

BIOLIQUEFACTION OF COAL SYNTHESIS GAS

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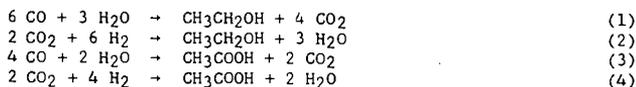
INTRODUCTION

Synthesis gas, a mixture of primarily CO, H₂ and CO₂, is a major building block in the production of fuels and chemicals. The gas may be produced from several sources, including coal, oil shale, tar sands, heavy residues, biomass or natural gas. Most synthesis gas is produced today by catalytic reforming of natural gas, although the partial oxidation of heavy liquids is also practiced (Graboski, 1984). Only a small percentage of the synthesis gas currently produced is by gasification of solid fuel. However, because of the large reserves of coal in the United States (300 year supply at the current consumption rate (Specks and Klussman, 1982)), synthesis gas production from coal will become an important technology in the future.

Coal gasification, which is a combination of pyrolysis and combustion reactions (Simbeck *et al.* 1982), produces a gas consisting of more than 50 percent H₂ and CO, the balance being a mixture of CO₂, CH₄, H₂S, COS and nitrogen compounds. The actual composition depends upon process conditions and the coal that is employed. The raw gas has a low to medium Btu content, with a heating value of 160-450 Btu/SCF, depending on whether air or oxygen is used during gasification (Coffin, 1984). Following quenching and purification, the synthesis gas contains 25-35 percent H₂, 40-65 percent CO, 1-20 percent CO₂, 0-7 percent CH₄ and other compounds in small quantities.

Catalytic processes may be used to convert syngas into a variety of fuels and chemicals, such as, methane, methanol, formaldehyde, acetic acid, etc. (Courty and Chaumette, 1987). Microorganisms may also be used to convert synthesis gas components into fuels and chemicals. Biological processes, although generally slower than chemical reactions, have several advantages over catalytic processes, such as higher specificity, higher yields, lower energy costs and generally greater resistance to poisoning. Furthermore, the irreversible character of biological reactions allows complete conversion and avoids thermodynamic equilibrium relationships.

Clostridium ljungdahlii, Strain PETC, was originally isolated from animal waste in the University of Arkansas laboratories, and is the only known organism capable of producing ethanol from CO, CO₂, and H₂ in synthesis gas (Barik *et al.* 1988). The overall stoichiometry for the formation of ethanol and acetate from CO and H₂/CO₂ has been established as (Vega *et al.* 1989a):



However, under optimal growth conditions, the organism produces acetate in favor of ethanol, with acetate:ethanol product ratios as high as 20:1 (Vega *et al.* 1989a). Research has concentrated on improving the product ratio in favor of ethanol using techniques found to be successful in boosting solvent production by other clostridial species. Improvements in solvent formation over acid production by clostridia have been obtained by utilizing nutrient limitation (Bahl *et al.*, 1986), reducing agent addition (Rao *et al.* 1987; Rao and Mutharasan, 1988), pH shift (Holt *et al.*, 1984; Huang *et al.*, 1986), hydrogen addition (Su *et al.*, 1981) and alternate medium constituents.

The purpose of this paper is to present results of batch and continuous laboratory studies with *C. ljungdahlii* in converting CO, CO₂ and H₂ in synthesis gas to ethanol. In addition, the effects of the sulfur gases H₂S and COS on growth, substrate uptake and product formation are presented and discussed.

MATERIALS AND METHODS

Organism and Medium. *Clostridium ljungdahlii*; Strain PETC, was originally isolated from chicken waste in the University of Arkansas laboratories, and later identified and characterized by Dr. R. S. Tanner, University of Oklahoma, Department of Botany and Microbiology. The culture was stored in a non-shaking incubator (Precision Scientific, Chicago, IL) at pH 5 and 37°C on a basal medium and synthesis gas (65% CO, 24% H₂ and 11% CO₂), and transferred every two weeks.

Equipment and Procedures. Medium preparation was carried in an atmosphere of 80% N₂ and 20% CO₂, as described by Hungate (1969) and Ljungdahl and Wiegel (1986). The initial pH was adjusted to 4.0-4.5 with HCl. Batch experiments were carried out in serum stoppered bottles with working volumes of 158 mL (Wheaton Scientific, Millville, NJ) or 1218 mL (Bellco Glass, Inc., Vineland, NJ). Continuous experiments were performed in Bioflo fermenters (New Brunswick Scientific, New Brunswick, NJ), modified for anaerobic operation. The medium used in the fermentations for the kinetic analyses contained yeast extract, vitamins, and minerals. The medium in continuous reactor studies and sulfur tolerance studies contained no yeast extract and minimal B-vitamins.

Analytical Procedures. Cell concentrations (in mg/L) were determined by comparing optical density readings at 580 nm in a Bausch and Lomb (Milton Roy Company, Rochester, NY) Spectronic 21 spectrophotometer with a standard calibration curve. Gas compositions were obtained by gas chromatography with a 180 cm Carbosphere, 60/80 mesh, column. Liquid analyses were performed by gas chromatography on previously acidified samples in a 60 cm column packed with Porapak QS at 180°C. 1-Propanol was used as the internal standard during liquid phase analysis after first verifying that 1-propanol was not present as a product.

RESULTS AND DISCUSSION

Development of a Kinetic Model. Figures 1 and 2 show cell concentration and substrate (CO) profiles for the conversion of CO to ethanol and acetate by *C. ljungdahlii* in batch culture. Initial CO partial pressures ranging from 1.0-1.6 atm in synthesis gas were used in order to study the effects of CO on cell growth and substrate uptake. A medium containing 0.01% yeast extract was used in this study.

Figure 1 shows that cell growth was essentially the same at each CO partial pressure up to a batch fermentation time of 100 h. At this time, the cell concentration increased with increasing CO partial pressure. The cell yield on CO, $Y_{X/S}$, was found to be 0.79 g cells/mol CO. The time for complete CO utilization was essentially constant with CO partial pressure (Figure 2). Also, the rate of CO utilization, as obtained from the slopes of the plots, was essentially constant with initial CO partial pressure. Product profiles (data not shown) showed ethanol to acetate molar product ratios of approximately 1:10 regardless of CO partial pressure due to the presence of yeast extract.

A kinetic analysis was performed on the data to determine kinetic parameters for growth and CO uptake utilizing a modified Monod model to include substrate inhibition (Andrews, 1969):

$$\mu = \frac{\mu_m P_{CO}^L}{K_p + P_{CO}^L + (P_{CO}^L)^2/W} \quad (5)$$

and

$$q_{CO} = \frac{q_m P_{CO}^L}{K'_p + P_{CO}^L + (P_{CO}^L)^2/W'} \quad (6)$$

The parameters μ_m , q_m , K_p , K'_p , W , and W' are kinetic parameters to be determined. A similar set of equations may be written for the uptake of H_2 , if desired.

The procedure for finding the kinetic parameters involves first finding the mass transfer coefficient, K_{La} , via material balance on the mass transfer-controlled gas-liquid system. The estimation of K_{La} involves finding the volumetric CO disappearance in the closed system, $-(1/V_L) dN_{CO}/dt$, and plotting it as a function of the partial pressure of CO in the gas phase. If part of the data fall on a straight line, mass transfer limiting conditions may be assumed. This generally occurs at low CO partial pressures or at high cell concentrations. The procedure is demonstrated in Figure 3. As noted in the figure, K_{La}/H equals 8.55 mmol CO/atm·L·h.

Once K_{La}/H is determined, the dissolved CO tension, P_{CO}^L (analogous to the dissolved CO concentration in the liquid phase), is found for situations where mass transfer is not controlling. The parameters in Equations (5) and (6) may then be found by rearranging the equations and performing a quadratic regression as illustrated in Figures 4 and 5 for the specific growth rate and specific uptake rate, respectively. A detailed presentation of this procedure has been shown previously for the bacterium *Peptostreptococcus productus* (Vega et al. 1989b).

Straight lines are obtained in plotting either P_{CO}^L/μ or P_{CO}^L/q as a function of P_{CO}^L (Figures 4 and 5), indicating that substrate inhibition was unimportant at least for $P_{CO}^L \leq 1.1$ atm. Furthermore, the intercepts on the

ordinates in both figures were essentially zero, indicating that K_p and K_p were negligible in comparison to P_{CO} . Thus, Equations (5) and (6) reduce to zero-order equations for *C. ljungdahlii* grown on CO, with $P_{CO} \leq 1.1$ atm.

$$\begin{aligned} \mu &= \mu_m = 0.04 \text{ h}^{-1} \\ \text{and} \\ q &= q_m = 42.7 \text{ mmol CO/g cell}\cdot\text{h} \end{aligned}$$

If the specific uptake rate of CO is converted to a carbon mass basis, a value of 0.22 g C/g cell·h is obtained for q_m , which is comparable to the rate of glucose uptake by *Saccharomyces cerevisiae* with a q_m of 0.27 g C/g cell·h (Vega, 1985). This rate indicates that *C. ljungdahlii* has reaction rates equivalent to other organisms that are used for commercial fermentations.

THE USE OF CELL RECYCLE IN THE CSTR

A cell recycle apparatus was used in conjunction with a standard CSTR as a method to increase the cell concentration inside the reactor. This is particularly important since total product formation with *C. ljungdahlii* has been shown to be proportional to the cell concentration inside the reactor.

Fermentations were carried out in a 1.6 L CSTR with cell recycle. The total liquid volume in the reactor was 1.0 L, consisting of basal medium without yeast extract and one-half B-vitamins. Ammonium phosphate dibasic was used to enhance cell growth. The temperature of the reactor was held constant at 37°C and the agitation rate was 400 rpm. The gas flow rate was 16.5 mL/min and the liquid flow rate was 300 mL/d.

Figures 6 and 7 show cell concentration and product concentration profiles for the CSTR with cell recycle. In these experiments, the CO conversion was rather low. As is shown in Figure 6, the maximum cell concentration reached was 1300 mg/L at 800 h, increasing significantly from the 200 mg/L concentration after 300 h. The product concentrations, shown in Figure 16, changed significantly with time. At a time of 300 h, the ethanol concentration was about 4 g/L and the acetate concentration was nearly 2 g/L. At a later fermentation time of 800 h, the ethanol concentration reached 15 g/L with an acetate concentration of 4 g/L. Other cell recycle studies have shown a 6 g/L ethanol concentration with a corresponding zero acetate concentration.

SULFUR GAS TOLERANCE OF *C. LJUNGDAHLII*

Many bacterial cultures capable of converting CO to products have been found to be quite tolerant of the sulfur gases H₂S and COS (Vega et al., 1990; Smith et al., 1991). *Peptostreptococcus productus*, for example, which converts CO to acetate, is able to successfully convert CO to acetate in the presence of 19.7 percent H₂S or COS after culture acclimation. The methanogen *Methanobacterium formicicum*, on the other hand, is able to tolerate only 6.6 percent H₂S or COS. However, even this latter result is encouraging, since typical coal-derived synthesis gas contains only 1-2 percent sulfur gases, mainly as H₂S.

C. ljungdahlii, grown in the presence of Na₂S in place of cysteine-HCl as the reducing agent for several weeks, was evaluated for its tolerance to H₂S and COS in batch bottle experiments. The 155 mL bottles containing 50 mL of liquid medium devoid of yeast extract and adjusted to pH 4.3, were first gassed with synthesis gas to a pressure of 10.7 psig. The desired amount of H₂S or COS (2.5 mL-20mL) at 1 atm was then added. This batch system was allowed to equilibrate overnight. As a final step 10 mL of *C. ljungdahlii* were added prior to incubation at 34°C.

The effects of H₂S on growth and substrate uptake by *C. ljungdahlii* are shown in Figures 8 and 9, respectively. As is noted in Figure 8, growth was not significantly slowed at H₂S concentrations below 5.2 percent. Upon the addition of 9.9 percent H₂S, however, growth essentially stopped. Similar results are noted with substrate uptake in the presence of H₂S (see Figure 9). The presence of H₂S slowed the rates of substrate uptake only slightly up to an H₂S concentration at 5.2 mole percent. Similar results were obtained with concentrations of COS up to 5.2 percent.

These concentrations are for in excess of maximum sulfur gas concentrations possible in coal synthesis gas. It should also be realized that dramatic effects can be obtained with prolonged sulfur gas acclimation. *P. productus*, for example, was only marginally tolerant of H₂S and COS in initial studies. Concentrations up to 20 percent were tolerated after a period of acclimation to the sulfur gases.

CONCLUSIONS

The anaerobic bacterium *Clostridium ljungdahlii* has been shown to be effective in converting CO, CO₂ and H₂ to ethanol. Rates of carbon uptake by *C. ljungdahlii* comparable to the rate of carbon uptake by the yeast *Saccharomyces cerevisiae* have been obtained. A CSTR cell recycle system has been shown to be effective in permitting the cell concentrations necessary for high concentrations of ethanol. An ethanol concentration of 13 g/L with a corresponding acetate concentration of 4 g/L has been attained. Alternatively, an ethanol concentration of 6 g/L without the presence of acetate has been reported. Finally, *C. ljungdahlii* has been shown to be tolerant of H₂S or COS in concentrations exceeding typical levels in synthesis gas.

LIST OF REFERENCES

- Andrews, J. F. (1969), *Biotechnol. Bioeng.* 10, 707.
Bahl, H., Gottwald, M., Kuhn, A., Rale, V., Andersch, W., and Gottschalk, G. (1986), *Appl. Environ. Microbiol.*, 52, 167.
Barik, S., Prieto, S., Harrison, S. B., Clausen, E. C., and Gaddy, J. L. (1988), *Appl. Biochem. Biotechnol.*, 18, 363.
Coffin, J. M., (1984), *Energy Progress*, 4, 131-137.
Courty, Ph. and Chaumette, P. (1987), *Energy Progress*, 7, 23.
Graboski, M. S., (1984) In Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals, R. G. Herman (ed.) Plenum Press, New York, pp. 37-50.
Holt, R. A., Stephens G. M., Morris, J. G. (1984), *Appl. Environ. Microbiol.*, 48, 1166.
Huang, L., Forsberg, C. W., and Gibbons, L. N. (1986), *Appl. Environ. Microbiol.* 51, 1230.

- Hungate, R.E. (1969), *Meth. Microbiol.* **3B**, 117.
- Ljungdahl, L. G., and Wiegel, J. (1986), Manual of Industrial Microbiology and Biotechnology (Demain, A. L., and Solomon, N. A., eds.), American Society for Microbiology, pp 84-96.
- Rao, G. Ward, P. J. and Mutharasan, R. (1987), *Annals N. Y. Acad. Sci.* **506**, 76.
- Rao, G. and Mutharasan, R. (1988), *Biotechnol. Letters*, **10**, 129.
- Simbeck, D. R., Dickenson, R. L., Moll, A. J. (1982), *Energy Progress*, **2**, 42.
- Smith, K. D., Klasson, K. T., Ackerson, M. D., Clausen E. C. and Gaddy, J. L. (1991) *Appl. Biochem. Biotechnol.*, **28/29**, 797.
- Specks, R. and Klussmann, A. (1982) *Energy Progress*, **2**, 60-65.
- Su, T. M., Lamed, R., and Lobos, J. H. (1981), "Effect of Stirring and H₂ on Ethanol Production by Thermophilic Fermentation," Proceedings of the Second World Congress of Chemical Engineering and World Chemical Exposition, Montreal, p. 356.
- Vega, J. L. (1985), M. S. Thesis, University of Arkansas.
- Vega, J. L., Prieto, S., Elmore, B. B., Clausen, E. C., and Gaddy, J. L. (1989a), *Appl. Biochem. Biotechnol.* **20/20**, 781.
- Vega, J. L., Clausen, E. C., and Gaddy, J. L. (1989b), *Biotechnol. Bioeng.* **34**, 774.
- Vega, J. L., Klasson, K. T., Kimmel, D. E., Clausen E. C. and Gaddy, J. L. (1990) *Appl. Biochem. Biotechnol.*, **24/25**, 329

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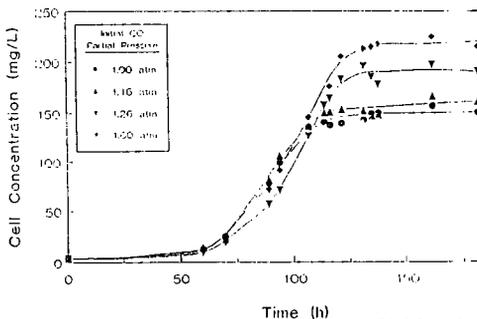


Figure 1. Cell Concentration Profile for the Fermentation of CO by *G. Ljungdahlii*

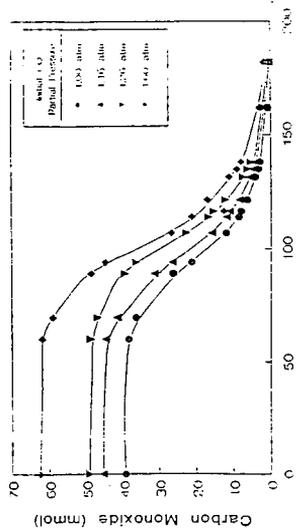


Figure 2. CO Profile for the Fermentation of CO by *S. limosus*.

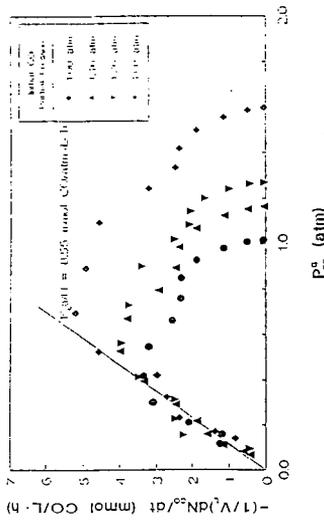


Figure 3. Determination of the Mass Transfer Coefficient for the Fermentation of CO by *S. limosus*.

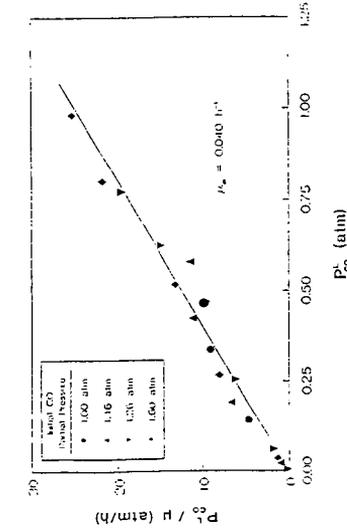


Figure 4. Determination of Monod Kinetics for the Rate of Cell Growth by *S. limosus*.

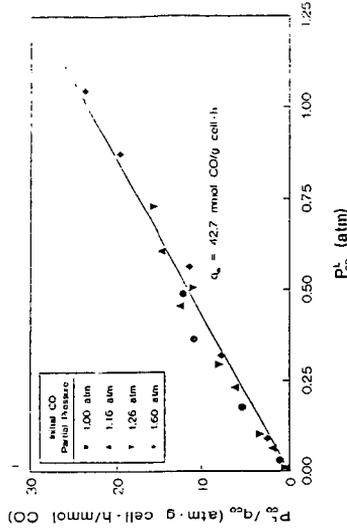


Figure 5. Determination of Monod Kinetics for the Rate of CO Uptake by *S. limosus*.

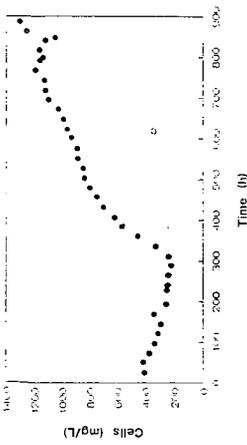


Figure 7. Ethanol and Acetic Acid Concentration Profiles for *E. Limbachi* in the CSTB with Cell Recycle

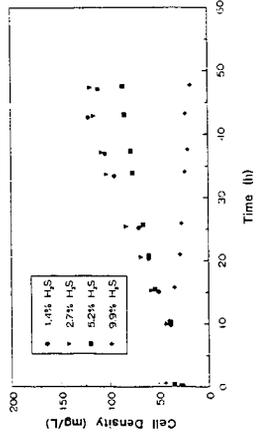


Figure 8. Cell Concentration Profile for *E. Limbachi* in the CSTB with Cell Recycle

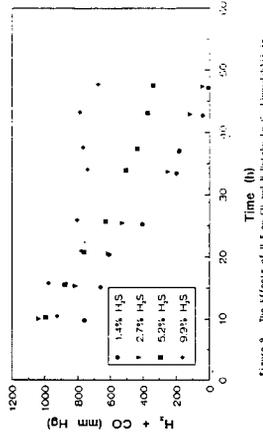


Figure 9. The Effects of H₂S on CO and H₂S in Batch Culture

