounts were detected. A GC-MS analysis of the organic compounds extracted from the black particulates and the solution phase was performed. Trace quantities of a large number of brominated aromatic and aliphatic compounds were identified.

This first apparatus was not suited to studying the reaction in great detail. In particular, bromine flow rates were not constant and there was no provision for accurately sampling the gaseous effluent. This in turn did not allow for a full material balance on the reaction.

Significant improvements were realized in a second design. A more versatile and reliable reactor test apparatus was successfully designed, built, and tested. The reactor did not experience plugging. The bromine delivery system was robust toward bromine corrosion. SRT's analytical methods for quantitating reaction products were greatly improved. Data were collected in seven different runs at different temperatures and varying reactant molar ratios. The data were significantly more complete than those collected previously, since the product gas stream (unreacted CH_4, CO, and CO_2) was collected and quantified with a GC. A spectroscopic method for determining Br_2 was developed as well.

The data are very encouraging. At 800 °C, conversion of methane and bromine to HBr was about 99% and 75%, respectively. The conversion of water to HBr was much less, only about 10%. This value will be increased if more water reacts with the carbonaceous material deposited in the reactor. Methane was typically the limiting reagent, while steam and bromine were essentially equimolar.

The improved reactor test apparatus has proven dependable in early testing. It will serve as a good test bed for scale-up testing for 1998.

SRT has performed a preliminary economic evaluation of the process and has found that it can produce hydrogen at small (76kSCFD) scales for a price of $9.57/MMBTU. The process is simple, robust, and is much safer than the previously studied solar driven reaction between bromine and steam. The process produces hydrogen as a pure gas under pressure, so that

compression is not required. SRT has compared its process to similar reactions researched by others and has concluded that technical risk for development is minimal.

In the SRT process, the electrical power required to split water is reduced effectively in half by the production of hydrogen bromide. The SRT concept is very attractive from an economic viewpoint as well. A reversible electrolytic fuel cell employed in the SRT process is capitalized via its use in load leveling by the utility. Thus, the price of SRT-produced hydrogen reflects only the cost of methane, reactor system capital costs and off-peak electrical power.

Since carbonaceous material is sometimes deposited in the reactor during operation (depending on conditions), SRT would like to explore the possibility that this method of hydrogen production from methane could be accomplished without generation of CO_2. This would be a method of reducing greenhouse gas emissions from the production of hydrogen. The carbon by-product could be used for other products, such as the production of carbon composite materials. SRT needs to determine under which conditions this conversion to carbon occurs. Reactors with increased surface area and/or characteristic residence times will be required. They will be evaluated over a range of operating conditions. This will serve to define the useful boundaries in parameter space for the subsequent scale-up design.

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I. Introduction

During the first two years of the cooperative research program DE-FC36-95GO10049 between SRT and the DOE, the solar-driven reaction between bromine and steam was studied. The goal was to make hydrobromic acid for hydrogen production and energy storage use via a reversible, high efficiency hydrogen/bromine fuel cell. While the reaction was technically successful and was demonstrated at NREL, it was determined to be uneconomical in today's economy due to present high capital costs of the solar hardware. In an effort to provide for an interim process that can be utilized to produce hydrogen and store energy until the cost of solar hardware decreases, SRT's process was modified to include the addition of methane. The new concept entails (i) reaction of bromine with methane and steam to produce hydrogen bromide and carbon dioxide and (ii) electrolysis of the stored hydrogen bromide for production of $H_{2(g)}$ and recovery of $Br_{2(l)}$. Electrolyzers are available today for the electrolysis of HBr. In addition, a vendor for a reversible H_2-Br_2 fuel has been identified. Most components of the envisioned system are commercially available. At present, the reactor needs the most development.

In the SRT process, the electrical power required to split water is reduced effectively in half by the production of hydrogen bromide. The SRT concept is very attractive from an economic viewpoint as well. A reversible electrolytic fuel cell employed in the SRT process is capitalized via its use in load leveling by the utility. Thus, the price of SRT-produced hydrogen reflects only the cost of methane, reactor system capital costs and off-peak electrical power.

Modified SRT Hydrogen Process

SRT investigated a reaction between bromine, methane and steam for producing HBr. It has great potential to reduce the capital cost inherent in using solar energy. It should make the approach more attractive to merchant hydrogen producers and to the natural gas/electricity industry. The overall reaction is:

$$\mathbf{2\,H_2O + 4\,Br_2 + CH_4 \rightarrow 8\,HBr + CO_2.\ \Delta H^\circ_{298} = -38.2\ kJ} \qquad \textbf{Equation 1}$$

SRT had been investigating several alternative reactions to produce HBr efficiently. Many involved the reaction of water and bromine with a carbonaceous material, such as charcoal, coal, or biomass. Previous work in this area indicated that bromine conversions of 95-100% could be attained at temperatures below 500 °C (773 K). The process is also expected to be exothermic, producing rather than requiring heat. A disadvantage of the prior work was that the carbonaceous material used was a solid, tending to complicate the processes to the point of being uneconomical.

Thermodynamic calculations performed by researchers at Sandia labs confirmed that the reaction had promise. SRT personnel built a laboratory sized bromine/steam/methane reactor and tested it. Preliminary results showed that the bromine conversion to HBr approached 95% at 750 °C. The reactor product stream was sampled and analyzed for HBr content. Concentrations up to 13 M in HBr were generated. This translates to 60 wt% HBr, which is a saturated fuming solution more concentrated than the commercially available azeotrope, which is 48 wt%.

Based on these early results, SRT has designed a new hydrogen production/energy storage process utilizing the bromine/steam/methane reaction. An electrolysis cell is presently used to take the place of the fuel cell as it is developed, the cell should be ready in 1999. The new system can generate hydrogen, but cannot be used for energy storage. The system however, even in this form, can have a positive impact on the hydrogen production marketplace. The system, when used to generate hydrogen from methane, water and electricity can compete favorably with delivered liquid hydrogen in small to medium sized installations. It is small, compact, and produces hydrogen as a pure gas, without the requirement for production of syngas intermediates or product separation and purification. Product separation and purification makes conventional steam/methane reforming uneconomical on a small scale. The process is illustrated in Figure 1.

Methane is mixed with steam and bromine in the reactor, where conversion to HBr and CO_2 takes place. The hot gases exit the reactor and go through heat exchangers. They capture some of the heat to pre-heat the incoming reactants. As the reaction is exothermic, excess heat is produced. The product gases then pass into an absorber, where the HBr is absorbed into water, raising the incoming HBr concentration from 20 wt% to 40 wt% upon exiting. The CO_2 is not absorbed to any appreciable extent and passes into the scrubber. In the scrubber, counterflowing water removes any residual HBr. The CO_2 exiting the process will be essentially pure and will have value as an inert gas or other chemical uses.

The 40 wt% HBr stream exiting the absorber will be pressurized by a pump and fed into the electrolyzer, producing H_2 and Br_2. Hydrogen exits the electrolyzer at high pressure, thus not requiring compression for storage. The liquid mixture leaving the electrolyzer will be depleted in HBr to 20 wt% and will have bromine dissolved into it. This liquid will be passed through a pressure reducing valve into a flash drum where the bromine will boil off, due its low boiling point. The bromine vapor will be conveyed back to the reactor after being reheated while the remaining liquid will return to the absorber, completing the cycle. For purposes of size visualization, at 76,000 scfd, the pump for the 40 wt% HBr stream has a capacity of 10 GPM.

A noteworthy feature of the process is that all of the components shown, even those that are required to be bromine compatible, are commercially available. The only exception is the reactor, which is expected to be constructed of glass-lined steel. Another noteworthy feature is that elemental bromine (Br_2) is only present in the flash drum and piping leading to the reactor. At all other times in the process cycle, bromine is present as HBr, a safer chemical to handle. The amount of elemental bromine present at any one time is small, and when the bromine is formed, it is immediately consumed in the reactor to make more HBr. Shutting down the electrolyzer (for example in the event of a power failure) would stop bromine production. This results in a safe system, with minimal potential for damage in the event of a failure in a piece of equipment.

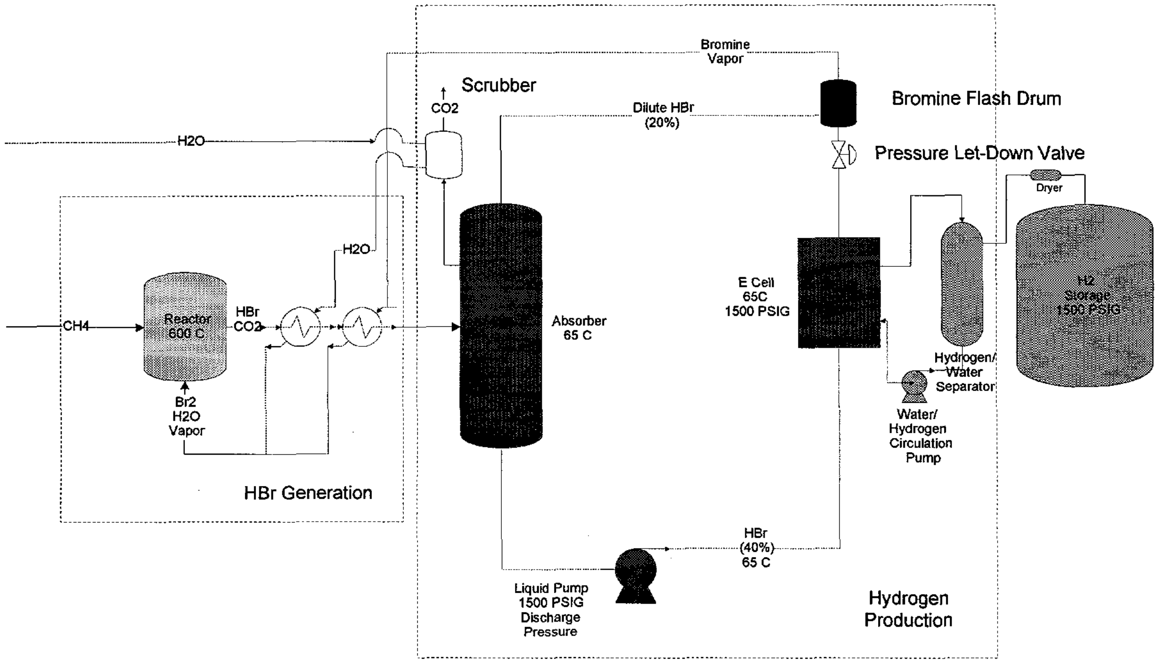

Figure 1 Hybrid Steam, Methane Electrolysis Process Flow Diagram

Steam/Bromine/Methane Research Program

In the 1997 effort to develop an energy storage/hydrogen production system, the focus was on reactor development. SRT set forth a series of experiments in which reactor-operating conditions were varied to determine the effect on the product mixture. Bromine conversion to HBr was to be optimized, while the amount of reaction by-products was to be minimized. Parameters included: (1) reactor temperature, (2) residence time, (3) H_2O:CH_4 molar ratio, (4) Br_2:CH_4 molar ratio, and (5) surface enhancement.

An apparatus for studying the bromine-methane-steam reaction was assembled. It consisted of a quartz tube reactor, bromine delivery system, steam generator, and sampling glassware. Initial results showed that bromine reacted readily with methane and steam to produce high concentrations of HBr. Reaction temperatures ranged between 650 and 900 °C. Gas exiting the sample capture tube was analyzed for CO and CO_2 with a GC; small amounts were detected. A GC-MS analysis of the organic compounds extracted from the black particulates and the solution phase was performed. Trace quantities of a large number of brominated aromatic and aliphatic compounds were identified.

This first apparatus was not suited to studying the reaction in detail. In particular, bromine flow rates were not constant and there was no provision for accurately sampling the gaseous effluent. This in turn did not allow for a full material balance on the reaction.

Significant improvements were realized in a second research effort. A more versatile and reliable reactor test apparatus was successfully designed, built, and tested. The reactor did not experience plugging at the flow rates used. The bromine delivery sub-system was robust toward bromine corrosion.

SRT's analytical methods for quantitating reaction products were greatly improved. Data have been collected in seven different runs at different temperatures and varying reactant molar ratios to date. The data were significantly more complete than those collected previously, since the product gas stream (unreacted CH_4, CO, and CO_2) was collected and quantified with a gas chromatograph (GC). A spectroscopic method for determining Br_2 was developed as well.

The data are very encouraging. At 800 °C, conversion of methane and bromine to HBr was 99 - 100% and 75%, respectively. The conversion of water to HBr was less, about 10%. This value will be increased if more water reacts with the carbonaceous material deposited in the reactor. Methane was typically the limiting reagent, while steam and bromine were essentially equimolar. A mass balance of bromine shows that some cannot be accounted for. The discrepancy can best be explained by a decrease in the bromine delivery rate during sampling (discussed later).

The improved reactor test apparatus has proven dependable in early testing. It will serve as a good test bed for an extensive testing program proposed for 1998. However, further up-grades are required. A more complete mass balance on the reaction products will require further system and analytical improvements. A technique for independently measuring the unreacted water in the product sample is needed. The carbonaceous material deposited in the reactor needs to be quantified as well. Modifications to the reactor and sampling system will needed. The analysis for organic compounds will be continued.

Before an extensive testing program is undertaken, two different reactor designs will be evaluated. Since carbonaceous material is deposited in the reactor during testing, SRT needs to determine under which conditions its conversion to useful products occurs. Reactors with increased surface area and/or characteristic residence times will be required. They will be evaluated over a range of operating conditions. This will serve to define the useful boundaries in parameter space for the subsequent statistical design experiment.

In the statistical design experiment, three variables will be varied simultaneously in a systematic fashion. It requires 16 separate runs, plus a few more at intermediate values. The data will be evaluated and a response surface generated. It should then be possible to predict where optimal reactor operating points lie. Further experiments at outlying or intermediate values will confirm this. Additionally, a more detailed economic model will provide valuable feedback/constraints. A method for measuring an empirical kinetic rate expression will have to be developed. The rate is crucial for designing a larger pilot-scale reactor system.

II Results to Date

The 1997 effort was a success. A new apparatus for studying the reaction was assembled. It consisted of a quartz tube reactor, bromine delivery system, steam generator, and sampling glassware. Initial experiments showed that bromine reacted readily with methane and steam to produce high concentrations of HBr. Analytical techniques for quantifying the reaction products were developed.

A more versatile and reliable reactor test apparatus was successfully designed, built, and tested. The reactor did not experience plugging at the flow rates used. The bromine delivery sub-system was robust toward bromine corrosion. SRT's analytical methods for quantitating reaction products were greatly improved. Data were collected in seven different runs at different temperatures and varying reactant molar ratios. The data were significantly more complete than those collected previously, since the product gas stream (unreacted CH_4, CO, and CO_2) was collected and quantified with a GC. A spectroscopic method for determining Br_2 was developed as well.

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First Reaction Studies

An apparatus for studying the bromine-methane-steam reaction was assembled. It consisted of a quartz tube reactor, bromine delivery system, steam generaror, and sampling glassware. Initial results showed that bromine reacted readily with methane and steam to produce high concentrations of HBr. Reaction temperatures ranged between 650 and 900 °C. Gas exiting the sample capture tube was analyzed for CO and CO_2 with a GC; small amounts were detected. A GC-MS analysis of the organic compounds extracted from the black particulates and the solution phase was performed. Trace quantities of a large number of brominated aromatic and aliphatic compounds were identified.

1. Apparatus and techniques.

Figure 2 shows SRT's first apparatus for studying the reaction between bromine, steam, and methane. Bromine was stored in a Tefzel-lined steel tank, whose change in mass was monitored by a load cell. Nitrogen (about 20 psig) was used to push bromine through the tank's dip tube, through a metering valve, and into a steam-jacketed heat exchanger, where it was vaporized. The reactor was run at atmospheric pressure. Steam was supplied by a commercial steam generator and metered by a metering valve. Methane (99.3%) was metered with a rotameter and pressure gauge.

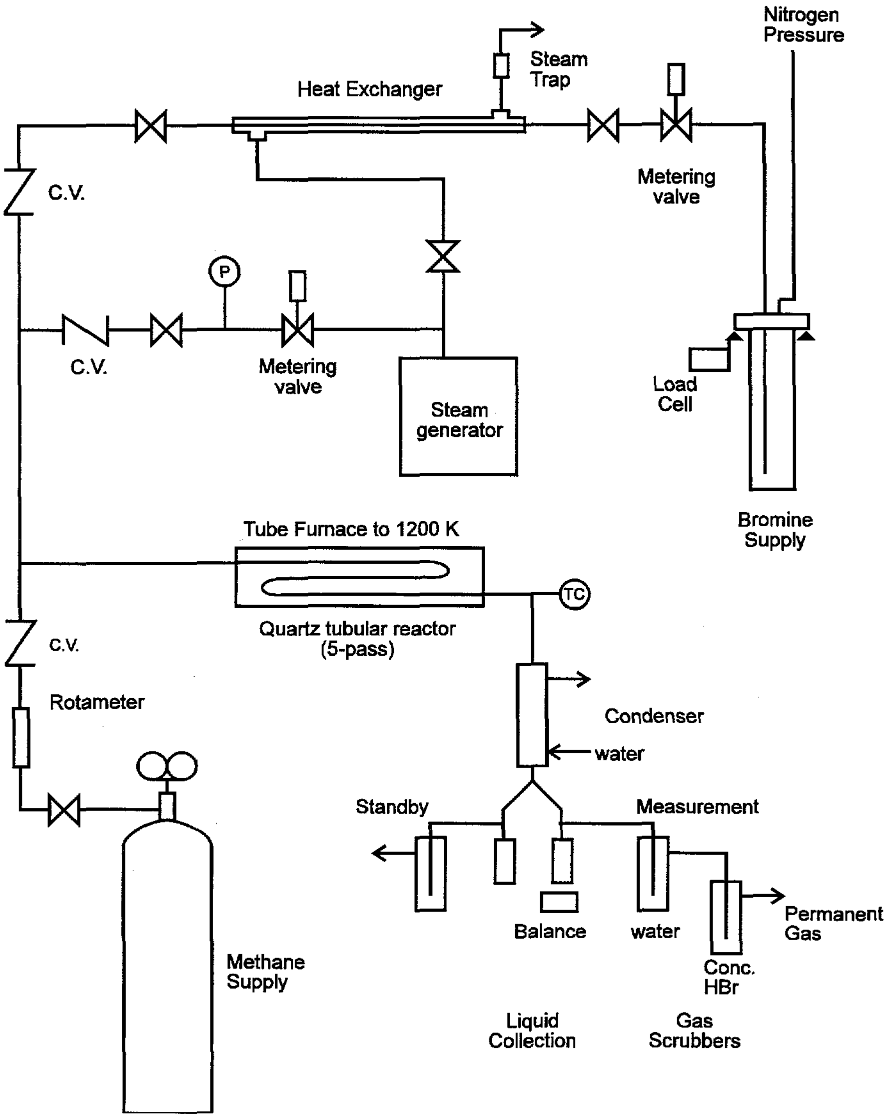

Figure 2 Apparatus used in the study of the reaction between steam, bromine, and methane.

In a second set of experiments, the configuration was slightly modified. The bromine metering valve was placed before the heat exchanger. It was thought that this would simplify operation and improve the uniformity of bromine delivery. A calibration leg for the bromine delivery was added after the heat exchanger. This did not result in significant improvement in delivery.

All three vapor streams were mixed in a heated manifold made of Kynar fittings and tubing. A medium porosity frit supplied about a 5 psi back pressure, sufficient to seat the three check valves in the input streams. The intent was to reduce upstream corrosion in both the bromine and steam lines.

The reactor was a quartz tube of 11 mm i.d. bent 4 times in a double-S configuration. Its empty volume was 200 ml. For a total molar flow rate of 0.25 mol/min and an 800 °C mean reactor temperature, this corresponds to a 0.54 second residence time. It was heated by an 18" long, 3" i.d. Omega tube furnace, controlled by a PID controller. The product gas stream was condensed in a water cooled condenser and sampled with a Pyrex adapter having a two-way valve. Samples were collected in 50 ml Erlenmeyer flasks with ground glass joints. They were weighed before and after the run, then stored in a refrigerator until analyzed. For the second set of experiments, a water scrubber solution (typically 225 ml) was added to an empty flask connected in series after the sample flask. The mass of the scrubber solution before and after a run was determined by mass difference and was stored in a tared Erlenmeyer flask.

A concentrated HBr solution was used to scrub any Br_2 passing through the water scrubber. In a third iteration of the sampling system, the product stream was bubbled through two water solutions before passing through the HBr solution in a cold trap and a second empty cold trap. Both cold traps were cooled to about -25 °C by a dry ice/ethylene glycol slush. A significant amount of gas not scrubbed by this last HBr solution was generated in the reactor. It was sampled with a gas syringe and injected into a gas chromatograph for analysis.

2. Analytical methods.

Samples in the first set of experiments were analyzed in the following manner: each sample was weighed, aqueous phase density determined, and then an aliquot (2 or 0.2 ml) titrated for H^+ with standardized NaOH solution. The pH was plotted as a function of ml NaOH added and the inflection point was used as the endpoint, as shown in Figure 30. In the second set of experimental runs, the water scrubber solutions were titrated instead. Since a large portion of the HBr generated did not condense in the first sample, the second scrubber bottle was critical for obtaining a more precise value for the total amount of HBr produced and attempting to close the mass balance.

3. Analysis and conclusions.

It was found that the concentration of HBr in samples was much higher when methane was flowed through the reactor than without, all other conditions constant (See Tables 13 and 14). In fact, the samples collected fumed in the presence of moist air. The 11 - 13 M concentration determined by titration was well above that of the commercially available HBr azeotrope, which is 48-49 wt% or 8.9 M. This is *very* encouraging, since HBr electrolysis is much more efficient at high acid concentrations.

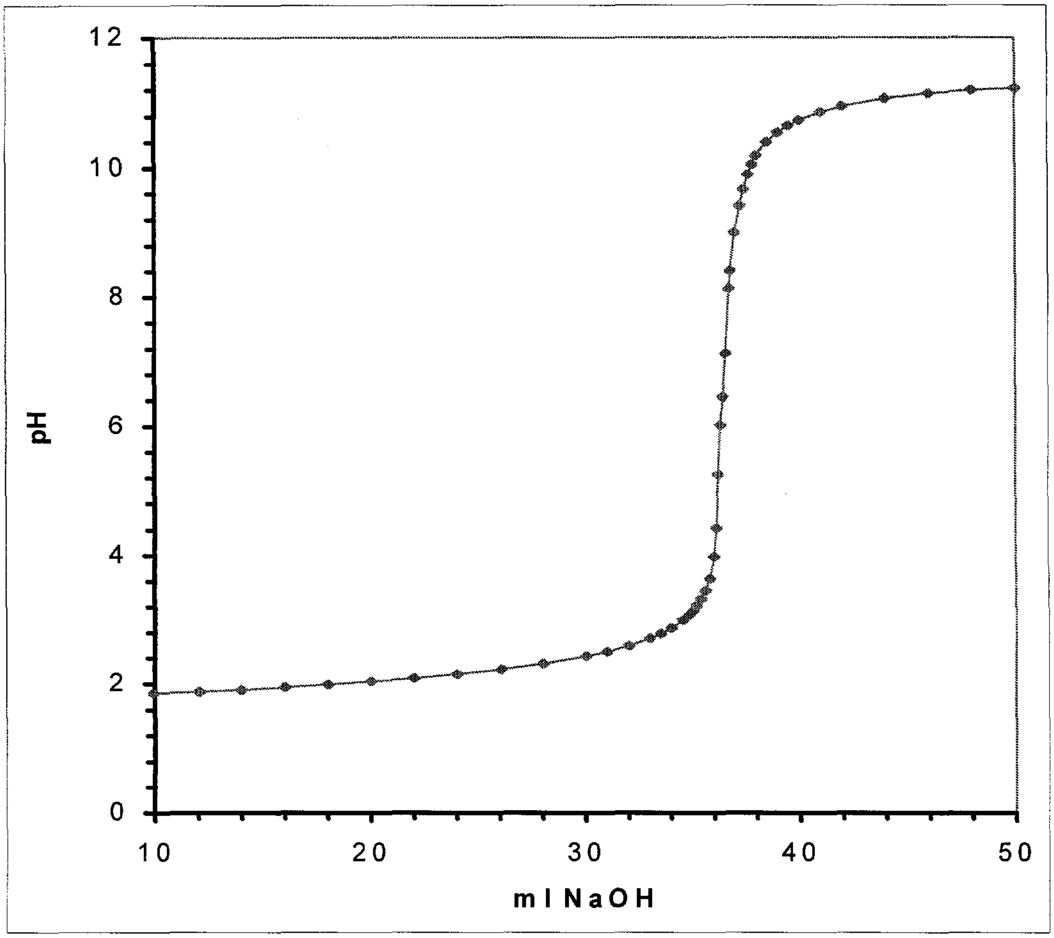

Figure 3 Titration curve for a 12.7 M HBr solution containing some Br_2.

It is apparent from Table 14 that an appreciable amount of HBr was collected in the scrubber solutions. This was reflected in an increase in their mass during the course of the experiment. In fact, the amount of HBr scrubbed was 2 - 3 times that collected in the samples for the highest methane flow rates. Reactant mole fractions were about 0.35 Br_2, 0.55 H_2O, and 0.1 CH_4. Bromine conversion efficiencies of 60% were attained. Higher values should be realized in future experiments through input mole fraction, temperature, residence times, and catalysts.

In a second set of experiments, bromine flow rates were reduced by a factor of 2 - 4 and methane by a factor of 5. In Table 15, these results are compared to those previously discussed. Experiments A and B refer to conditions of higher flow, while C, D, and E are for the lower rates. By running the reactor methane rich, it was possible to obtain very little free bromine in Experiments C, D, and E. This made the analysis much simpler. In particular, the organic impurities could readily be extracted without the need for distilling off large amounts of bromine. The conversion of bromine to HBr realized was comparable to the former two experiments, i.e.

between 30 and 70%. The 92% conversion for Experiment E, Sample 1 is an upper limit, based on reasonable values for the bromine delivery rate, which varied.

Sample #	XBr_2	XH_2O	XCH_4	[HBr] (M)
2	0.479	0.521	0.0	0.46
3	0.467	0.533	0.0	0.50
4	0.433	0.493	0.074	11.3
5	0.433	0.493	0.074	11.3

Table 1. Bromine-steam-methane reaction, reactor exit temperature = 650 °C.

Note that no water scrubber solution was used.

Sample No.	XBr_2	XH_2O	XCH_4	[HBr] Sample	[HBr] Scrub	n_{scrub}/n_{sample}	Conversion. %
1	0.433	0.567	0.0	1.82	0.0	0.0	2.3
2	0.433	0.567	0.0	1.82	0.0	0.0	2.2
3	0.352	0.559	0.089	12.7	0.668	2.47	6.2
5	0.352	0.559	0.089	13.1	0.678	3.15	59
6	0.368	0.585	0.047	8.1	0.159	0.548	30
7	0.368	0.585	0.047	8.91	0.154	0.495	30

Table 2. Bromine-steam-methane reaction, reactor exit temperature = 800 °C.

The column n_{scrub}/n_{sample} refers to ratio of moles HBr in scrubber solution to those in the concentrated sample.

Since it is difficult to accurately measure gas temperatures in a tube furnace, the two temperatures listed in Table 15 are upper and lower bounds to the effective temperature. The furnace temperature was measured by the controller thermocouple. The exit temperature was measured by a thermocouple in a well bathed by the exit gas stream. It was just inside the end of the furnace.

Exp.	Run	T_{set} (C)	T_{exit} (C)	XBr_2	XCH_4	XH_2O	XBr_2/ XCH_4	% Br_2 Conversion.
A	4	750	650	0.43	0.07	0.49	5.8	24
	5	750	650	0.43	0.07	0.49	5.8	25
B	3	900	790	0.35	0.09	0.56	4.0	62
	4	900	790	0.35	0.09	0.56	4.0	
	5	900	790	0.35	0.09	0.56	4.0	59
	6	900	790	0.37	0.05	0.59	8.0	30
	7	900	790	0.37	0.05	0.59	8.0	30
C	1	650	500	0.28	0.09	0.64	3.3	33
D	1	950	815	0.51	0.09	0.43	5.5	67
E	1	750	650	0.16	0.08	0.76	1.8	**92**
	2	750	650	0.21	0.08	0.71	2.5	54

Table 15 Summary of SRT's Preliminary Studies of the Bromine-steam-methane reaction. T_{set} and T_{exit} refer to the furnace and exit gas temperatures, respectively.

A disadvantage of Reaction (12) as studied were side reactions leading to the production of hydrocarbon and brominated hydrocarbon compounds. This was manifested by the appearance of a black residue in the sampling system and a characteristic odor. A white solid condensed on the walls when $HBr/Br_2/H_2O$ samples were distilled. At lower reactor exit temperatures (650 °C), the black residue was more tarry and settled at the bottom of the sample bottle with unreacted bromine. At higher temperatures (800 °C), the residue consisted of smaller particulates and there was very little unreacted bromine at the bottom of the sample flasks. This organic residue may be eliminated via two approaches: (1) operate the reactor at higher gas temperatures, or (2) employ a catalyst to destroy the organic species. A candidate for (2) is iron oxide, Fe_3O_4. A similar catalyst was successfully used for the work with charcoal described in the related research section in Appendix 3.

Based on the residual product distributions, it will be possible to elucidate the reaction mechanism. Once understood, it will be possible to greatly reduce their production. These compounds occur at trace levels, and much of the black filtrate collected is carbon in the form of soot or graphite. More careful analytical work will be required to quantify their total amount. This will allow SRT to close the material mass balance for the reaction.

20 - 50% of the mass flowing through the reactor could not be accounted for. We estimate that 5 - 10% of the discrepancy was due to the black residues coating the sampling apparatus. The remainder was likely due to a mixture of gases passing through the system: CH_4, O_2, CO_2,

CH_3Br, ethane, propane, and others. A change in bromine flow rate of 10 - 20% during experiments was possible as well.

B. *Economic Analysis*

The modified hydrogen production process of Figure 1 was evaluated by SRT for its economic potential as a hydrogen production system. The analysis involved a spreadsheet model of the process containing input costs and output prices. It is patterned after a similar analysis performed by Energetics Inc. for the energy storage/hydrogen production system. The base scenario assumes:

- 76,000 SCFD production (18 hours/ day production time)
- Electrolyzer cost of $400/kW
- Off-Peak electricity cost of $ 0.01/kWh
- Natural gas cost of $2.70/MMBTU
- After tax Internal Rate of Return (IRR) of 15% or more

Given these constraints, the process of Figure 28 can provide hydrogen at a price of $9.57/MMBTU.

Figure 31 shows how the IRR varies as a function of plant size, Figure 32 shows how IRR varies with electricity costs, and Figure 33 shows the effect of natural gas cost.

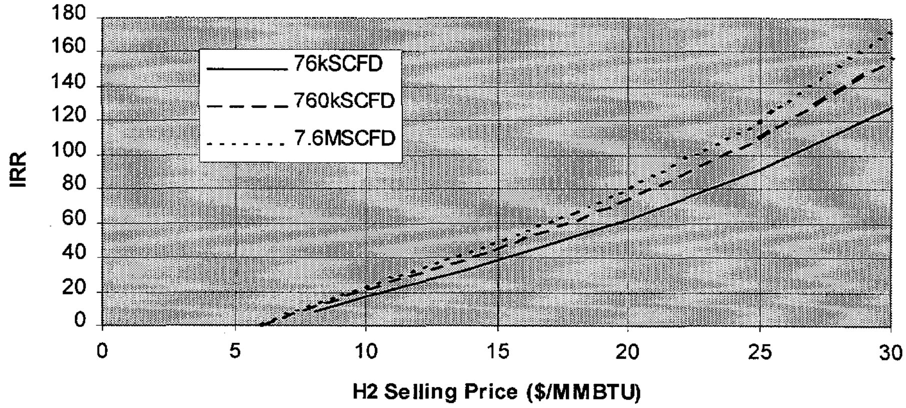

Figure 4 Effect of plant size on IRR

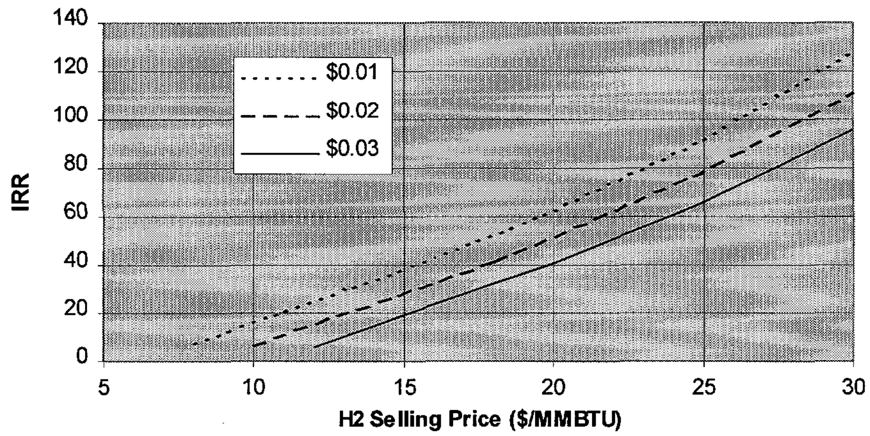

Figure 5 Effect of off peak electricity cost ($/kWh) on IRR

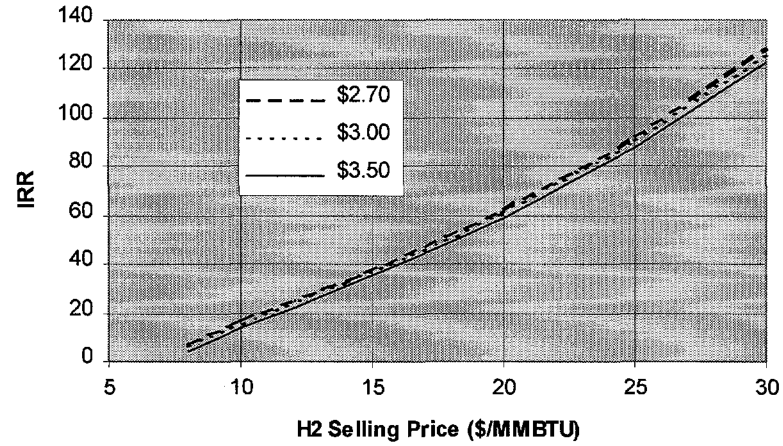

Figure 6 Effect of natural gas price ($/MMBTU) on IRR

SRT examined markets for hydrogen and found that in many cases, companies are paying up to $25.00/MMBTU for hydrogen delivered to their plant. These customers consume from 50 to 100kSCFD, so these companies would make good candidates for this technology. Plants could be situated on-site for maximum economic return.

In discussing the economic viability SRT's concept, it is important to estimate the overall thermal and chemical efficiency of the process. That is, the estimated amount of energy input compared to the heating value of the H_2 produced and that of the CH_4 consumed. For the purposes of illustration, we assume complete reaction according to

$$2\ H_2O + 4\ Br_2 + CH_4 \rightarrow 8\ HBr + CO_2.\ \Delta H^{\circ}_{298} = -38.2\ kJ \qquad \textbf{Equation 10}$$

This can be compared to the enthalpies for the following two combustion reactions:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O, \quad \Delta H^\circ_{298} = -\,890\ \text{kJ} \qquad \textbf{Equation 2}$$

and

$$2\,H_2 + O_2 \rightarrow 2\,H_2O, \quad \Delta H^\circ_{298} = -571.6\ \text{kJ}. \qquad \textbf{Equation 3}$$

The enthalpy of reaction (2) at 1200 K is -239.9 kJ/mole of CH_4 consumed. Assuming 1.0 mole/min of CH_4 reacting completely according to (2), forming 8.0 mol/min HBr, which is electrolyzed to yield 4.0 mol/min H_2, the energy terms are as follows:

Heat of reactant vaporization	3.5 kW
Average Specific heat (300 - 1200 °C)	3.7 kW
Heat of Reaction (1200 K)	-4.0 kW
Heating value of CH_4 consumed	14.8 kW
Electrical energy input ($E^\circ = 0.80$ V)	10.3 kW
Total energy input	28.3 kW
Heating value of H_2 produced	19.0 kW

If one defines the energy efficiency η as follows

$$\eta = \textbf{H2 heating value/Total energy inputs} \qquad \textbf{Equation 4}$$

then the $\eta = 0.67$, which is a surprisingly high value. In this treatment, it was assumed that the heat of vaporization of H_2O and B_2 was supplied by a very efficient heat exchanger.

One can modi19the assumptions to include system inefficiencies: additional heating/vaporization energy inputs, electrolyzer inefficiencies (e.g. higher potentials and current efficiencies < 100%), parasitic energy requirements (for pumping, separation, cooling, etc.), heat for bringing the reactor up to temperature, which all result in somewhat lower overall energy efficiencies. Due to the early stage of SRT's work, it is premature to estimate these losses from a preliminary process flow sheet. This value however, is significantly higher than the 49% value cited in the Rockwell International report on the production of H_2 from Br_2, H_2O and biomass (Darnell, *et al.*, 1983).

Subsequent Experimental Program

Significant improvements were realized in a second research effort. A more versatile and reliable reactor test apparatus was successfully designed, built, and tested. The reactor did not experience plugging at the flow rates used. The bromine delivery sub-system was robust toward bromine corrosion. SRT's analytical methods for quantitating reaction products were greatly improved. Data were collected in seven different runs at different temperatures and varying reactant molar ratios. The data were significantly more complete than those collected previously, since the product gas stream (unreacted CH_4, CO, and CO_2) was collected and quantified with a GC. A spectroscopic method for determining Br_2 was developed as well.

Apparatus

The entire apparatus was installed inside a large stand-up fume hood. In case of a bromine spill, it protected personnel from irritating bromine vapors. All controls and displays were located on a control panel outside the hood. Each reactant (Br_2, steam, and CH_4) was metered separately in separate flow loops. The pressure in each loop was kept greater than the downstream pressure. This ensured that small changes in sampling system back pressure did not affect the metering rate.

If bromine is allowed to absorb moisture, it will corrode most metals severely. To prevent corrosion and protect operators, a special flow loop was built to safely transfer, store, and handle bromine. A supply tank, lined with chemically resistant Tefzel, held about 1.5 liters of bromine (see Figure 7). The tank was a 2" diameter piece of carbon steel pipe that was sealed with a weld cap on one end and a flange on the other. The tank lid was cut from a solid piece of PVDF (Kynar) and machined to the dimensions of the flange. Threaded ports were drilled and tapped into the lid for the various connections. The three top bolts mated the lid to the tank flange with the plastic liner serving as a gasket. All tank fittings were Monel; connections between the tank

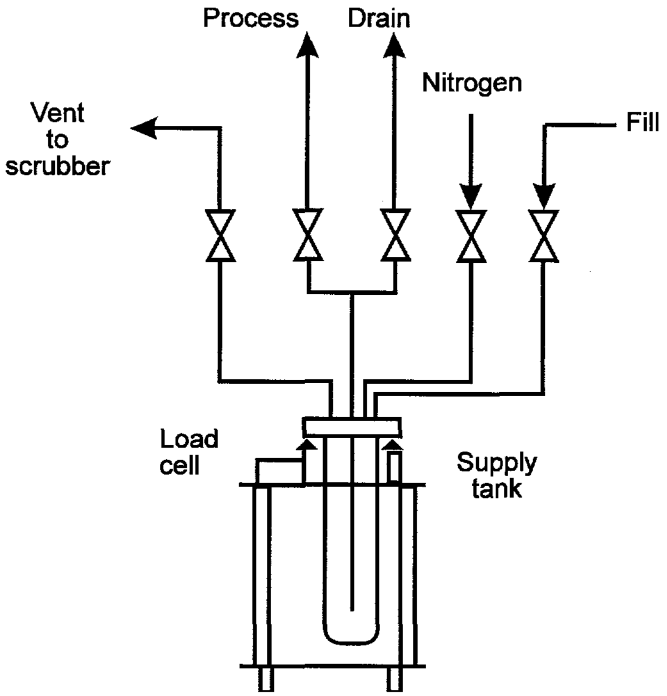

Figure 7 Bromine Supply Tank

and the apparatus were made with flexible PFA tubing.

Three support struts, welded to the body of the tank, allowed the tank to sit in a support stand. One of mounting points was a load cell, which recorded the tank weight. Each standoff contained a recess or seat for a ball bearing, which rode between the tank and stand. They allowed the tank to sit level in the stand.

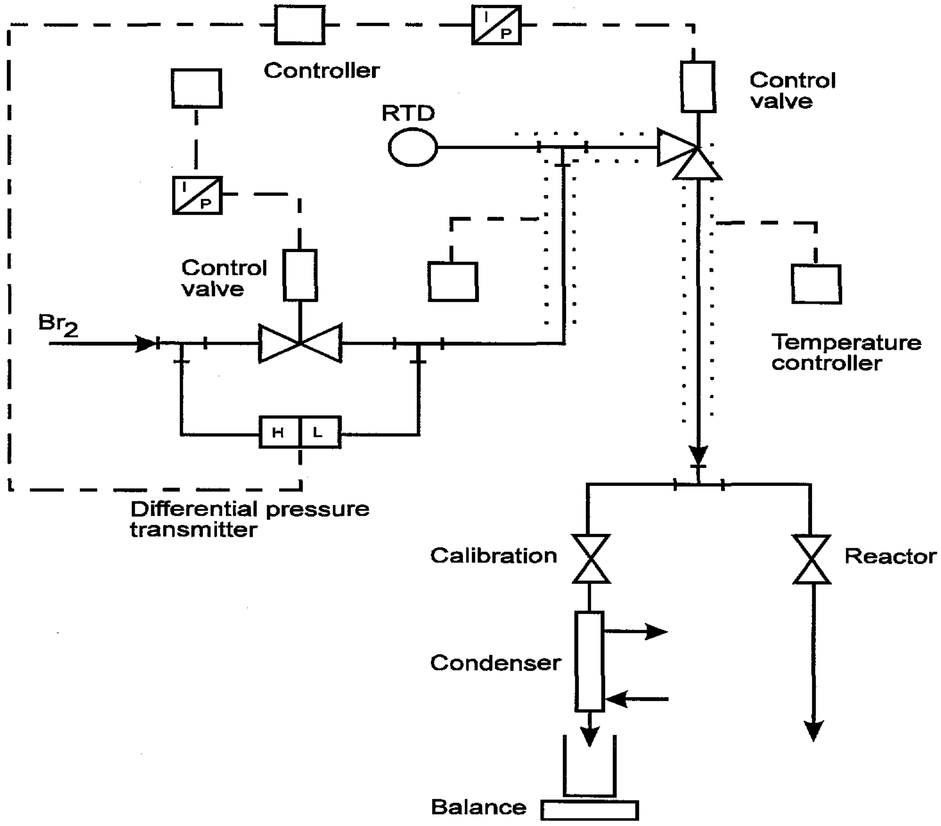

Figure 8 Bromine flow loop.

Bromine (Great Lakes Chemical, 99.8%) was loaded into the tank by vacuum and stored under dry nitrogen (BOC, UHP grade) at all times. Pressurizing the supply tank with nitrogen forced bromine out through the dip tube and into the flow loop.

Bromine is a liquid at room temperature and must be vaporized before it enters the reactor. It was most convenient to meter bromine as a liquid. It was heated under pressure to a temperature above its boiling point. The pressure was then dropped, flashing the liquid to a vapor (See

Figure 8).

Liquid bromine (at 26 psi) flowed through a pneumatic Hastelloy control valve (CV1) that acted as an adjustable orifice. All lines in the flow loop were 1/4" Monel tubing. Each side of CV1 was connected to a differential pressure transmitter. As bromine flowed through CV1, the transmitter read the pressure drop, normally 1 to 10 inches of water. It could be increased or decreased by changing the position of the valve stem. The differential pressure transmitter sent a current signal to a P.I.D. controller, which displayed a numerical value for the pressure drop.

Bromine then flowed through a vertical section of tubing wrapped with a heating tapes (heat exchanger). The tapes were connected to two time proportional controllers. The thermocouples for these controllers were mounted between the Monel tubing and the heater tapes. The temperature of liquid bromine was measured with a RTD in a Monel sheath. It was inserted into one end of the tee at the top of heat exchanger. The heat exchanger temperature was maintained between 65 - 70 °C. Since the boiling point of bromine at one atmosphere is 59 °C, the nitrogen pressure was kept above the vapor pressure (26 psi) to prevent boiling.

The liquid, now slightly superheated, flowed through a second control valve (CV2). This valve controlled the actual flow rate to the reactor. CV2 was the same size as CV1, but had an angle style flow pattern. Since the pressure downstream from CV2 was essentially atmospheric, the superheated liquid flashed to form a vapor as it flowed through the valve.

The vapor was then directed either to a calibration condenser or to the reactor. The switchover valves were housed in an insulated enclosure. It was heated with steam-traced lines and electrical heater elements. A fan circulated the hot air.

The bromine flow rate was measured during calibration by condensing the vapor and recording the mass of liquid collected versus time. An electronic balance and a stopwatch were used. In practice, the flowrate did not remain constant, although a high delivery pressure was used. Future work will be directed to tuning the PID controller for CV2 with the signal from the differential pressure transmitter.

Methane was supplied by a high purity compressed gas cylinder (BOC Gases, 99.3%), See

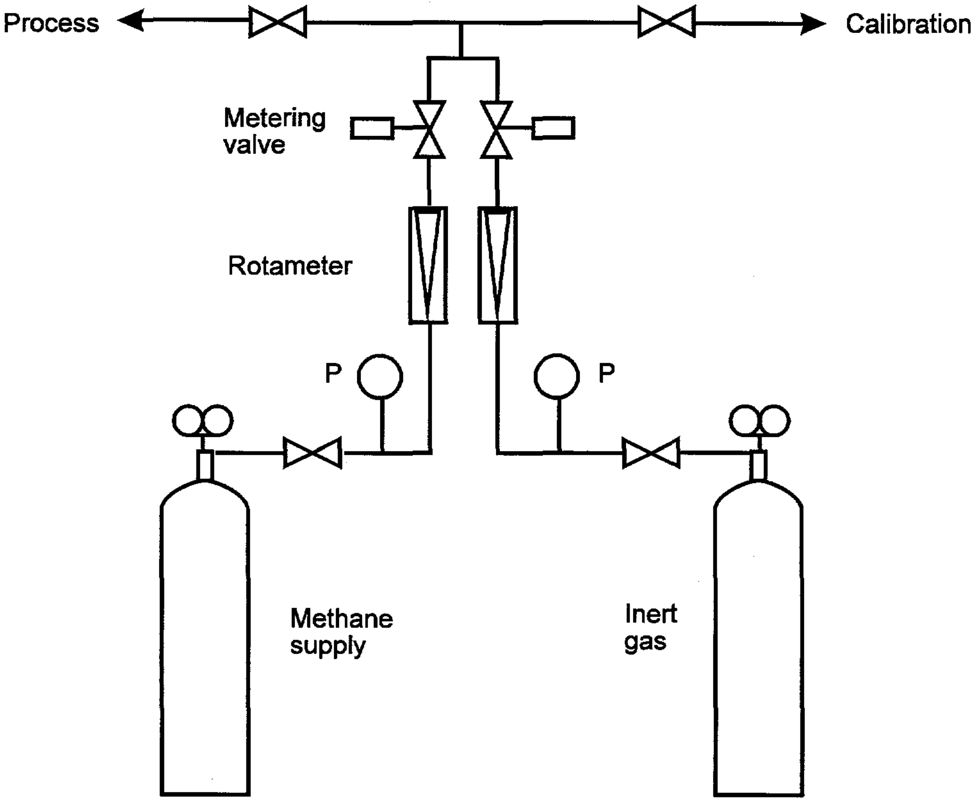

Figure 9 Methane Flow Loop

Figure 9. The flow rate was measured with a rotameter, which had a high-resolution metering valve located on its exit side. The rotameter contained two flow tubes. This allowed blending an inert gas into the reactor. The inert gas was used to control the molar ratio of two components (e.g., steam vs. bromine) while the third (e.g., methane) is varied. Because of the high supply pressure (50 psi), the methane flowrate was unaffected by changes in the downstream pressure.

A small commercial steam generator (Reimers, 220V, 6 kW), which had an automatic water feed and its own temperature control, supplied steam continuously throughout the experimental run (See Figure 10). The generator was operated at pressures higher than those needed for the reactor feed. This somewhat superheated steam was used for steam tracing the reactor feed lines. Steam line condensate was drained automatically with steam traps. A small metering valve with a vernier handle was used to adjust the flowrate to the reactor. The pressure upstream of the valve was kept constant with a pressure regulator. Steam exiting the metering valve was directed either to a calibration leg fitted with a condenser or the reactor. The flow rate was determined by the mass collected from the condenser in a fixed time interval.

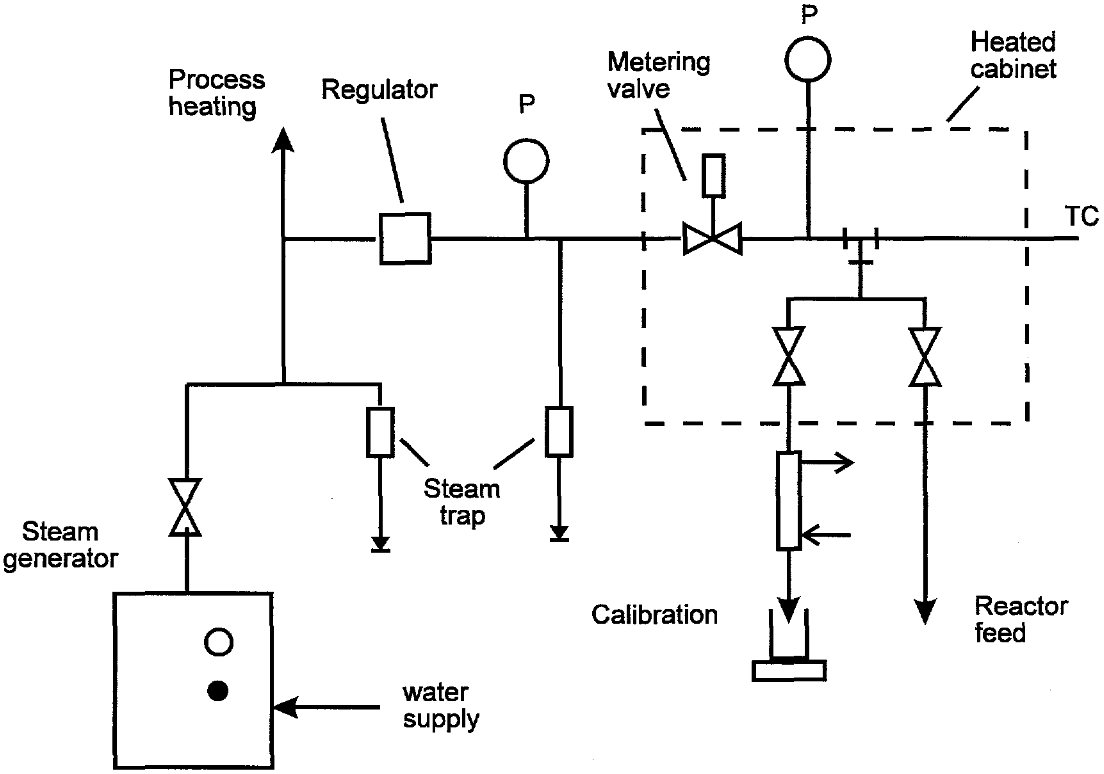

Figure 10 Steam Flow Loop

Two independently controlled furnaces, mounted vertically end-to-end in a support frame, held the reactor assembly (See Figure 11). The frame and furnaces could be removed as a unit from the hood for disassembly. The quartz reactor assembly had three different regions. The first was a heat transfer zone. It contained two coils of identical length. Steam and methane flowed through one coil, while bromine flowed through the other. The coils were housed in the lower tube furnace. It was 18" long with a 3" i.d. The reactant gases mixed in the second region, located between the two furnaces. They then flowed into the third zone, the reaction zone. It was housed in the upper tube furnace, which was 12" long with a 4" i.d. Ceramic plates, an integral part of the assembly, aligned the two furnaces and held them together. They also positioned and supported the complete reactor assembly. The plates measured 11.5" x 11.5" (🖹 and 1" thickness). They split apart and contained holes for several thermocouples and the reactor feed and exit tubes.

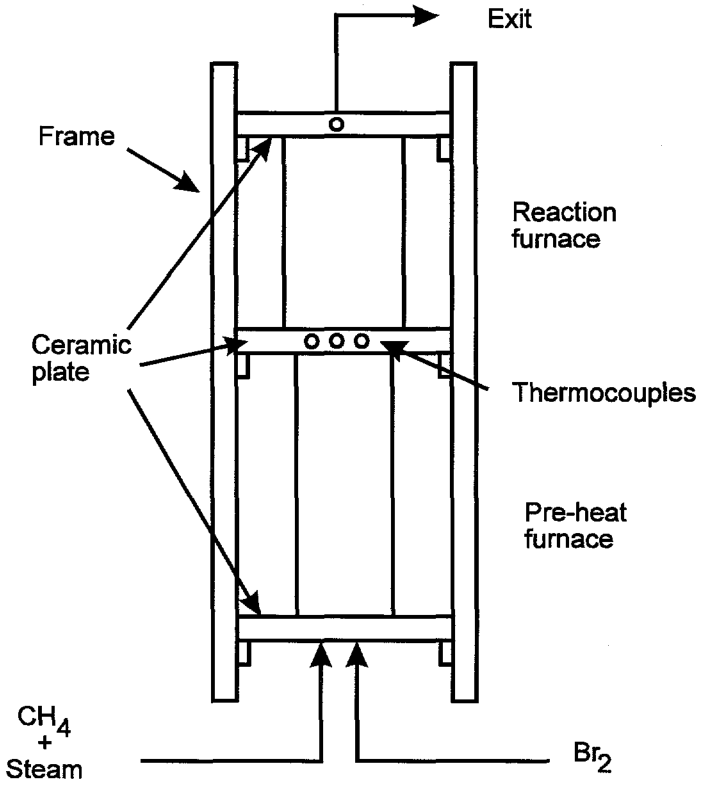

Figure 11 Configuration of Assembled Furnaces

The configuration of the reaction zone furnace is shown in detail in Figure 12. The center plate, which was 1" thick, shielded the reactor furnace from the coils of the preheater furnace. A cavity in the plate supported the mixing region of the reactor, which was its only vertical support inside the furnaces. Through holes in the top and bottom plates centered the reactor in the two furnaces. Due to insufficient power at the ends of the reactor furnace, the temperature dropped off rapidly from the middle. To improve the temperature profile, split disk shaped ceramic heaters were added at each end. The power supplied to each of these end heaters was fixed, while the furnace controller varied the power to the reactor furnace. This arrangement resulted in a profile that was essentially flat over the length of the furnace (± 20 K).

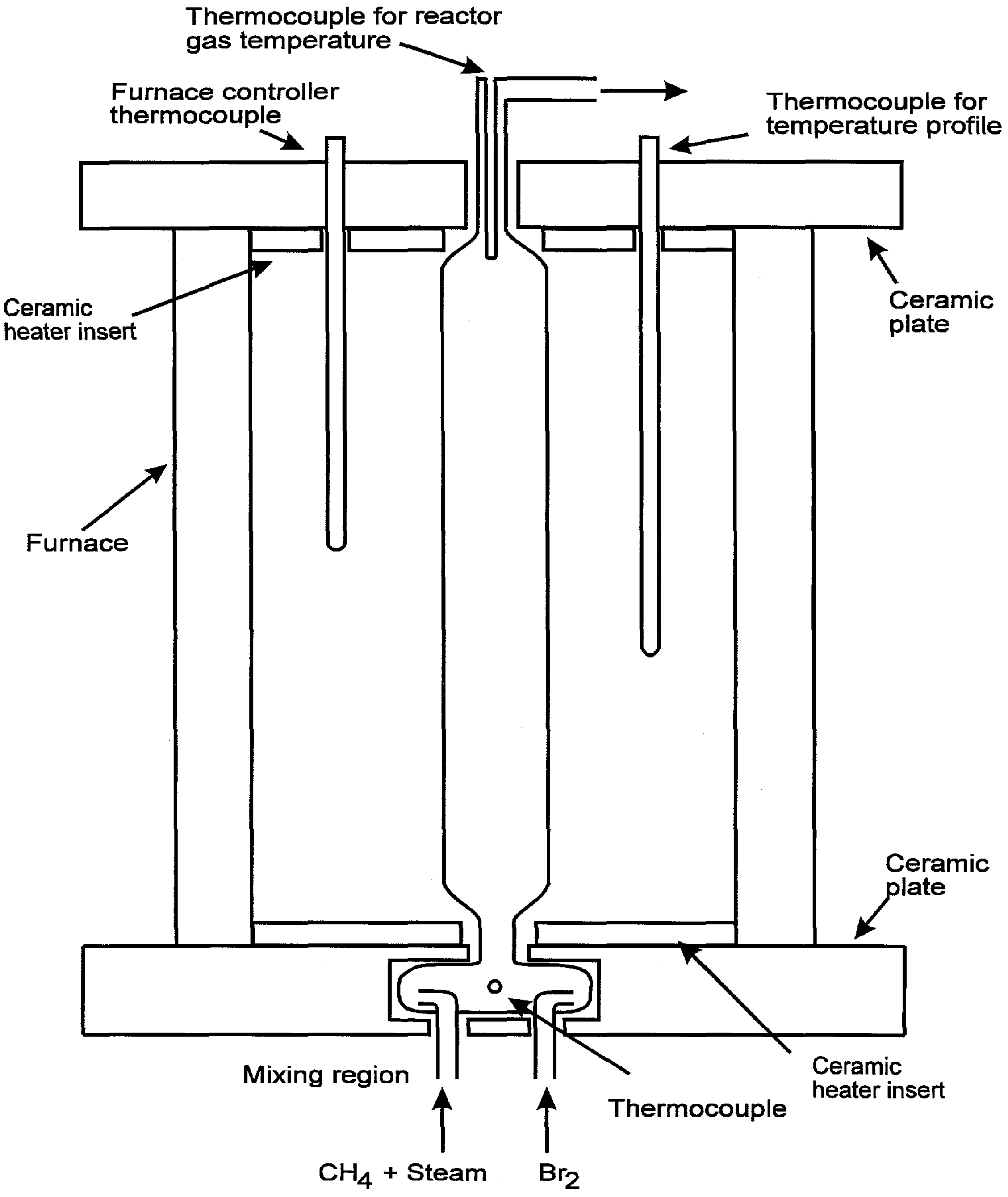

Figure 12 Reaction Zone Furnace

The mixing zone in the reactor contained a quartz well. It was aligned with a through hole in the middle plate. A bare junction thermocouple, inserted into the well from the outside edge of the plate, measured gas temperatures just before the reaction zone. It was supported by a two-holed ceramic tube, which facilitated seating in the well. The measured gas temperature could be increased or decreased by changing the set point of the lower furnace. This thermocouple was shielded by the middle plate from radiative heating by the preheater and reaction zone furnaces. A more accurate measurement was obtained than if it had not been shielded in this manner.

Once the gases exited the lower furnace, they cooled, due to imperfect insulation. To quantify the amount of cooling, the middle plate contained several thermocouple wells located at different radii from the center of the mixing cavity. They facilitated a determination of the temperature profile from the mixing region outward.

The gases exiting the reactor were cooled rapidly in a heated transfer tube. They then passed through a heated particulates filter, composed of a removable 90 degree bend loosely packed with glass wool. The gas stream then entered the sampling manifold. There, the flow could be directed into any one of four sample bubblers. The bubblers, which contained a known amount of weakly acidified water, dissolved HBr and any unreacted bromine. They were kept cool with an ice water bath. To prevent HBr or bromine loss, a second bubbler was connected after each of the first bubblers.

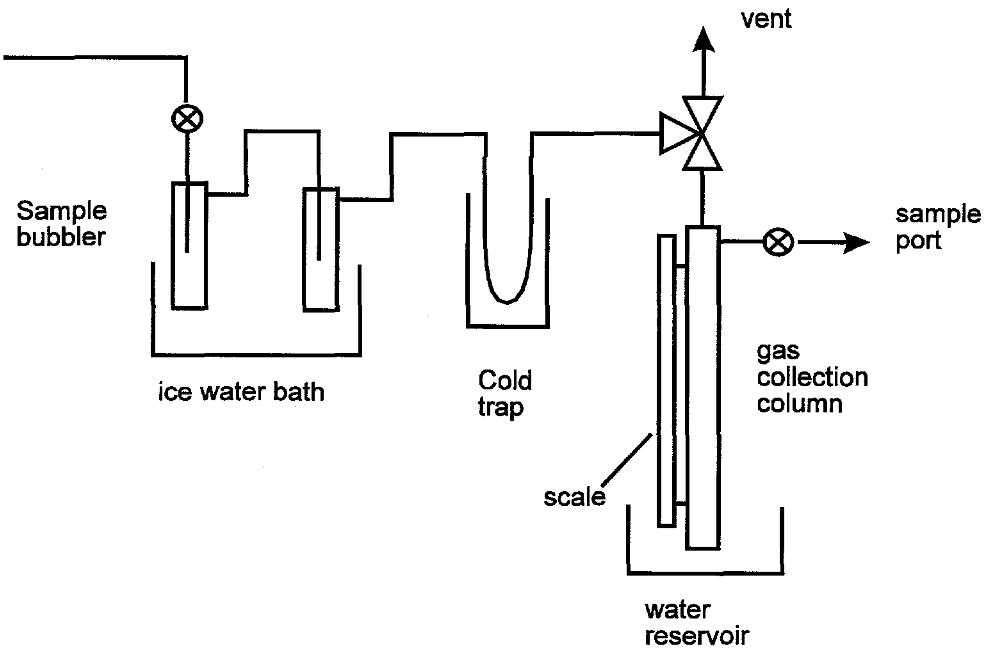

Figure 13 Sampling System

The gas stream exiting the second bubbler was assumed to contain only non-condensable gasses and water vapor. Four glass U-tubes were immersed in a dry ice-ethylene glycol slush (-25 °C) to remove water vapor. The hold-up volume of these cold traps was kept small (about 5 ml) to reduce the amount of air initially present in the gas sampling system. A check valve after each U-tube prevented back flow.

The gas stream then entered a gas collection column, initially filled with water, where it was trapped. The rate at which water was displaced from the collection column was measured. The flow rate of non-condensable gases exiting the reactor was determined using this method. Gas samples were withdrawn through a syringe port fitted before the collection column. The gas composition in the syringe was then related to the concentration of gases exiting the reactor by analysis with a GC.

Analytical methods.

Significant effort was expended by SRT personnel to improve an analytical technique for quantifying the compounds in the product reaction stream. The masses of the sample collection tubes were measured. Those containing black particulates were filtered. The aqueous solution density was determined. A spectrophotometric method using two wavelengths for determining the bromine concentration in aqueous solutions containing HBr was developed. The titration of HBr with NaOH was improved by using a derivative of the titration curve. Non-condensable gases were analyzed with a GC method.

Sample tube analysis. Liquid samples were collected in a primary and a secondary bubbler tube. The primary sample bubbler tubes usually contained carbon residue which passed through the heated transfer tube and filter after the reactor. Each primary bubbler was first weighed to yield a total mass of sample, which included the black residue. The sample was filtered through glass wool into a tared Erlenmeyer flask, yielding the aqueous sample mass. The secondary bubblers were also weighed after sampling. Since no carbon residue was present, this was the secondary bubbler sample mass. The bubbler solution density (primary and secondary) was determined for each sample using a 10 mL pycnometer (Ace Glass).

Primary bubblers contained aqueous Br_2, H_3O^+, and Br^-. The samples taken from the gas collection tube contained unpurged air, CO, CO_2, and unreacted CH_4, as well as water vapor. The secondary bubblers contained trace amounts of Br_2, H_3O^+, and Br^-.

Acid titration. Aliquots of 5.000 mL of each filtered primary bubbler solution were titrated using standardized 1 M NaOH as the titrant. An Orion Research Digital Ionalyzer (Model 801A) equipped with a Cole-Palmer combination glass pH electrode was used for this purpose. Titration curves of solutions of HBr, which contain aqueous Br2, exhibit two endpoints. The first endpoint is for HBr. Previous titration curves of pseudo-unknown solutions prepared with equivalent HBr concentrations but prepared both with and without bromine exhibited the same HBr endpoints. This indicated that it is possible to titrate for HBr in the presence of Br_2. Each primary bubbler solution was titrated in duplicate. Suitable calculations yielded the concentration of HBr in each primary sample bubbler. A derivative of titration curves allowed a more precise determination of the endpoint when bromine was present.

The pH of each secondary bubbler solution was likewise measured. It was typically between 3 and 4, making direct titration with concentrated base difficult. For these solutions, the concentration of the hydronium ion was approximated using the definition of pH: $pH = -\log[H_3O^+]$. The concentration of HBr in each secondary bubbler was found to be insignificant in comparison to the concentration present in its corresponding primary bubbler.

Bromine determination. A spectrophotometric method was employed to determine the total concentration of bromine in each bubbler solution. In the presence of bromide ion, bromine undergoes the following equilibrium reaction to form the tribromide ion:

$$Br_2 + Br^- \leftrightarrow Br_3^-, \quad K_{eq} = 16.8 \qquad \textbf{Equation 5}$$

Both Br_2 and Br_3^- absorb in the UV, their absorption spectra have been published (Raphael, 1988). Since both species absorb in the wavelength range 330 to 400 nm, a simultaneous equations method was used for quantitation.

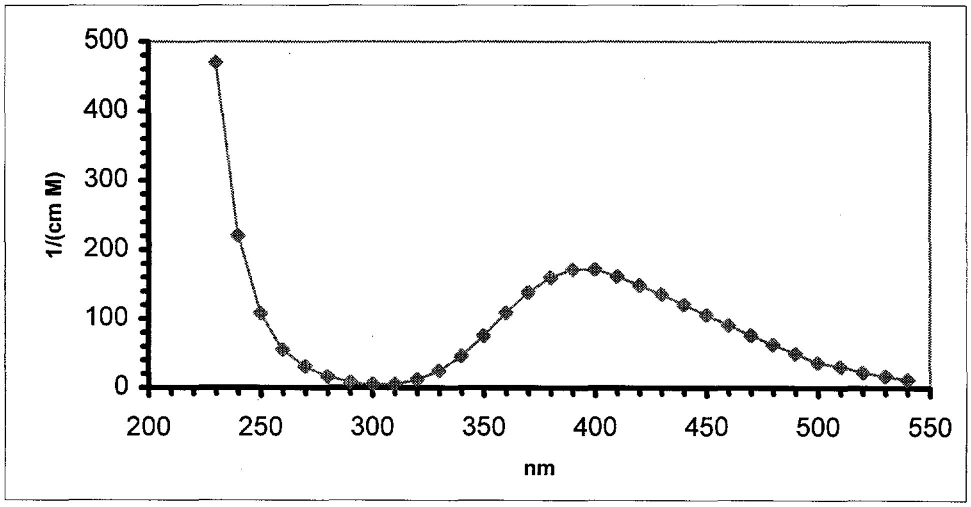

Figure 14a. Absorption spectrum of Br_2 in aqueous solution (Raphael, 1988).

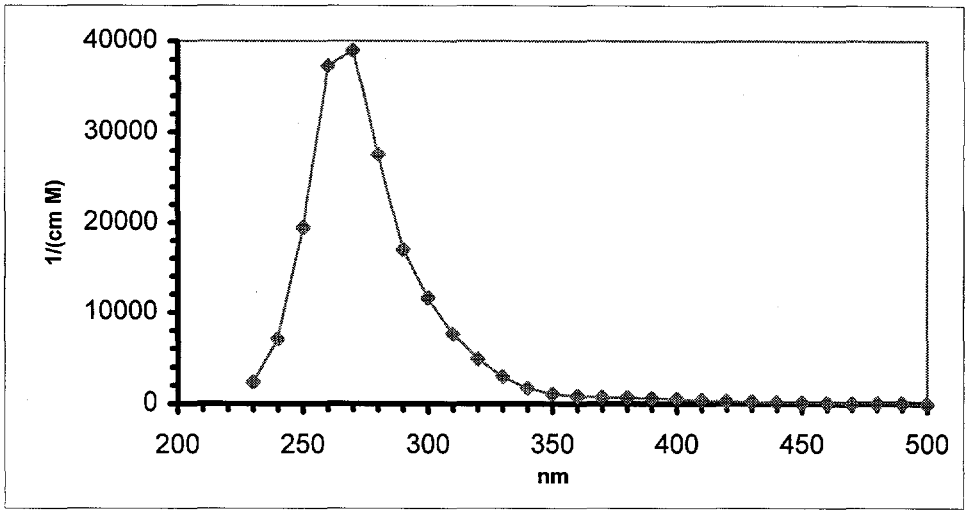

Figure 14b. Absorption spectrum of Br_3^- in solution (Raphael, 1988).

For any solution containing two absorbing species, both obeying Beer's law at two different wavelengths, their absorbances are additive. For species x and y at wavelengths 1 and 2:

$$A_{1,total} = A_{1,x} + A_{1,y} \qquad \text{Equation 6a}$$

$$A_{2,total} = A_{2,x} + A_{2,y}, \qquad \text{Equation 6b}$$

where $A_{i,j}$ is the absorbance at wavelength i for species j. According to Beer's law:

$$A = \varepsilon bC, \qquad \text{Equation 7}$$

where ε is the extinction coefficient, b the pathlength, and C the concentration. If b = 1 cm, the simultaneous equations reduce to:

$$A_1 = \varepsilon_{1,x}C_x + \varepsilon_{1,y}C_y \qquad \text{Equation 8a}$$

$$A_2 = \varepsilon_{2,x}C_x + \varepsilon_{2,y}C_y. \qquad \text{Equation 8b}$$

The published molar absorptivities (See Figure 14) for each species at 340 and 390 nm were then substituted into Equations 8a and 8b. A_1 and A_2 were measured, and two equations with two unknowns resulted. The total Br_2 concentration in solution was obtained by adding C_x and C_y.

Each primary bubbler solution was diluted using deionized water until reasonable total absorbance values were measured at the two wavelengths of interest. All absorbance measurements were made in quartz cuvettes using a Beckman DU spectrophotometer equipped with Gilford electronics. The light source was a tungsten lamp. The instrument was blanked at each wavelength using deionized water. It was calibrated weekly for lamp and electronic drift with a standard potassium dichromate solution.

The secondary bubbler solutions were analyzed for total bromine concentration by the same method. However, due to the low bromine concentrations, no dilution was necessary prior to absorbance measurements. The same method of simultaneous equations revealed that the total concentration of bromine in each secondary bubbler was negligible compared to the primary bubbler.

GC analysis. Gas chromatography was used to determine the concentrations of non-condensable gases collected in the gas collection tube, i.e.: air, CO, CH_4 and CO_2. The instrumental set-up consisted of a Tracor gas chromatograph (Model 550) fitted with a 1/8" stainless steel column of length 7.7 meters packed with silica gel (40/50 mesh). High-purity helium was used as the carrier gas with the flow rate set to 25 ml per minute at a column temperature of 80°C. The detector used for all measurements was a Gow-Mac Thermal Conductivity Detector cell (TCD) operated at a bridge current of 150 mA and a cell temperature of 215°C. Sample chromatograms were obtained via a chart recorder.

For adequate separation of these compounds, it was necessary to employ temperature programming. The temperature program consisted of initial isothermal elution at 80 °C for 12 minutes, then temperature ramping elution at 25°C per minute to 250°C. The column was then held at 250°C for several minutes. The air peak eluted first, followed by CO and CH_4; at higher temperature (250 °C) CO_2 eluted. There was no evidence for measurable amounts of organic compounds eluting from the column, unless they were under the other peaks, which is very unlikely. A typical plot is shown in Figure 15; note the relatively large CO and CO_2 peaks compared to the very small CH_4 peak.

Gas samples were withdrawn from the syringe port of the gas flow calibration tube (See Figure 13). SGE syringes (5 or 25 ml) with Teflon-coated plungers and valves behind the needle were used. If a 25 ml sample was withdrawn, the needle and valve assembly was replaced with a septum adapter. A 5 ml aliquot was then withdrawn with a 5 ml valved SGE syringe and injected into the GC. In this way, several replicate analytical runs could be performed.

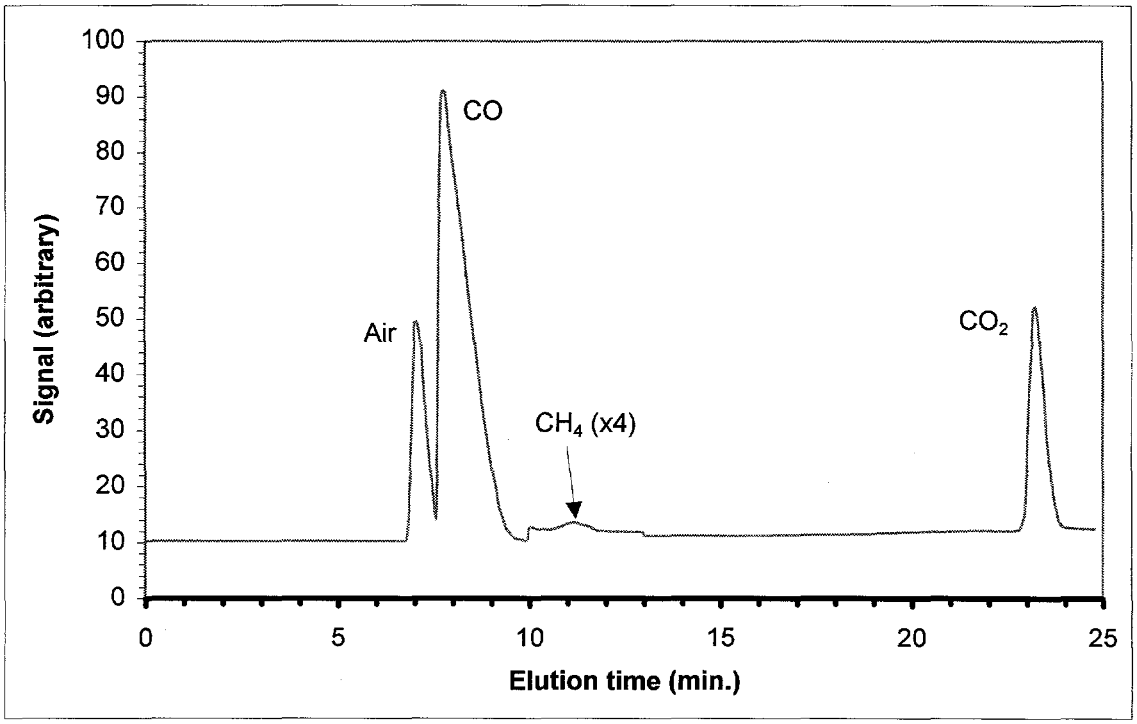

Figure 15. Typical GC elution plot (Sample G5); 5 ml gas injected.

Aliquots (5 ml) of gas from the gas collection tube were injected into the GC using this temperature program. The normalized area for each peak was calculated. Previously determined calibration plots of normalized peak area versus injected moles of gas yielded the number of moles of each gas in the unknown sample. This was then divided by the injected volume to calculate its concentration and mole fraction.

Gas flow analysis. During an experimental run, the reactor output was directed through the Bubbler pair #4, which was used in stand-by mode operation. The reactor was allowed to equilibrate for at least 5 minutes. The flow meter tube was filled with water to a predetermined mark near the top. The reactor flow was switched over to Bubbler pair #1 (Sample #1) for 3 - 4 minutes. When Sample #1 was collected, flow was switched over to Bubbler pair #2, then Bubbler pair #3.

The decrease in water level was measured as a function of time for 1 - 3 minutes. The total gas flow rate was calculated according to:

$$-dn/dt = (\pi r^2/RT)[p_{atm} - p_{H2O}(T) - \rho gz](dz/dt), \qquad \textbf{Equation 9}$$

where dn/dt is the molar flow rate, r the column radius, R the ideal gas constant, T the absolute temperature, p_{atm} laboratory barometric pressure, $p_{H2O}(T)$ the vapor pressure of water at T, ρ the density of water, g the acceleration due to gravity, z the column height, and dz/dt the rate of column movement. Sample flow rates were typically 50 cm^3/min and the total column volume was 700 ml.

Data analysis procedure.

Individual analytical measurements were processed in Excel spreadsheets. The results were then entered into a Microsoft Access data base developed by SRT. It allows one to edit the data and view it in a series of formats. A report summarizing the data, i.e. containing the reactant and measured product molar flow rates, was generated. The product yields were calculated as well.

Results and discussion.

Nine experimental runs at various temperatures and molar ratios have been completed to date. Eight are listed in Table 4; during Run E a reactor plug developed. Three (replicate) samples were collected each time, except in Run F (6 samples). However, only Runs D, F, G, and H proved satisfactory. In the earlier runs, problems with the gas flow measurement technique were being worked out.

Run	T (°C)	Total mole/min	CH_4 ratio	Br_2 ratio	H_2O ratio
A	650	0.1398	1.00	3.26	2.14
B	650	0.0975	1.00	2.19	0.93
C	800	0.0637	1.00	3.55	3.86
D	800	0.0659	1.00	4.02	4.18
F	800	0.0649	1.00	3.92	3.75
G	650	0.0580	1.00	2.92	3.81
H1	800	0.0602	0.00	1.00	1.19
H2	800	0.0678	1.00	3.67	4.36
I1	850	0.0560	0.00	1.00	1.56
I2	850	0.0627	1.00	3.27	5.09

Table 4. Bromine-Methane-Steam Run Conditions; H1 and I1 refer to runs without and H2 and I2 with methane, respectively.

The sampling time was noted and the liquid and gas samples processed as described in previous sections. The molar flow rates for the products and unreacted bromine and methane are shown in Tables 5a and 5b for Runs D, F, G, H, and I. The characteristic residence time was typically 1.0 sec. The unreacted water was not determined directly; it was inferred from the amount of CO and CO_2 produced.

The HBr production rates are the most constant of the data presented in Tables 5a and 5b with only a 5% variation within runs. *This is significantly better than the data obtained in the first experimental effort.* The variation in unreacted bromine is not strongly correlated with HBr, as would be expected if the inlet bromine flow varied significantly between samples. Due to the volatile nature of bromine, fluctuations in sampling pressure and variations in the analytical technique could account for some of this variability. The amount of unreacted CH_4 exiting the reactor in runs D, F, H, and I was almost negligible compared to that entering, typically 0.006 mol/min. The ratio of CO_2:CO produced was about 1:10. The consistency within runs points to the great improvements made in SRT's gas sampling method. It is interesting to note in Run G (650 °C) that the amount of unreacted CH_4 was greater than in D and F. The ratio of CO2:CO was 1:4. This ratio will undoubtedly shed some light on the reaction mechanism of bromine with steam and carbon as more data is collected.

Sample	HBr (mol/min)	Br_2 (mol/min)	CH_4 (mole/min)	CO_2 (mole/min)	CO (mole/min)
D1	0.0352	0.0062	7.15E-05	2.54E-04	2.275E-03
D2	0.0320	0.0049	2.31E-05	2.29E-04	2.051E-03
D3	0.0338	0.0044	4.91E-05	2.56E-04	2.418E-03
F1	0.0291	0.0091	1.23E-05	5.36E-04	4.981E-04
F2	0.0305	0.0094	8.88E-07	2.65E-04	2.292E-03
F3	0.0296	0.0108	0.00	2.86E-04	2.639E-03
F5	0.0318	0.0160	2.49E-06	2.49E-04	2.205E-03
F6	0.0293	0.0075	4.08E-06	5.43E-05	1.998E-03
F7	0.0318	0.0072	0.00	2.15E-04	2.212E-03
G1	0.0222	0.0046	5.40E-04	1.88E-04	6.474E-04
G2	0.0225	0.0050	6.12E-04	2.28E-04	8.073E-04
G3	0.0239	0.0041	5.70E-04	1.82E-04	6.753E-04

Table 5a. Molar flow rates for Runs D, F, and G.

Sample	HBr (mol/min)	Br_2 (mol/min)	CH_4 (mole/min)	CO_2 (mole/min)	CO (mole/min)
H1	4.86E-04	0.0287	0.00	0.00	0.00
H2	6.67E-04	0.0305	0.00	0.00	0.00
H3	5.86E-04	0.0280	0.00	0.00	0.00
H4	0.0305	0.0094	2.37E-04	2.50E-04	2.060E-03
H5	0.0332	0.0047	9.04E-05	2.64E-04	2.737E-03
H6	0.0380	0.0095	0.00	3.43E-04	3.350E-03
I1	8.2E-04	0.0198	0.00	0.00	0.00
I2	2.10E-03	0.0130	0.00	0.00	0.00
I3	7.8E-04	0.0105	0.00	0.00	0.00
I4	0.0308	0.0136	6.95E-05	3.18E-04	2.001E-03
I5	0.0320	0.0052	7.62E-05	3.69E-04	3.318E-03
I6	0.0278	0.0019	8.65E-05	2.13E-04	2.647E-03

Table 5b. Molar flow rates for Runs H and I.

The reaction conversions for CH_4, Br_2, and H_2O are shown in Table 6. For CH_4, it was calculated as follows:

$$Y_{CH4} = (n_{CH4,in} - n_{CH4,out})/ n_{CH4,in}, \qquad \textbf{Equation 10}$$

where Y is the conversion, and n are the molar flow rates. Due to the potential inaccuracy of the bromine input flow rate, the conversion reported here was based on the sum of HBr and unreacted Br_2 determined in each sample:

$$Y_{Br2} = n_{HBr}/(n_{HBr} + 2n_{Br2,out}). \qquad \textbf{Equation 11}$$

The conversion of water to HBr was inferred from the amount of CO and CO_2 produced. It was calculated as follows:

$$Y_{H2O} = (n_{CO} + 2n_{CO2})/n_{H2O,in}. \qquad \textbf{Equation 12a}$$

For the samples in Runs H and I without methane, the water conversion was calculated as:

$$Y_{H2O} = n_{HBr}/(2n_{H2O,in}). \qquad \textbf{Equation 12b}$$

In the previous three equations, the formation of organic by-products containing C, H, Br, and O atoms is assumed to be negligible.

Sample	**%Conv. CH_4**	**%Conv. Br_2**	**%Conv. H_2O**
D1	99.0	73.9	9.30
D2	99.7	76.6	8.38
D3	99.3	79.3	9.78
Run D Average	**99.33**	**76.60**	**9.15**
F1	99.8	61.5	5.59
F2	100.0	61.9	10.06
F3	100.0	57.8	11.45
F5	100.0	49.8	9.63
F6	99.9	66.1	7.51
F7	100.0	68.8	9.41
Run F Average	**99.97**	**61.57**	**8.85**
G1	92.8	70.7	3.58
G2	91.8	69.2	4.41
G3	92.4	74.5	3.63
Run G Average	**92.33**	**71.47**	**3.87**

Table 6a. Reaction conversions for Runs D, F, and G.

Sample	%Conv. CH_4	%Conv. Br_2	%Conv. H_2O
H1	0.00	0.84	0.74
H2	0.00	1.08	1.02
H3	0.00	1.04	0.90
Run H1 Average	**0.00**	**0.99**	**0.89**
H4	96.8	62.0	7.83
H5	98.8	77.9	9.98
H6	100.0	66.7	12.3
Run H2 Average	**98.53**	**68.87**	**10.04**
I1	0.00	2.03	1.20
I2	0.00	7.47	0.31
I3	0.00	3.58	1.14
Run I1 Average	**0.00**	**4.36**	**0.88**
I4	99.0	53.1	7.73
I5	98.9	75.4	11.9
I6	98.7	88.0	9.01
Run I2 Average	**98.87**	**72.17**	**9.55**

Table 6b. Reaction conversions for Runs H and I.

The 98 - 100% conversion for CH_4 and approximately 75% for Br_2 at 800 - 850 °C in Tables 6a and 6b is very encouraging. The 10% conversions for H_2O will need to be increased so that little unreacted carbonaceous material remains in the reactor. If it is difficult to react most of the carbon with bromine and steam, the methane stream may be pulsed. In Run G at 650 °C, the methane conversion was lower (only 92%), while the bromine conversion was about the same as before. Not surprisingly, the water conversion was lower (4%). The incomplete methane conversion to product may be reflected in some organic bromine compounds not converted to HBr and C.

Thermochemical Predictions. Predicted reaction conversions for runs D, F, G, H1, H2, I1, and I2 were calculated using a thermochemical equilibrium program[1]. This program operates by minimizing the Gibbs free energy for a system of reaction products, given the starting molar concentrations of the reactants and the temperature and pressure of the reaction. The reaction

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[1] EQS for Windows, Ver 1.1.6, Mathtrek Systems

conversions are given in Table 7, and the complete product decks from the simulations are shown in Appendix 1.

Run	T (oC)	Predicted CH_4 conversion	Predicted Br_2 conversion	Predicted H_2O conversion
D	800	100.00%	99.47%	47.81%
F	800	100.00%	99.97%	52.60%
G	650	99.97%	100.00%	47.75%
H1	800	N/A	5.10%	3.51%
H2	800	100.00%	99.99%	43.93%
I1	850	N/A	7.89%	4.01%
I2	850	100.00%	100.00%	36.15%

Table 7 Conversion Rates Predicted From Thermochemistry

It is important to note that the predicted conversion rates for water in table 7 are not 100% because water was in excess of the stoichiometric amount for these reactions. Thermochemical equilibrium predictions are based on an assumption that the reaction kinetics are infinitely fast, or that the reaction has had an infinite amount of time to come to equilibrium at the (isothermal) temperature and (isobaric) pressure conditions. As reactions in the real world are not infinitely fast or have infinite residence times in the reactor, in most cases the real world reaction conversions will be lower than corresponding thermochemical predictions. Nonetheless, it is instructive to rank the actual conversions against the thermochemical predictions to arrive at a measure of the reaction efficiency in terms of percent of theoretical conversion. This efficiency is presented in Table 8.

Run	T (oC)	CH_4 conversion	Br_2 conversion	H_2O conversion
D	800	99.33%	77.01%	19.95%
F	800	99.97%	61.59%	16.82%
G	650	92.42%	74.50%	7.60%
H1	800	N/A	19.34%	25.29%
H2	800	98.53%	68.87%	22.85%
I1	850	N/A	55.28%	22.02%
I2	850	98.87%	72.17%	26.41%

Table 8 Actual Reaction Efficiency In Terms of Percent of Theoretical Conversion

The data in table 8 indicate that the reaction mixtures have not reached equilibrium. In particular, water conversions are low, which leads to lower bromine conversions. This indicates that a longer residence time would probable improve the overall conversion rates.

Mole balance. Since carbon and unreacted water were not quantified in SRT's current analytical technique, only a mole balance of Br_2 could realistically be undertaken. The moles of bromine flowing into the reactor were typically greater than those exiting as HBr and unreacted bromine (See Tables 9a and 9b). It is unlikely that such a large discrepancy (-10 to -30%) was due to bromine loss as a vapor or in the form of organic products. A decrease in the bromine flow is a more plausible cause.

Recall that the inlet flow rate was measured in a calibration condensor *before* samples were collected. It was assumed not to change when bromine was flowed into the reactor with methane and steam. While testing SRT's nominal 10 kW reactor at NREL's High Flux Solar Furnace, a similar version of the bromine delivery system was used. The bromine flow rate in the calibration condenser was usually higher than that measured from the change in load cell mass as a function of time. The latter corresponded to bromine and steam flowing together through the reactor.

This emphasizes the importance of holding the bromine flow rate through control valve CV2 constant with active feedback from the differential pressure transmitter (See Figure 8). Otherwise, the value measured in the calibration leg will be significantly different than that during an experiment. If this method proves unsatisfactory, then the mass change in the bromine reservoir must be measured during experimental runs. A smaller and lighter intermediate holding tank with a more precise load cell would be required.

Sample	% Change Br_2	% Change H_2	% Change C
D1	-17.4	+1.3	-63.8
D2	-27.4	-1.9	-68.0
D3	-26.0	-0.8	-62.2
F1	-19.6	-4.6	-86.0
F2	-16.2	-6.0	-65.9
F3	-12.9	-7.9	-61.0
F5	+ 8.5	-4.2	-67.2
F6	-24.7	-5.7	-72.6
F7	-21.4	-4.0	-67.7
G1	-28.3	-8.8	-81.7
G2	-25.8	-8.7	-78.0
G3	-26.7	-6.8	-81.0

Table 9a. Preliminary mole balance for Runs D, F, and G.

Sample	% Change Br_2	% Change H_2	% Change C
H1	+5.1		0.00
H2	+12.0		0.00
H3	+2.9		0.00
H4	-10.2	-3.9	-66.0
H5	-22.5	-3.1	-58.8
H6	+3.6	-0.1	-50.8
I1	-7.8		0.00
I2	-35.6		0.00
I3	-50.2		0.00
I4	+32.4	-1.0	-64.4
I5	-3.2	-2.7	-43.8
I6	-27.9	-5.1	-56.0

Table 9b. Preliminary mole balance for Runs H and I.

A check on the moles of hydrogen flowing into (as CH_4 and H_2O) and out of (as unreacted CH_4, unreacted H_2O, and HBr) the reactor was done. Here, it was assumed that the moles of water reacted equalled the moles of CO plus twice the moles of CO_2 produced. If the moles of CO and CO_2 result in additional HBr, then this should be reflected in the mass balance. According to Tables 7a and 7b, this was indeed the case. In Run D, the mole balance agrees to within 2%, while in Runs F, G, H, and I it was greater. There may have been a small change in the steam or methane flow rate during the course of those experiments.

The mole balance for carbon is only meant to be instructive. Much was retained in the reactor and the transfer line leading to the bubbler tubes. The rest was filtered out from the samples. The percentage was surprisingly consistent, between -60 and -80%.

Reaction mechanism. Based on experimental observations, SRT believes the methane-bromine-steam reaction occurs as a sequence of sub-reactions. First, bromine reacts with methane to yield a large distribution of brominated hydrocarbons. At high enough temperatures, most of them are pyrolyzed. The role of water in this process is not understood at this time. If one assumes 100% pyrolysis, the net reaction is, under ideal conditions:

$$CH_4 + 2\,Br_2 \rightarrow\rightarrow C + 4\,HBr \qquad \textbf{Equation 13}$$

The carbon deposited in the reactor can then react with steam to produce CO and CO_2:

$$C + H_2O \rightarrow CO + H_2 \qquad \textbf{Equation 14}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \textbf{Equation 15}$$

If excess bromine is present, the hydrogen of Equations 14 and 15 is converted to HBr via Equation 17. If CO_2 is indeed produced from CO via Equation 15, and 15 proceeds to a lesser extent than Equation 14, then the CO:CO_2 molar ratio of 10 observed at 800 °C can be explained. Thermodynamically, Equation 14 is slightly endothermic at 800 °C (21 kJ/mol), while Equation 15 is slightly exothermic (-9.6 kJ/mol). The kinetics of the second reaction may be slower, however.

Another reaction that produces H_2 is of course steam-methane reforming:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad \textbf{Equation 16}$$

When just methane and steam were passed through the clean reactor at 800 °C, essentially no methane was reacted. Industrial steam methane reforming units use nickel catalysts and operate at 750 °C and up to 500 psi. Such high pressures are not favorable for product equilibrium, but are necessary for making the downstream CO separation and heat recovery economical. The lack of appreciable methane reforming in SRT's reactor, which lacks a catalyst, is thus not surprising.

One can appreciate that the H_2 formed in Equations 14 - 16 reacts almost immediately with unreacted bromine:

$$H_2 + Br_2 \rightarrow 2\,HBr \qquad \textbf{Equation 17}$$

If this scenario is correct, then it might be advantageous to direct UV light onto the reactor to promote Br radical reactions in the formation of HBr.

The result of Equations 13 through 17 would be a mixture of CO, CO_2, HBr, C, and unreacted H_2O and Br_2. This is indeed observed in experiments. However, there are also small amounts of organic compounds produced.

There is another possible reaction contribution. Based on previous SRT research, the reaction between bromine and steam yields increasingly larger amounts of oxygen at temperatures above about 750 °C:

$$2\,H_2O + 2\,Br_2 \rightarrow 4\,HBr + O_2 \qquad \textbf{Equation 18}$$

This oxygen will oxidize the carbon from Equation 13:

$$2\,C + O_2 \rightarrow 2\,CO \qquad \textbf{Equation 19}$$

$$C + O_2 \rightarrow CO_2. \qquad \textbf{Equation 20}$$

The extent of the contribution of this reaction pathway is probably quite small, since Equations 13 + 14 and 15 are probably more kinetically favored.

This rather simplistic treatment of sequential reactions probably does not accurately describe the actual process. There may be reactions in which steam directly reacts with brominated organic intermediates during pyrolysis. However, it points out that research into the reaction between carbon, steam, and bromine must be undertaken in the very near future.

Conclusions and recommendations. The data from these first few runs with the new reactor and apparatus are very encouraging. The data within experimental runs have been very reproducible. At 800 °C, 100% CH_4 and 75% Br_2 were converted to HBr. At 650 °C, 92% CH_4 was converted. However, the amount of H_2O converted was much lower: 10% at 800 °C and 4% at 650 °C. This value needs to be increased in future work. Since water was in excess compared to CH_4, this represents a significant amount of unreacted carbonaceous material in the reactor.

The formation of carbon deposits in the reactor points out the need for research into reactor design. In particular, larger surface areas and longer residence times are in order. Pulsed methane delivery is another interesting avenue of investigation. This would allow carbon deposits to build up for a brief period of time, then be removed in the reaction with bromine and steam. An understanding of the reaction between bromine, steam, and carbon is required. The conditions for fast reaction need to be understood as well as the dependence of the $CO:CO_2$ ratio on feed conditions and temperature.

A preliminary molar balance of reactant and product flow rates shows that a significant amount of bromine cannot be accounted for. This is most likely due to a change in bromine flow rate when steam and methane are admixed. A better control of the bromine flow rate is required, or a means for measuring the mass delivered in real-time. Analytical methods for determining the amounts of unreacted water, carbon, and organic compounds in the product stream need to be developed for a complete reactor mass balance.

III. Recommended Further Work

The research program proposed for 1998 includes a series of ambitious reactor scale up tests. The test-bed apparatus will require minor up-grades. Sample analytical methods need to be improved so that a better reactor mass balance is obtained. Unreacted water and carbonaceous material need to be measured. The organic by-products formed need to be quantified. Given the large amount of data generated in extensive testing, data processing will have to be streamlined as well.

Testing in 1997 has raised several important questions that must be answered *before* an extensive experimental effort is undertaken to elucidate optimum reactor design/operation. An amount of carbonaceous material deposits on reactor walls during operation. If it can be reacted with steam and bromine in an efficient manner, more HBr will be produced. **Alternatively, if water is removed from the reaction mix, HBr can be generated without concomitant CO_2 generation, which could be important as a means of alleviating greenhouse gas release during hydrogen production.** A modified reactor with increased surface area and residence time will be tested under a range of operating conditions. Pulsed methane delivery will also be investigated.

An extensive statistical design experiment will yield a response surface. This will show the best point for reactor operation based on that data set. It will also show where more data needs to be collected. Further questions will be addressed in additional experiments. For example, the reaction of carbon with steam and bromine needs to be understood. The effect of surface area and pressure should also be important.

Apparatus Up-Grades

Minor modifications to the research set-up will be made to allow for improved sampling and precision. The sampling system may need some modifications to reduce the air hold-up and to accommodate smaller samples.

Analytical Improvements

The present analytical methods for determining HBr, Br_2, CO_2, CO, and CH_4 are satisfactory. However, H_2O in the product mixture needs to be determined independently to improve confidence in the mass balance. At present, it is assumed that the water consumed only produces CO and CO_2. Some of it could also form organic by-products. The amount of water will most likely be determined by a very careful mass balance.

Larger amounts of samples could be collected in an evacuated cold trap, allowed to warm up, and then will be separated, and analyzed. The gas in the head space will be amenable to GC-MS analysis. The amount and nature of organic constituents will be qualitatively determined.

SRT has not attempted to quantify the amount of carbon produced in the reactor. This results in a significant gap in the mass balance. One way of measuring it is with a clever reactor + sampling design. Possibly two reactors would be run in parallel in the same tube furnace, one of which is in "stand-by" mode, while the other is only used once. The total mass change in the latter is recorded and the carbon material rinsed, washed, dried, and weighed. Or it could be burned off with O_2, and the amount of CO_2 produced determined.

The organic content of the carbonaceous material and the aqueous sample phases needs to be estimated. They will be extracted with suitable solvents (e.g., methylene chloride, petroleum ether, methanol, ethanol, and pentane) and subjected to GC-MS analysis. They will be quantified in a series of procedures for organic compounds. The total amount of organic compounds generated may be needed in future work.

Data Analysis Streamlining

Sample analysis has been the bottleneck in SRT's work on this project. Improvements have steadily been made over prior methods. However, given the large number of samples to be collected, further improvements are necessary. The present analytical apparatus is not automated and is tedious to operate. Several pieces of equipment, such as a GC and a UV-VIS spectrometer, have been budgeted. A HP data logger will be purchased for collecting reactor temperatures and other process values. These pieces of equipment will be cost-effective as they will reduce analysis time required and will increase analyst productivity.

Exploratory Experiments

Before an extensive scale up testing program is undertaken, one or two different reactor designs will be evaluated. Since carbonaceous material is deposited in the reactor during testing, SRT needs to improve its conversion to HBr when bromine and steam are passed over it. Reactors with increased surface area and/or characteristic residence times will be required. They will be evaluated over a range of operating conditions.

The first design involves quartz tubes with a known surface area that are fused into the reactor. This will provide a larger surface area for steam and bromine to react with the carbonaceous material that deposits in the reactor. The residence time can be increased with a larger reactor volume. The relative surface area should be held constant, if two reactors are compared. Only slight changes in the apparatus are anticipated.

Further Reactor Testing

In further reactor tests, the optimal reactor design identified in exploratory work will be used. Three process variables (reactor temperature, $H_2O:CH_4$, and $Br_2:CH_4$) will be studied in a systematic fashion. Temperatures will range from 600 to 1000 °C, with $H_2O:CH_4$ between 1.0 to 5.0 and $Br_2:CH_4$ between 1.0 and 6.0.

The data will be evaluated and a response surface generated. It should then be possible to predict where optimal reactor operating points could lie. Further experiments at outlying or intermediate values will confirm this. Additionally, a more detailed economic model will provide valuable feedback/constraints.

The "optimal" operation point may involve more than several compromises, some of which will be dictated by economics. A large percentage conversion of bromine and methane to HBr will be important. Likewise, the amount of carbon and organic by-products produced should be minimized. It is anticipated that higher $H_2O:CH_4$ ratios (running with excess steam) will reduce carbon reactor deposits, as is done in steam methane reforming.

Approach to Scale-Up

In anticipation of integration with electrolysis, SRT will test an Electrosynthesis lab-scale electrolyzer. The effect of bromine concentration on the electrochemical potential will be measured. Its operation will be compared to that specified by the manufacturer and predicted by electrochemistry. In an industrial process, solid particulates containing carbon can be filtered. However, if water-soluble organics are formed, they could affect electrolyzer operation. This is unlikely, but needs to be verified. A larger test electrolyzer (ca. 1 ft^2 stack) supplied by a suitable vendor will be integrated with an SRT reactor and tested by DIT in a subcontract.

IV. Conclusions

An alternative to SRT's former hydrogen generating concept, in which Br_2 and H_2O react at high temperatures to yield HBr, involves the addition of a carbon source. This makes the reaction quite exothermic. SRT has chosen methane as a gaseous source of carbon and hydrogen. Preliminary research has shown that the reaction proceeds at favorable rates at 700 - 900 °C. The beauty of the reaction with methane is the production of only a minimal amount of reaction by-products/waste if the system can be fully optimized. Other sources of carbon, such as coal and biomass, would result in more ash residues, translating into a greater waste disposal problem.

Improved operation was experienced with increased reactor surface area, longer residence time, proper reactant molar ratios, and sufficient heat transfer area. HBr concentrations of 11 - 13 M, well above those of the commercially available HBr azeotrope (9M), were produced in a first series of tests.

In order to better characterize the reaction, an improved flow delivery system, reactor, sampling system, and sample analytical scheme were designed and implemented. The data show that at 800 °C, conversion of methane and bromine to HBr was about 99% and 75%, respectively. The conversion of water to HBr was much less, only about 10%. This value will be increased if more water reacts with the carbonaceous material deposited in the reactor.

A goal will be to decrease carbonaceous reactor deposits with corresponding increase in water conversion to HBr, or alternatively operating the system to produce solid carbon only, without production of CO_2.

In parallel with the reactor scale up program, SRT will study aqueous phase electrolysis of HBr. The technology is fairly mature, and in consultation with vendors, existing PEM based cells will be used with minor modification. This represents an integrated approach toward developing a viable near-term hydrogen production process, with energy storage to be added in 1999. The hydrogen production process also holds promise for being competitive with small-scale steam methane reforming (~$9/MMBTU). This effort is an important step forward in the U.S. realization of energy self-sufficiency and clean fuel technology, with implications for our balance of trade.

V. References

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APPENDIX 1

Thermochemical Equilibrium Reaction Simulations

Run D

Temperature (C):
800.
Pressure (bar): 1.

Species	Moles	Mole Fraction	μ (kJ/mol)
Br(g)	4.51E-05	5.62E-04	-2.80E+01
BrH(g)	5.72E-02	7.13E-01	-6.44E+01
Br2(g)	1.53E-04	1.91E-03	-5.60E+01
C(g)	3.53E-36	4.40E-35	-1.57E+02
CBr(g)	2.86E-29	3.56E-28	-1.85E+02
CBr4(g)	3.14E-21	3.91E-20	-2.69E+02
CH(g)	2.90E-34	3.62E-33	-1.93E+02
CHO(g)	3.47E-17	4.32E-16	-3.24E+02
CH2(g)	5.87E-29	7.31E-28	-2.30E+02
CH2O(g)	3.47E-15	4.33E-14	-3.60E+02
CH3(g)	1.26E-22	1.57E-21	-2.66E+02
CH4(g)	7.12E-18	8.88E-17	-3.02E+02
CO(g)	9.74E-06	1.21E-04	-2.87E+02
CO2(g)	7.15E-03	8.91E-02	-4.18E+02
H(g)	1.92E-11	2.39E-10	-3.64E+01
HO(g)	5.06E-11	6.31E-10	-1.67E+02
HO2(g)	9.94E-19	1.24E-17	-2.97E+02
H2(g)	2.32E-05	2.89E-04	-7.28E+01
H2O(g)	1.56E-02	1.95E-01	-2.03E+02
H2O2(g)	4.67E-17	5.82E-16	-3.34E+02
O(g)	4.54E-17	5.66E-16	-1.30E+02
O2(g)	1.64E-14	2.05E-13	-2.61E+02
O3(g)	2.09E-31	2.61E-30	-3.91E+02
C(p,s)	0.00E+00	0.00E+00	0.00E+00
C(p,s)	0.00E+00	0.00E+00	6.30E+00

Total
Moles:
Gas: 8.0248564E-02

Run F

Temperature (C):
800.
Pressure (bar): 1.

Species	Moles	Mole Fraction	μ (kJ/mol)
Br(g)	1.10E-05	1.37E-04	-4.06E+0
BrH(g)	5.87E-02	7.34E-01	-6.41E+0
Br2(g)	9.10E-06	1.14E-04	-8.11E+0
C(g)	1.55E-33	1.94E-32	-1.02E+0
CBr(g)	3.07E-27	3.84E-26	-1.43E+0
CBr4(g)	4.91E-21	6.14E-20	-2.65E+0
CH(g)	5.37E-31	6.72E-30	-1.26E+0
CHO(g)	3.09E-15	3.87E-14	-2.84E+0
CH2(g)	4.58E-25	5.73E-24	-1.50E+0
CH2O(g)	1.31E-12	1.63E-11	-3.07E+0
CH3(g)	4.14E-18	5.18E-17	-1.73E+0
CH4(g)	9.88E-13	1.24E-11	-1.97E+0
CO(g)	2.06E-04	2.58E-03	-2.60E+0
CO2(g)	7.28E-03	9.11E-02	-4.17E+0
H(g)	8.04E-11	1.01E-09	-2.36E+0
HO(g)	1.02E-11	1.28E-10	-1.81E+0
HO2(g)	9.66E-21	1.21E-19	-3.39E+0
H2(g)	4.10E-04	5.13E-03	-4.72E+0
H2O(g)	1.33E-02	1.67E-01	-2.05E+0
H2O2(g)	1.91E-18	2.40E-17	-3.62E+0
O(g)	2.17E-18	2.72E-17	-1.57E+0
O2(g)	3.79E-17	4.74E-16	-3.15E+0
O3(g)	2.32E-35	2.91E-34	-4.72E+0
C(p,s)	0.00E+00	0.00E+00	0.00E+0
C(p,s)	0.00E+00	0.00E+00	6.30E+0

Total
Moles:
Gas: 7.9877488E-02

Run G

Temperature (C):
650.
Pressure (bar): 1.

Inert
Moles:
Gas: 0.0000000E+00

Species	Moles	Mole Fraction	μ (kJ/mol)
Br(g)	1.21E-07	1.66E-06	-5.51E+01
BrH(g)	4.38E-02	6.00E-01	-6.43E+01
Br2(g)	4.32E-08	5.91E-07	-1.10E+02
C(g)	3.62E-36	4.96E-35	-3.34E+01
CBr(g)	3.02E-29	4.13E-28	-8.85E+01
CBr4(g)	1.63E-22	2.24E-21	-2.54E+02
CH(g)	5.30E-32	7.26E-31	-4.26E+01
CHO(g)	5.48E-15	7.51E-14	-2.33E+02
CH2(g)	8.98E-24	1.23E-22	-5.18E+01
CH2O(g)	1.95E-10	2.68E-09	-2.42E+02
CH3(g)	2.96E-14	4.05E-13	-6.10E+01
CH4(g)	1.88E-06	2.57E-05	-7.02E+01
CO(g)	1.35E-03	1.85E-02	-2.24E+02
CO2(g)	6.15E-03	8.42E-02	-4.15E+02
H(g)	5.45E-12	7.47E-11	-9.19E+00
HO(g)	1.48E-14	2.02E-13	-2.00E+02
HO2(g)	2.15E-26	2.94E-25	-3.91E+02
H2(g)	6.74E-03	9.24E-02	-1.84E+01
H2O(g)	1.49E-02	2.05E-01	-2.09E+02
H2O2(g)	2.27E-22	3.12E-21	-4.00E+02
O(g)	1.49E-23	2.04E-22	-1.91E+02
O2(g)	1.94E-23	2.65E-22	-3.81E+02
O3(g)	0.00E+00	0.00E+00	-5.72E+02
C(p,s)	0.00E+00	0.00E+00	0.00E+00
C(p,s)	0.00E+00	0.00E+00	5.62E+00

Total
Moles:
Gas: 7.3001303E-02
Run H2

Run H1

Temperature (C):
800.
Pressure (bar): 1.

Inert
Moles:
Gas: 0.0000000E+00

Species	Moles	Mole Fraction	μ (kJ/mol)
Br(g)	5.13E-04	8.41E-03	-3.85E+00
BrH(g)	2.29E-03	3.76E-02	-9.07E+01
Br2(g)	2.61E-02	4.27E-01	-7.70E+00
C(g)	0.00E+00	0.00E+00	2.22E+22
CBr(g)	0.00E+00	0.00E+00	2.22E+22
CBr4(g)	0.00E+00	0.00E+00	2.22E+22
CH(g)	0.00E+00	0.00E+00	2.22E+22
CHO(g)	0.00E+00	0.00E+00	2.22E+22
CH2(g)	0.00E+00	0.00E+00	2.22E+22
CH2O(g)	0.00E+00	0.00E+00	2.22E+22
CH3(g)	0.00E+00	0.00E+00	2.22E+22
CH4(g)	0.00E+00	0.00E+00	2.22E+22
CO(g)	0.00E+00	0.00E+00	2.22E+22
CO2(g)	0.00E+00	0.00E+00	2.22E+22
H(g)	5.13E-14	8.41E-13	-8.68E+01
HO(g)	2.90E-08	4.76E-07	-1.08E+02
HO2(g)	1.22E-10	2.00E-09	-1.29E+02
H2(g)	2.18E-10	3.58E-09	-1.74E+02
H2O(g)	3.16E-02	5.17E-01	-1.95E+02
H2O2(g)	2.02E-11	3.31E-10	-2.15E+02
O(g)	7.39E-12	1.21E-10	-2.09E+01
O2(g)	5.73E-04	9.39E-03	-4.18E+01
O3(g)	1.56E-15	2.56E-14	-6.27E+01
C(p,s)	0.00E+00	0.00E+00	2.22E+22
C(p,s)	0.00E+00	0.00E+00	2.22E+22

Total
Moles:
Gas: 6.1029833E-02
Run I1

Temperature (C):
800.
Pressure (bar): 1.

Inert
Moles:
Gas: 0.0000000E+00

Species	Moles	Mole Fraction	μ (kJ/mol)
Br(g)	4.94E-06	5.97E-05	-4.80E+01
BrH(g)	5.51E-02	6.65E-01	-6.50E+01
Br2(g)	1.78E-06	2.15E-05	-9.60E+01
C(g)	1.56E-32	1.89E-31	-8.22E+01
CBr(g)	1.34E-26	1.62E-25	-1.30E+02
CBr4(g)	1.76E-21	2.13E-20	-2.74E+02
CH(g)	1.13E-29	1.36E-28	-9.92E+01
CHO(g)	1.99E-14	2.40E-13	-2.67E+02
CH2(g)	2.01E-23	2.42E-22	-1.16E+02
CH2O(g)	1.75E-11	2.11E-10	-2.84E+02
CH3(g)	3.78E-16	4.56E-15	-1.33E+02
CH4(g)	1.88E-10	2.27E-09	-1.50E+02
CO(g)	6.35E-04	7.67E-03	-2.50E+02
CO2(g)	6.87E-03	8.30E-02	-4.18E+02
H(g)	1.74E-10	2.10E-09	-1.70E+01
HO(g)	6.76E-12	8.17E-11	-1.85E+02
HO2(g)	1.96E-21	2.36E-20	-3.53E+02
H2(g)	1.85E-03	2.23E-02	-3.41E+01
H2O(g)	1.84E-02	2.22E-01	-2.02E+02
H2O2(g)	8.08E-19	9.76E-18	-3.70E+02
O(g)	6.90E-19	8.33E-18	-1.68E+02
O2(g)	3.68E-18	4.45E-17	-3.36E+02
O3(g)	6.91E-37	8.34E-36	-5.04E+02
C(p,s)	0.00E+00	0.00E+00	0.00E+00
C(p,s)	0.00E+00	0.00E+00	6.30E+00

Total
Moles:
Gas: 8.2817473E-02
Run I2

Temperature (C):
850.
Pressure (bar): 1.

Inert
Moles:
Gas: 0.0000000E+00

Species	Moles	Mole Fraction	μ (kJ/mol)
Br(g)	7.12E-04	1.25E-02	-4.92E+00
BrH(g)	2.74E-03	4.80E-02	-9.01E+01
Br2(g)	2.01E-02	3.53E-01	-9.84E+00
C(g)	0.00E+00	0.00E+00	2.22E+22
CBr(g)	0.00E+00	0.00E+00	2.22E+22
CBr4(g)	0.00E+00	0.00E+00	2.22E+22
CH(g)	0.00E+00	0.00E+00	2.22E+22
CHO(g)	0.00E+00	0.00E+00	2.22E+22
CH2(g)	0.00E+00	0.00E+00	2.22E+22
CH2O(g)	0.00E+00	0.00E+00	2.22E+22
CH3(g)	0.00E+00	0.00E+00	2.22E+22
CH4(g)	0.00E+00	0.00E+00	2.22E+22
CO(g)	0.00E+00	0.00E+00	2.22E+22
CO2(g)	0.00E+00	0.00E+00	2.22E+22
H(g)	2.69E-13	4.71E-12	-8.52E+01
HO(g)	6.83E-08	1.20E-06	-1.06E+02
HO2(g)	2.66E-10	4.67E-09	-1.27E+02
H2(g)	6.93E-10	1.21E-08	-1.70E+02
H2O(g)	3.28E-02	5.74E-01	-1.91E+02
H2O2(g)	4.06E-11	7.12E-10	-2.12E+02
O(g)	2.76E-11	4.84E-10	-2.07E+01
O2(g)	6.85E-04	1.20E-02	-4.14E+01
O3(g)	4.32E-15	7.58E-14	-6.21E+01
C(p,s)	0.00E+00	0.00E+00	2.22E+22

Total
Moles:
Gas: 5.7040639E-02

Temperature (C):
850.
Pressure (bar): 1.

Inert
Moles:
Gas: 0.0000000E+00

Species	Moles	Mole Fraction	μ (kJ/mol)
Br(g)	5.60E-06	7.36E-05	-5.29E+01
BrH(g)	4.38E-02	5.76E-01	-6.69E+01
Br2(g)	9.35E-07	1.23E-05	-1.06E+02
C(g)	8.46E-31	1.11E-29	-8.14E+01
CBr(g)	1.80E-25	2.37E-24	-1.34E+02
CBr4(g)	8.45E-22	1.11E-20	-2.93E+02
CH(g)	4.88E-28	6.42E-27	-9.55E+01
CHO(g)	1.07E-13	1.41E-12	-2.65E+02
CH2(g)	4.54E-22	5.96E-21	-1.09E+02
CH2O(g)	6.24E-11	8.20E-10	-2.79E+02
CH3(g)	3.78E-15	4.97E-14	-1.24E+02
CH4(g)	9.08E-10	1.19E-08	-1.38E+02
CO(g)	1.07E-03	1.41E-02	-2.51E+02
CO2(g)	5.63E-03	7.39E-02	-4.20E+02
H(g)	7.29E-10	9.58E-09	-1.40E+01
HO(g)	2.23E-11	2.93E-10	-1.84E+02
HO2(g)	1.05E-20	1.38E-19	-3.53E+02
H2(g)	3.82E-03	5.02E-02	-2.81E+01
H2O(g)	2.18E-02	2.86E-01	-1.98E+02
H2O2(g)	3.25E-18	4.27E-17	-3.67E+02
O(g)	4.44E-18	5.83E-17	-1.69E+02
O2(g)	1.33E-17	1.74E-16	-3.39E+02
O3(g)	1.01E-35	1.33E-34	-5.08E+02
C(p,s)	0.00E+00	0.00E+00	0.00E+00

Total
Moles:
Gas: 7.6100796E-02