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PROJECT STATUS REPORT

April 10, 1993

Report No. 3-1
Reporting Period:
January 1, 1993
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GRANT NUMBER AND TITLE

Biological Conversion of Synthesis Gas
U. S. Department of Energy: DE-FG21-90MC27225

GRANT PERIOD

September 4, 1990 - September 3, 1993

Task 1. Test Plan

Task has been completed.

Task 2. Culture Development

Task has been completed.

Task 3. Mass Transfer/Kinetics Studies

Task has been completed.

Task 4. Bioreactor Studies

A continuous stirred tank reactor with and without sulfur recovery has been operated using *Chlorobium thiosulfatophilum* for the conversion of H_2S to elemental sulfur. In operating the reactor system with sulfur recovery, a gas retention time of 40 min was required to obtain a 100 percent conversion of H_2S to elemental sulfur. Essentially no SO_4^{2-}, an undesirable product, was produced under these conditions. Significant reductions in the gas retention time are expected by employing cell recycle after sulfur recovery, and by using increased pressure.

Technical Discussion

The anaerobic, photosynthetic bacterium *Chlorobium thiosulfatophilum* converts H_2S and COS in coal synthesis gas to elemental sulfur by the equations:

$$2\ H_2S + CO_2 \xrightarrow{\text{light}} \underset{\text{(biomass)}}{(CH_2O)} + 2\ S + H_2O \tag{1}$$

$$COS + H_2O \rightarrow H_2S + CO_2$$

Under conditions where excessive light or minimal H_2S is supplied to the bacterium, the final product is SO_4^{2-} instead of elemental sulfur. Thus, a process for converting H_2S and COS to elemental sulfur requires minimal light intensity and sufficient H_2S to prevent SO_4^{2-} formation.

A CSTR system has been designed and operated for the conversion of H_2S (and later COS) to elemental sulfur. The fermenter is a 1.25 L New Brunswick Scientific Bioflo chemostat equipped with agitation and temperature control. The fermenter has been modified to operate under strict anaerobic conditions with both continuous gas and liquid flow. The fermenter is maintained at 29-31°C by housing the system in a constant temperature environment. Light is supplied to the culture using 2 60W bulbs mounted approximately 8 in from the reactor. Liquid effluent from the reactor contains elemental sulfur, which may be separated from the medium by gravity, if desired. A 475 mL separatory flask with a side arm is used for the rapid separation of solid sulfur from the balance of the effluent.

The system was first operated without sulfur recovery at a constant gas flow rate of 20 standard mL/min (62.5 min gas retention time), while varying the dilution rate (inverse liquid retention time), D, from 0.4 to 2.0 days^{-1}. The gas contained 2.5 percent H_2S, 10 percent CO_2 and 15 percent CH_4 in helium. The use of two 60 W bulbs for light intensity had been shown in preliminary studies to give a high yield of elemental sulfur while minimizing SO_4^{2-} formation. Figure 1 shows the results of the liquid dilution rate study with cell concentration, H_2S conversion and liquid sulfur species (S^{2-}, SO_4^{2-} and S^o) concentrations plotted as a function of dilution rate, D. As is noted in the figure, the H_2S conversion was essentially 100 percent for all of the dilution rates studied. The exception to this result is the dip in conversion found while operating at dilution rates of 0.7 - 1.0 $days^{-1}$. Cell concentration showed typical Monod behavior with dilution rate increasing from 350 mg/L at a 0.4 $days^{-1}$ dilution rate to 450 mg/L at a 1.3 $days^{-1}$ dilution rate before falling gradually as the dilution rate was further increased. The dissolved S^{2-} concentration, corresponding to the accumulated H_2S dissolved in the liquid phase, remained near zero for all dilution rates. Almost all of the sulfur product was present as elemental sulfur (400 - 1000 mg/L), while the sulfate concentration remained at 0 - 100 mg/L. In fact, the SO_4^{2-} concentration was 0 at dilution rates below 1.20 $days^{-1}$.

A second study was performed in the CSTR without sulfur recovery in which the gas retention time was varied at a constant liquid dilution rate of 1.25 $days^{-1}$. Figure 2 shows the results of this study, where cell concentration, H_2S conversion and sulfur species concentrations are plotted as a function of gas retention time. As is noted in the figure, the H_2S conversion increased almost linearly with gas retention time, ranging from just under 60 percent at a 20 min gas retention time to 100 percent at a 75 min gas retention time. As expected, the cell concentration was not affected by gas retention time, maintaining a constant concentration of 350 mg/L. Similarly, the liquid phase S^{2-} concentration stayed very low at 0-50 mg/L, the SO_4^{2-} concentration remained low at 0-60 mg/L and the elemental sulfur concentration ranged from 600-800 mg/L.

Finally, a third study was performed in the CSTR, but this time with the sulfur recovery device. As is shown in Figure 3, cell concentration, H_2S conversion and sulfur species concentrations are plotted as a function of gas retention time for a liquid dilution rate of 1.25 $days^{-1}$. In this study, the H_2S conversion ranged from 60-100 percent, reaching 100 percent conversion at a gas retention time of 45 min. Thus, conversions were higher at a given retention time with sulfur recovery. The cell concentration was constant at 350 mg/L, a similar level as in the previous study. The S^{2-} and SO_4^{2-} concentrations were again quite low and the sulfur concentration in the effluent (not the total sulfur produced) ranged from 200-350 mg/L. Thus, sulfur recovery significantly improves H_2S conversion and thereby sulfur production.

Future studies with the reactor and sulfur separator will include cell recycle to increase the concentration of cells inside the reactor. A hollow fiber membrane system compatible with the sulfur species is being sought. It is also believed that increased pressure will improve the performance of the *C. thiosulfatophilum* system.

Task 5. Limiting Conditions/Scale-up

Continuous reactor studies are being carried out in the CSTR in order to study the performance of *Rhodospirillum rubrum* under a variety of limiting conditions. Results from these studies will be presented during the next reporting period.

Task 6. Economic Evaluations

No work was scheduled on this task during the reporting period.

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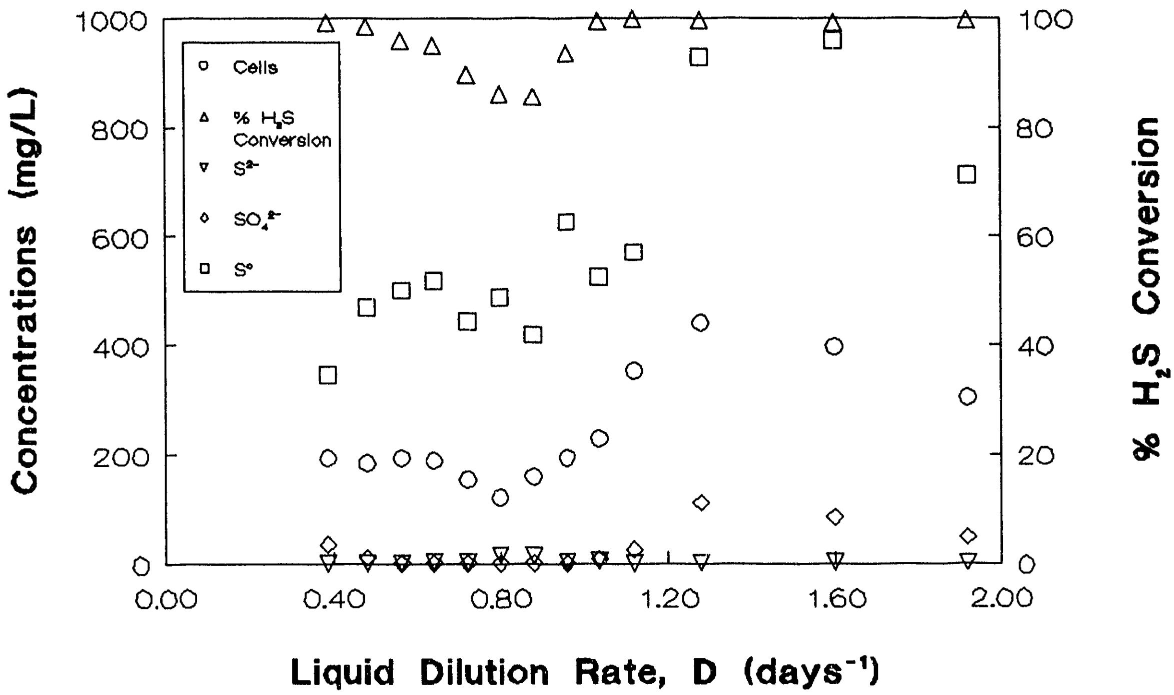

Figure 1. Performance of CSTR without Sulfur Recovery using *C. thiosulfatophilum* at Various Liquid Dilution Rates (Gas Retention Time: 62.5 min).

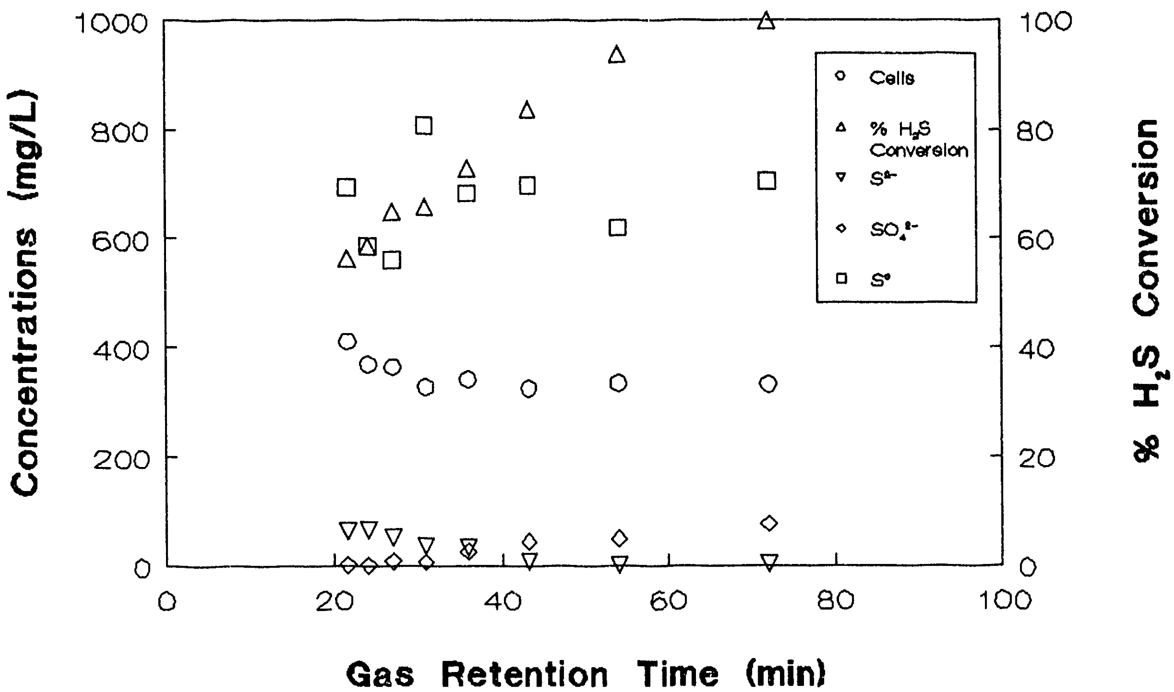

Figure 2. Performance of CSTR without Sulfur Recovery using *C. thiosulfatophilum* at Various Gas Retention Times (Liquid Dilution Rate: 1.25 $days^{-1}$).

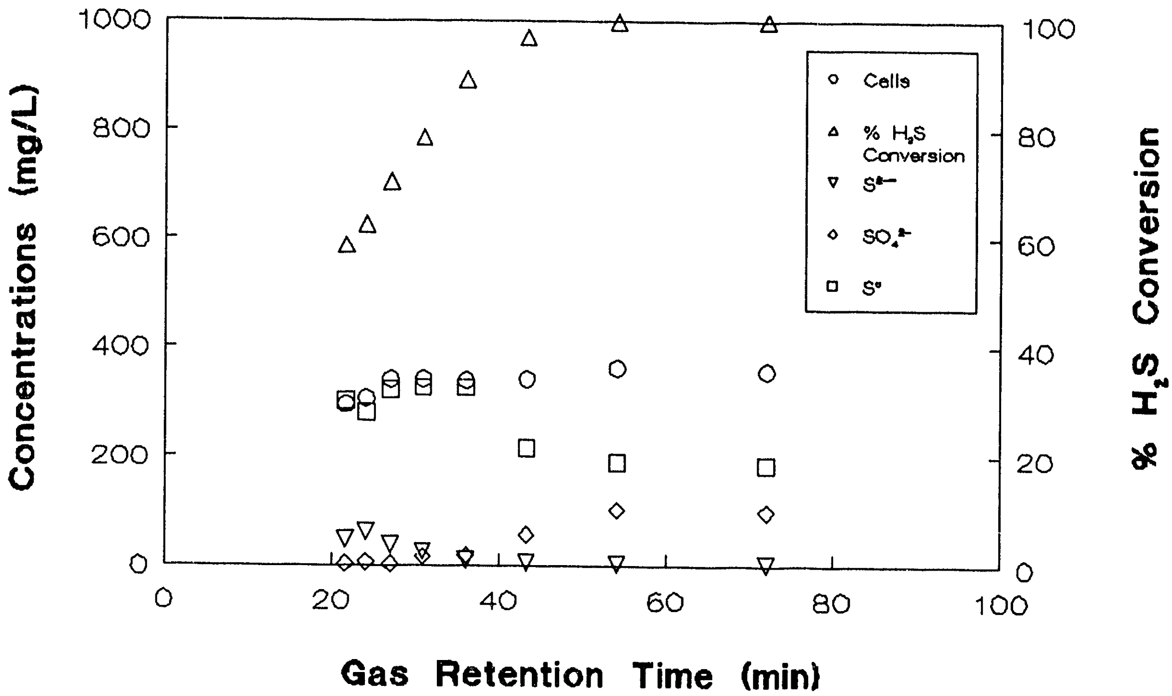

Figure 3. Performance of CSTR with Sulfur Recovery using *C. thiosulfatophilum* at Various Gas Retention Times (Liquid Dilution Rate: 1.25 $days^{-1}$).

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