BIOLOGICAL CONVERSION OF SYNTHESIS GAS

Topical Report: Bioreactor Studies

by

R. Basu
K.T. Klasson
E.C. Clausen
J.L. Gaddy

September, 1993

Work performed under Grant No. DE-FG21-90MC27225

for

U.S. Department of Energy
Morgantown Energy Technology Center
Morgantown, WV

by

University of Arkansas
Fayetteville, AR

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ACKNOWLEDGMENT

Financial support for this work has been provided by the Morgantown Energy Technology Center, U. S. Department of Energy under grant number DE-FG21-90MC27225

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1.0 INTRODUCTION

Synthesis gas, a mixture of primarily CO, H₂ and CO₂, is a major building block in the production of fuels and chemicals. The gas is derived from non-gaseous raw materials such as coal, shale oil, tar sands, heavy residue and biomass. The composition of synthesis gas is dependent upon the raw material used and the gasification process. Coal-derived gas is rich in CO and H₂, with lower concentrations of CO₂ and CH₄ and traces of H₂S and COS (1).

Synthesis gas may be used in the production of both gaseous and liquid fuels. The conventional method of producing gaseous fuel first employs the catalytic shift reaction. In this reaction, CO and H₂O are converted into H₂ and CO₂. Following the removal of excess CO₂ and sulfur contaminants such as H₂S and COS, the H₂ and CO₂ are catalytically methanated to CH₄ and H₂O. After drying, the product gas contains 95-98% CH₄.

Most methanation processes require temperatures of 300-700°C and operating pressures of 3-20 atm (2). The catalysts used for the methanation step include nickel and potassium-based catalysts, as well as mixtures of iron/chromium oxides and zinc/copper oxides (3,4). Poisons for these catalysts include chlorine and sulfur (5,6). In addition, chemical catalytic processes are known to produce by-products such as methanol, formaldehyde and acetic acid (7).

A wide variety of both liquid and gaseous fuels may be produced from synthesis gas using Fischer-Tropsch synthesis including light hydrocarbons (methane, ethane), fuel range hydrocarbon distillates and heavy waxes. The stoichiometry for product formation may be ideally represented by the equation:

However, based on actual yields in a Synthol entrained flow reactor, the overall stoichiometry is better characterized by the empirical relation (8):

As is noted in Equations (1.1) and (1.2), about 2 moles of H_2 are required for every mole of CO .

The H_2/CO ratio in synthesis gas is dependent upon both the grade of coal used in the feed and the type of gasifier employed. Modern gasifiers produce synthesis gas with a H_2/CO ratio as low as 0.6. Therefore, an increase in the H_2 content of synthesis gas is usually necessary prior to Fischer-Tropsch synthesis, which requires coupling water gas shift and gasification.

The utilization of coal to produce liquid fuels by Fischer-Tropsch synthesis is a multi-step process. After gasification at $700\text{-}2000^\circ\text{C}$ (9), the raw gas is quenched and scrubbed to condense tars and oils and to remove dust and water soluble materials from the gas stream such as phenols, chloride, ammonia, cyanide, thiocyanate, and perhaps some H_2S (10). A catalytic water-gas shift conversion at about 225°C is then used to adjust the H_2/CO ratio:

A high H_2/CO ratio is not only necessary to satisfy the stoichiometry of the Fischer-Tropsch synthesis, but is beneficial in controlling carbon deposition and reducing associated catalyst deactivation (11).

Following shift conversion, the gas contains primarily H_2 , CO , CO_2 , H_2O , sulfur gases and possibly methane, although small amounts of higher aliphatic hydrocarbons and light oils are sometimes present. The sulfur is present as H_2S and COS , with smaller amounts of organic sulfides or mercaptans. These "acid gases", including CO_2 , are removed using a variety of processes, including Claus, absorption, or liquid phase oxidation processes. The sulfur

concentration must be reduced to less than 0.1 ppm to protect sensitive downstream catalysts (10). Following purification, the gas is then available for conversion to C₁-C₃₅ hydrocarbons in a Fischer-Tropsch synthesis reactor at 225-365°C.

There are several limitations with water gas shift, purification and Fischer-Tropsch synthesis. Each of these operations are conducted in separate steps, at different conditions requiring intermediate adjustment of temperature or pressure, which results in a very complex and expensive process. Also, these processes are carried out at elevated temperatures and pressures, and thus suffer from low thermal efficiencies. The catalysts used in the Fischer-Tropsch synthesis are particularly sensitive to the presence of sulfur gases or carbon deposition and deteriorate rapidly. Carbon deposition, as was mentioned previously, is enhanced by low H₂/CO ratios in the synthesis gas. Finally, more specific catalysts are required to avoid production of a broad array of chemicals and fuels and to improve raw material yields from Fischer-Tropsch synthesis.

1.1 Biological Synthesis Gas Conversion

Biological processes may be utilized as an alternative to the traditional methods of producing fuels from raw synthesis gas. Biological processes operate at near ambient temperatures, and yields and energy efficiencies are high. Many microorganisms (biocatalysts) are not sensitive to the presence of low concentrations of toxic gas compounds found in synthesis gas (12,13). In addition, biological reactions are very specific, and often a single product is produced as a result of biosynthesis.

A single reaction vessel can often be used to carry out several biological reactions in series or parallel. Therefore, one reactor might be

used for water gas shift, gas purification (sulfur and CO₂ removal) and product formation (Fischer-Tropsch synthesis or methanation) by utilizing a co-culture or mixed culture. As is shown in Figure 1.1, the process for biological production of hydrocarbons from synthesis gas could be very simple. Following gasification, the gas temperature would be reduced to 95-135°F, with the opportunity for heat recovery and improved energy efficiency. The cool gases would then be bubbled through a biological reactor, where a culture of microorganisms would be maintained to produce H₂ and remove sulfur gases and CO₂. Cultures may be developed that utilize CO, CO₂ and H₂ as substrates to produce hydrocarbons, such that adjustment of the H₂/CO ratio in the synthesis gas is not essential. Also, the removal of CO₂ may not be necessary if a liquid product is produced in the reactor. High conversions in the reactor will be necessary to avoid recycle. Therefore, significant potential exists for developing a simple, more economical biological process for hydrocarbon production from coal.

The disadvantages of biological processes include slower reactions and the need for sterile conditions to prevent contamination. When utilizing synthesis gas, sterility is insured by the presence of CO, which is toxic to most microorganisms. Biological reactions involving gaseous substrates may be operated under mass transfer limiting conditions, where mass transfer controls the rate of transport of gaseous reactants and, consequently, reactor size. Reactor rates have been found to be proportional to pressure, and the use of special bioreactors at moderate pressures (150 psia) have resulted in residence times for near complete conversion of synthesis gas of only a few minutes (14,15). Therefore, fast reaction rates and small reactors can be achieved by the appropriate bioreactor design.

Figure 1.1. Comparison of Conventional and biological routes for methane production from coal.

1.2 Brief Statement of Purpose

The purpose of the proposed research is to develop a technically and economically feasible process for biologically producing H_2 from synthesis gas while, at the same time, removing harmful sulfur gas compounds. This research builds upon previous research studies carried out in the University of Arkansas laboratories where the technical and economic feasibility of biologically producing CH_4 from synthesis gas components has been demonstrated. Six major tasks are being studied:

1. Culture development, where the best cultures are selected and conditions optimized for simultaneous hydrogen production and sulfur gas removal;
2. Mass transfer and kinetic studies in which equations necessary for process design are developed;
3. Bioreactor design studies, where the cultures chosen in Task 1 are utilized in continuous reaction vessels to demonstrate process feasibility and define operating conditions;
4. Evaluation of biological synthesis gas conversion under limiting conditions in preparation for industrial demonstration studies;
5. Process scale-up where laboratory data are scaled to larger-size units in preparation for process demonstration in a pilot-scale unit; and
6. Economic evaluation, where process simulations are used to project process economics and identify high cost areas during sensitivity analyses.

The bioconversion studies are built upon previous experimental work performed under DOE contract. A strong foundation in gaseous substrate fermentation with a major emphasis on continuous bioreactor design and operation has been achieved. Although the technical feasibility of biological

methane production from synthesis gas has been demonstrated, several important pieces of information are needed prior to recommending a demonstration unit for this biological conversion. These process development studies can be grouped into three categories:

1. Culture development under industrial conditions;
 2. Investigation of alternate reactor systems to minimize capital costs;
- and
3. Process scale-up measurements.

Culture development studies under industrial conditions involve operating the cultures under less than optimum conditions in order to define operating limits for the cultures. The effects of trace quantities of oxygen in the feed on the strict anaerobes will be quantified. In addition, synthesis gas contaminants other than sulfur gases will be added to the gas stream to measure the effects of these materials on cell growth, substrate consumption and product formation. The effects of various CO/H₂ ratios on product yield and fermentation rates will be measured. Finally, efforts will be directed toward developing a cheap minimal media for synthesis gas fermentation.

An economic evaluation of various reactor alternatives has shown that the use of traditional mass transfer equipment yields high capital costs due to relatively poor gas-liquid mass transfer. A reaction system with mass transfer capabilities that minimize capital costs is thus sought. Various reaction systems are potential candidates and will be tested, including modified trickle-bed reactors and pulse and airlift fermenters. Also, various compounds will be added to the fermentation media in an effort to increase the mass transfer coefficient by changing physical properties.

Scale-up measurements involve several experiments. First, physical properties of the fermentation media will be evaluated under a variety of fermentation conditions. Two physical properties, medium viscosity and surface tension, are thought to change significantly with increasing cell density during the fermentation. Methods for handling these changes during process scale-up will be addressed. SEcondly, the limiting conditions of gas-liquid fermentation need to be defined. The maximum operable cell density and the performance of the cultures under extreme agitation rates, cell densities, operating pressure and high product concentrations will be evaluated. Finally, the scale-up correlations used in the economic analysis will be tested in larger bench-scale continuous reactors prior to recommending orocess demonstration in a PDU.

The production of hydrogen from CO and water can be carried out biologically by the facultative photosynthetic bacterium *Rhodospirillum rubrum* as an alternative to the water gas shift reaction. H₂ production is essentially in adjusting the H₂/CO ratio for further utilization of the syngas. Experiments in the University of Arkansas laboratories have shown that this bacterium is fast growing, exhibits fast CO uptake and is table in the presence of high CO and sulfur gas compositions. *R. rubrum* requires a tungsten light source for growth; however, the actual chemical reaction can be carried out in the dark. Therefore, only a small bioreactor for bacterial growth is required, thereby reducing capital and radiant energy costs.

Sulfur gas removal may be carried out by the anaerobic bacterium *Chlorobium thiosulfatophilum* (16,17). *C. thiosulfatophilum*, a phototropic sulfur bacterium, has the advantage of producing sulfur which could be easily

separated as a solid by-product. It has also been shown to utilize COS in conjunction with the chemical reaction

on *C. thiosulfatophilum* is superior to other sulfur gas-utilizing species such as *Thiobacillus denitrificans*, which produces sulfate as the product in H₂S conversion (18,19).

1.2.1 Purpose

The purpose of this report is to present results from bioreactor studies involving H₂ production by water gas shift and H₂S removal to produce elemental sulfur. Many of the results for H₂ production by *R. rubrum* has been presented during earlier contracts. Thus, this report will concentrate mainly on H₂S conversion to elemental sulfur by *R. rubrum*.

2.0 MATERIALS AND METHODS

2.1 Organisms and Culture

Rhodospirillum rubrum, ATCC 25903, was obtained from the American Type Culture Collection, Rockville, MD. The medium used for stock cultures, transfers and experiments contained per 100 mL: Pfennig mineral solution (20), 5 mL; Pfennig trace metal solution (20) with the addition of 10 mg/l Na₂SeO₃ (21), 0.1 mL; B-vitamin solution (21), 0.5 mL; yeast extract (Difco), 0.1 g; NaCH₃COO·3H₂O, 0.58 g; NH₄Cl, 0.27 g; and NaHCO₃, 0.4 g. Stock cultures were kept anaerobically under tungsten light at 30°C and transferred every 2-3 weeks. Seed cultures used for inoculation of the bioreactors were prepared by transferring 5 mL of stock culture to 75 mL of fresh medium reduced with 1.5 mL of Na₂S (2.5%). Typically the seed culture was grown for 48 hours before an aliquot of 5 mL was used for inoculation of the reactor.

The medium for the studies with *C. thiosulfatophilum* contained per 100 mL: Phennig mineral solution (20), 5 mL; Pfennig trace metals solution (20), 0.1 mL; B-vitamins solution (21), 0.5 mL; yeast extract (Difco), 0.05 g; and NaHCO_3 , 0.4 g. Before sterilization, 75 mL of medium were added to each bottle under a N_2/CO_2 (80%/20%) atmosphere. The bottles were autoclaved at 15 psig for 20 minutes. Once sterile, the bottles were flushed with He/CO_2 (60%/40%) to remove any traces of O_2 and inoculated with 5 mL of seed culture. Gaseous H_2S was then added to the bottles in the desired amounts. The seed culture was grown for 72 h before being used for inoculation into the bottles.

2.2 Batch Bioreactors and Operating Conditions

Batch fermentations were carried out in 150 mL glass serum bottles (Wheaton Glass Co., Millville, NJ). The bottles were sealed using butyl rubber septum stoppers and aluminum crimp seals (Bellco Glass Co., Vineland, NJ). Before sterilization, 75 mL of medium were added to each bottle under a He/CO_2 (75%/25%) atmosphere. The bottles were autoclaved at 15 psig for 20 minutes.

Once sterile, the bottles were reduced with 1.5 mL of Na_2S (2.5%) and inoculated with 5 mL of seed culture. After inoculation the desired gas phases were introduced by flushing with CO/CO_2 (80%/20%) for 3 minutes using an appropriate check valve to achieve the desired pressure. Argon (20 mL) was then added to each bottle as an inert tracer gas with a gas-tight syringe. This procedure allowed calculation of the amounts of each gas component through the fermentation.

The experiments were carried out in a modified incubator shaker (Model G25, New Brunswick Scientific Co., Edison, NJ) at 150 rpm and 30°C. Tungsten light, necessary for growth, was supplied in excess in the shaker.

The experiments involving light intensity were also carried out in a modified incubator shaker (Model G25, New Brunswick Scientific Co., Edison, NJ) at 150 rpm and 30°C. Tungsten light, necessary for growth, was supplied in the shaker. Each bottle was placed horizontally into a dark box, contained in the shaker incubator, with a light reduction filter (Kodak Wratten Gelatin Filter, Eastman Kodak Company, Rochester, NY) in the lid to control light intensity. Light intensities in the boxes were measured with a LX-101 Digital Lux Meter (Cole-Parmer, Chicago, IL).

2.3 Continuous Bioreactor and Operating Conditions

The continuous stirred-tank reactor used was a New Brunswick Scientific (Edison, NJ) BioFlo II fermenter equipped with temperature, pH and agitation control. The liquid working volume was 1250 mL and the overhead gas volume was 350 mL. Illumination necessary for growth was supplied by two tungsten lights (40W) directed towards the glass fermentation jar. Experiments were carried out at 30°C and pH 7. The feed gas used was a mixture of H₂, Ar, CO and CO₂ (20/15/55/10%) and was continuously fed to the reactor. Liquid feed was also supplied on a continuous basis. A schematic of the equipment set-up is shown in Figure 2.1.

Typically experiments were started with constant agitation rate and gas flow rate. During an experimental run, the liquid flow rate was reduced from a high to low setting. This procedure induced an increase in cell concentration and CO conversion with time as the culture strived to reach a steady state for growth limited by medium composition, liquid flow rate and illumination. The conversion of CO was monitored and experiments were considered complete when the gas conversion leveled off. The liquid flow rate was then increased and the cell concentration allowed to decrease to a low level before starting a new experiment.

Figure 2.1. Schematic Set-up of the CSTR Reactor System using *R. rubrum*
 Legend: 1- Feed reservoir; 2- Feed pump; 3- Fermenter;
 4- Gas supply tank; 5- Rotameter; 6- Effluent reservoir;
 7- Exit gas.

An effort has been made to develop a mixed culture of *R. rubrum* and *C. thiosulfatophilum*. 75 ml of basal medium with the addition of ammonium chloride and sodium acetate (medium used for *R. rubrum*) was added to 150 ml serum bottles. 1.5 ml of 2.5% sodium sulfide was then added to reduce any traces of oxygen. The bottles were purged with CO/CO₂ (80%/20%) for five minutes and 5 ml of H₂S were added. Pure cultures of *R. rubrum* and *C. thiosulfatophilum* (5 ml each) were added to the bottles.

It was observed that for all experiments the performance of the mixed culture was not as good as with pure cultures in terms of H₂ production, CO uptake, and H₂S consumption. The rates were much slower than when using the pure cultures. While for pure cultures, complete CO uptake and H₂S consumption required between 24 and 48 hours, for the mixed culture it required about 7 days.

In the future, it is proposed to utilize pure cultures in CSTRs in series for both H₂ production and H₂S removal. In this arrangement, the first CSTR containing *C. thiosulfatophilum* will consume H₂S (or at least reduce the level of H₂S to tolerable levels). The second CSTR in series containing *R. rubrum* will produce H₂ from CO. While the gas stream passes from the first reactor to the second, the liquid streams in the CSTRs will be separate and parallel.

2.4 Analytical Techniques

Liquid and gas samples, 1.5 mL and 0.4 mL, respectively, were withdrawn from the reactors during the fermentation and analyzed for cell concentration and gas phase composition. The dry cell weight concentration for *R. rubrum* was obtained by measuring light scatter at 540 nm in a Spectronic 21 (Milton

Roy Co., Rochester, NY) and converting it to cell density using a calibration curve ($DCW(mg/l) = 395.4 \cdot ABS_{540}$). Cell concentration measurements for *C. thiosulfatophilum* are discussed later.

Gas analyses of CO, CO₂ and H₂ were performed on a gas chromatograph (Perkin-Elmer Sigma 300, Norwalk, CT) using an 1.8 m stainless steel column packed with Carbosphere, 60/80 mesh. The oven temperature was held constant at 135°C while the injector and thermal conductivity detector temperatures were 175°C. Helium was used as the carrier gas at a flow rate of 40 mL/min.

The gas phase H₂S concentrations were measured by gas chromatography using a Hewlett-Packard (Kennett Square, PA) HP 5890 Series II gas chromatograph and an HP 7673 integrator equipped with a thermal conductivity detector. The column was a 1/8" x 6' teflon column packed with Chromosorb 107, 80/100 mesh (Altech Assoc., Inc., Deerfield, IL). The oven temperature was 80°C, and the detector and injector temperatures were kept at 175°C. The carrier gas was helium at a flow rate of 30 mL/min. Liquid phase sulfur concentrations (H₂S(l), HS⁻, S²⁻) were measured using a Corning Silver/Sulfide Electrode (Corning Glass Works, Medfield, MA) and an Orion Specific Ion meter (Orion Research, Inc., Cambridge, MA).

3.0 H₂S CONVERSION BY CHLOROBIVM THIOSULFATOPHILUM

The anaerobic, photosynthetic bacterium *Chlorobium thiosulfatophilum* is able to convert H₂S and COS in synthesis gas to elemental sulfur. The bacterium grows on CO₂ as its carbon source at 30°C. In the absence of sulfide, the formed elemental sulfur is converted to sulfate. Thus, bioreactor designs must incorporate sulfur removal as an integral part of the bioprocess.

3.1 Conversion Without Sulfur Removal

In this initial study, *C. thiosulfatophilum* was used to convert H_2S to elemental sulfur in a continuous stirred tank reactor (CSTR) with continuous gas and liquid feed. Sulfur removal was not part of this initial system design, but will be an added feature in future work. The gas used in this study contained 2.52 percent H_2S , 10.00 percent CO_2 , 14.99 percent CH_4 (as a tracer) and 72.49 percent He. The liquid flow rate to the 1380 mL reactor volume ranged from 10.8-23.6 mL/min and was a variable in the study. The initial gas flow rate was 11.6 standard mL/min, although it was also changed twice during the study. The temperature was maintained at 31°C and the agitation rate was held at 200 rpm in the Bioflo reactor.

Cell density was monitored by the chlorophyll method and gas composition was monitored by gas-solid chromatography. Light at 2200 lux was supplied using two 40W tungsten light bulbs on the outside of the glass reactor vessel. The light intensity was measured at the front of the reactor vessel, but was not uniform around the reactor.

Figures 3.1 and 3.2 show cell concentration and H_2S conversion measurements in the CSTR with *C. thiosulfatophilum*. Several changes were made during the course of the experiment as is noted on the two figures. Complete H_2S conversion was noted at a gas flow rate of 11 standard mL/min (2.09 hr gas retention time). The gas conversion fell at increased gas flow rates, mainly due, however, to temperature control problems.

Two problems were noted in operating the system. First, the use of external light in the temperature controlled room caused a temperature increase inside the reactor, thus lowering the H_2S conversion and cell concentration. Secondly, a yellowish color was observed in the reactor after

Figure 3.1. Cell Concentration Measurements for H_2S Conversion by *C. thiosulfatophilum* in the CSTR.

Figure 3.2. H_2S Conversion Measurements for H_2S Removal by *C. thiosulfatophilum* in the CSTR.

several hours of operation due to the accumulation of sulfur in the reactor. Both of these problems will be addressed in future studies.

A chiller will be installed in the cooling water line to help control the cooling water temperature. Light intensity will be controlled by installing a variable autotransformer with the lights.

Sulfur will be removed from the system by employing a separatory funnel and a recycle loop between the reactor and the separator. The cell culture with suspended sulfur will be pumped into the separatory funnel. Another pump will recirculate the cell culture back to the reactor. An overflow line on the funnel will take care of the flow imbalances between the pumps. Settled sulfur will be removed from the bottom of the funnel as needed.

3.2 H₂S Conversion in the CSTR With Sulfur Recovery by Gravity Separation

A CSTR system has been designed and operated for the conversion of H₂S (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 3.3 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^0) 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 $0.7 - 1.0 \text{ days}^{-1}$. 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 3.4 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

Figure 3.3. Performance of CSTR without Sulfur Recovery using *C. thiosulfatophilum* at Various Liquid Dilution Rates (Gas Retention Time: 62.5 min).

Figure 3.4. Performance of CSTR without Sulfur Recovery using *C. thiosulfatophilum* at Various Gas Retention Times (Liquid Dilution Rate: 1.25 days⁻¹).

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 3.5, 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.

Additional experiments were carried out in the stirred tank reactor with the sulfur settler at varying light intensities and gas flow rates to observe maximum H_2S removal. A schematic of the equipment set-up is shown in Figure 3.6. Results from the study are summarized in Table 3.1. As is noted, the gas retention time for complete H_2S removal was minimized at 20 min when using two 200 W light sources. Also, it is observed that the S^{2-} concentration

Figure 3.5. Performance of CSTR with Sulfur Recovery using *C. thiosulfatophilum* at Various Gas Retention Times (Liquid Dilution Rate: 1.25 days⁻¹).

Figure 3.6. Schematic Diagram of the Experimental Set-up for H_2S Removal and Sulfur Production

Table 3.1

Performance of the CSTR with Sulfur Recovery Using *C. thiosulfatophilum* at Different Light Intensities
(Liquid Dilution Rate: 1.25 days⁻¹)

Light	Gas Retention Time, min	Cell Conc. mg/L	% H ₂ S Conversion	S ²⁻ mg/L	SO ₄ ²⁻ mg/L	S° mg/L
2X60W	43	339	99.2	0	1	292
2X75W	43	409	99.9	1	182	327
2X75W	36	433	99.8	2	240	327
2X75W	31	460	97.8	0	183	402
2X100W	31	463	99.5	2	214	449
2X100W	27	441	95.5	2	135	516
2X150W	27	391	99.5	2	117	496
2X150W	24	408	98.5	2	89	572
2X150W	22	412	96.5	2	62	501
2X200W	22	422	99.9	2	100	539
2X200W	20	453	99.9	2	115	440

remained essentially at zero. It was also possible to maintain the SO_4^{2-} concentration at levels below 100 mg/L. The sulfur concentration in the liquid at this gas retention time remained between 500-600 mg/L. Higher light intensities are expected to permit higher H_2S removal rates. However, because of physical limitations in providing sufficient reactor cooling, experiments were not carried out at higher light intensities.

After determining the optimum liquid dilution rate, gas flow rate, and light intensity to maximize H_2S removal in the system, an experiment was performed for an extended time period at these optimum conditions (1.25 days⁻¹ liquid dilution rate, 19.6 min gas retention time, and two 200W light sources) to establish the stability of the process. The results of this experiment over a period of 39⁷ hrs are shown in Figure 3.7. It can be seen from this figure that the reactor performance was quite stable during this period. However, the settler was not efficient in removing all of the elemental sulfur particles present in the reactor effluent. The effluent contained 425-550 mg/L elemental sulfur. The H_2S removal rate during this operation was 57 micromol/min/L which is about 1.5 times the maximum value reported by Kim and Chang.

3.3 H_2S Conversion with Cell Recycle and Sulfur Recovery

The continuous stirred tank reactor system was modified to include both sulfur recovery and cell recycle using ceramic tubular membranes (Membralox ceramic membranes, U.S. Filter, Warrendale, PA; membrane area: 55 cm²). Ceramic membranes were chosen due to their resistance to H_2S and other sulfur species. The sulfur recovery filter (5.0 micron pore size) was first installed in front of the cell recycle filter (0.2 micron pore size) due to the larger size of the sulfur particles in comparison to cells. But however,

Figure 3.7. Long Term Behavior of the CSTR with Sulfur Recovery using *C. thiosulfatophilum* (Liquid Dilution Rate: 1.25 days⁻¹; Gas Retention Time: 19.6 min)

the sulfur recovery filter was found to block after 15-30 minutes of operation. It is possible to regenerate the filter by backflushing with water. The frequent backflushing disturbs the reactor system and makes the process impractical.

The continuous stirred tank reactor system was also operated along with a sulfur settler and a polysulfone hollow fiber membrane module (0.45 micron microfiltration cartridge, 465 cm² membrane area, fiber lumen i.d. 0.75 mm, A/G Technology, Needham, MA) for cell recycle. Results for four different cases (denoted as Case I to Case IV) of operation are presented in Table 3.2. In case I, the reactor was operated with the settler only (recycle rate = 70 mL/min) and no cell recycle membrane was installed. In case II, the settler and the hollow fiber module were in the same loop (recycle rate = 450 mL/min) and the liquid discharge from the reactor was taken completely as the membrane permeate. This causes gradual accumulation of cells in the reactor and the reactor performance in terms of H₂S conversion drops. In case III, 50 percent of the reactor discharge was taken as bleed and 50 percent as membrane permeate. This caused improvement in reactor performance. However, keeping the settler and the filter in the same loop with a high recycle rate causes a higher concentration of suspended S⁰ in the reactor. In case IV, the settling of sulfur was improved by separating the cell recycle (recycle rate = 450 mL/min) and the sulfur settling (recycle rate = 70 mL/min) loops. Fifty percent of the reactor discharge was as bleed. This change resulted in a significant improvement in H₂S conversion with a lower gas retention time.

4.0 CONCLUSIONS

The CSTR with sulfur recovery and cell recycle using *C. thiosulfatophilum* was shown to be very effective in removing H₂S from syngas streams. A gas

Table 3.2

Performance of the CSTR with the Sulfur Settler and Cell
Recycle Using *C. thiosulfatophilum*

Time h,	Light Intensity	D, day ⁻¹	Gas RT Min	X, mg/L	%H ₂ S conv.	SO ₄ ²⁻ mg/L	S° mg/L	S ²⁻ mg/L
Case I								
96	2X60W	1.12	36	605	99.6	47	655	1
Case II								
24	2X60W	1.12	36	802	98.7	58	1275	1
48	2X60W	1.12	36	1595	99.9	107	1762	1
72	2X60W	1.12	31	1782	99.7	108	1488	1
96	2X60W	1.12	27	2125	92.6	42	2733	1
120	2X60W	1.12	27	2554	94.0	25	3255	1
144	2X60W	1.30	27	2799	79.1	4	2294	1
168	2X60W	1.30	27	3244	70.0	4		1
192	2X75W	1.30	27	3300	88.8	8	1795	1
Case III								
24	2X75W	1.30	27	3993	80.4	1	2016	1
48	2X75W	1.30	27	3190	77.0	4		1
72	2X75W	1.30	27	2854	79.0	0.5	3046	1
96	2X75W	1.30	27	2324	79.3	4	2381	1
168	2X75W	1.30	27	1911	94.0	0.5	2317	1
192	2X75W	1.30	27	1887	96.1	0.5	1684	1
Case IV								
24	2X75W	1.30	27	2036	99.9	6	757	1
48	2X75W	1.30	24	2149	99.8	76	591	1
144	2X75W	1.30	20	1778	98.1	5	876	2
168	2X75W	1.30	20	1754	98.1	7	852	7

Case I : Reactor with settler (recycle rate = 70 mL/min)

Case II : Reactor with cell recycle and settler in the same loop (recycle rate = 450 mL/min).

Case III: Reactor with cell recycle and settler in the same loop (recycle rate = 450 mL/min) and 50% bleed.

Case IV : Reactor with cell recycle (recycle rate = 450 mL/min) and settler (recycle rate = 70 mL/min) in different loop and 50% bleed.

retention time of only 20 min was required to remove essentially 100 percent of the H_2S from a synthetic syngas stream containing 2.5 percent H_2S . Just as important essentially 100 percent of the sulfur product was produced as elemental sulfur instead of sulfate. The *C. thiosulfatophilum* system will be very useful along with *R. rubrum* in removing H_2S and converting CO and water to H_2 .

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