AIIM

Association for Information and Image Management
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

2

DOE/PC/92117--T8

Report No. PETC-SYN 25-94

BIOCONVERSION OF COAL DERIVED SYNTHESIS GAS TO LIQUID FUELS

Contract No. DE-AC22-92PC92117

Quarterly Technical Progress Report
January 1, 1994 - March 31, 1994

Contract Date: September 29, 1992
Anticipated Completion Date: September 28, 1994
Government Award for 1993-94; $215,085

Program Manager
Dr. Malvina Farcasiu
Department of Energy
Pittsburgh Energy Technology Center

Contracting Officer's Representative (COR)
Dr. Shelby Rogers
DOE-PETC

Principal Investigators
Mahendra K. Jain
R. Mark Worden
Hans Grethlein

Project Personnel
Dan Beacom
Michael Guettler
Lois Cutting
Andrew Grethlein

Michigan Biotechnology Institute
3900 Collins Road, P.O. Box 27609
Lansing, MI 48910-7609
Tele.: 517-336-4626
Fax: 517-337-2122

April 15, 1994

OBJECTIVES:

The overall objective of the project is to develop an integrated two-stage fermentation process for conversion of coal-derived synthesis gas to a mixture of alcohols. This is achieved in two steps. In the first step, *Butyribacterium methylotrophicum* converts carbon monoxide (CO) to butyric and acetic acids. Subsequent fermentation of the acids by *Clostridium acetobutylicum* leads to the production of butanol and ethanol.

The tasks for this quarter were:

- Development / isolation of superior strains for fermentation of syngas.
- Optimization of process conditions for fermentation of syngas.
- Evaluation of bioreactor configuration for improved mass transfer of syngas.
- Selection of cell-support material for gas lift fermentation.
- Recovery of carbon and electrons from H_2-CO_2.

SUMMARY OF TECHNICAL PROGRESS

- Isolation of CO-utilizing anaerobic strains is in progress.
- Syngas batch fermentation pH shift used to maximize butyrate production.
- H_2/CO_2 (50/50) batch fermentation resulted in acetate production.
- Celite selected for cell-support materials for gas lift fermentation.
- Cell recycle fermentation on syngas initiated.

TECHNICAL PROGRESS REPORT

2. Development of Superior Strains

No new isolates or strains superior than the current *B. methylotrophicum* strain has been obtained yet. The isolation and mutation work is being continued.

3. Development and Optimization of Process Conditions for Fermentation of Syngas Containing Sulfur Gases in a Chemostat Fermentation System

3a. Batch Fermentation of Synthesis Gas

Our initial studies on syngas batch fermentation by *B. methylotrophicum* showed that pH regulation during the stationary phase increased the final butyrate to acetate ratio from < 0.1 to 0.2 (Annual Report to DOE, No. PETC-SYN-17-93). It was hypothesized that the effect of shifting the pH from 6.8 to 6.0 on butyrate to acetate ratio might be more dramatic if the shift occurred late in the growth phase. To examine the effect of pH shift during late growth phase, syngas was batch fermented in a 2-liter fermentor. Figure 1 exhibits an immediate and very significant change in product profile during the course of fermentation. *B. methylotrophicum* also showed better growth on syngas than on 100%

CO. Figure 2 represents the effect of pH shift on the ratio of butyrate to acetate. The final butyrate to acetate ratio of 1.3 demonstrates a significant shift of carbon and electrons towards butyrate. The timing of the pH shift seems to play a significant role in selectivity towards butyrate.

4. Integrate, Operate and Optimize the Two-Stage Fermentation of Synthesis Gas to Alcohols on the Bench-Scale

A cell recycle system as used by Grethlein (1991) was constructed as the first stage of the two-stage fermentation of synthesis gas. During this stage synthesis gas is converted to acids and alcohols by the CO strain of *B. methylotrophicum*. A schematic of the system is shown in Figure 3.

Initially the pH is set at 6.8. Once steady-state is reached (4-5 weeks), the pH is varied to determine the effect on the fermentation profile. Figure 4 shows the product profile during the initial two weeks of fermentation under the cell recycle system. Mechanical difficulties resulted in the loss of the culture after day 17. The system has been reset and the fermentation is in progress.

5. Evaluation of Bioreactor Configuration for Improved Mass Transfer of Syngas.

Gas lift and trickle bed reactors using immobilized *B. methylotrophicum* cells will be used to maximize mass transfer.

Gas-Lift Fermentor Design and Operation

Based on *B. methylotrophicum* immobilization and support fluidization properties, celite (14 mesh) has been chosen over molecular sieves, alumina, ion exchange resin as the immobilization support for the gas lift fermentation system. Alumina was eliminated due to difficulty in fluidization. Molecular sieves and ion exchange resin were poorer in immobilization of *B. methylotrophicum*. Celite was chosen for its superior cell immobilization properties and adequate fluidization.

8. Develop Process Conditions and Optimization of Fermentation of H_2-CO_2 by *B. methyltrophicum* to Reduce Loss of Carbon and Electrons.

After the consumption of CO, the exit synthesis gas will be rich in lost carbon (CO_2) and electrons (H_2). The purpose is to recover the lost carbon and electrons. Previous batch fermentations of H_2-CO_2 performed on 80/20 mixtures showed that *B. methylotrophicum* can ferment the H_2/CO_2 mixture (DOE Report, PETC-SYN-17-93). Calculation based on the composition of raw synthesis gas shows that the ratio of H_2 and CO_2 in the exit gas would be closer to 50:50. Using a *B. methylotrophicum* adapted on H_2-CO_2 fermentation was conducted to verify recovery of carbon and electrons from the H_2:CO_2 (50:50) mixture. Figure 5 exhibits the fermentation product profile at pH 6.8. The fermentation was highly selective for acetate. In a second batch fermentation pH will be regulated under the late log phase of growth to determine if butyrate selectivity is increased. Based on these data, we will calculate the extent of carbon and electron recovery under these conditions.

D. DIFFICULTIES/PROBLEMS

Sulfur gas containing synthesis gas is very chemically harsh on natural rubber tubing. We have switched to the more chemically resistant viton tubing. Viton tubing has poorer elasticity and mechanical strength resulting in operational difficulties of longer term systems.

E. PERSONNEL CHANGES

Dr. Hans Grethlein, Senior Engineer, retired during this quarter. Dr. Andrew Grethlein will provide additional support in the task related to pervaporation.

REFERENCES

1. Grethlein, Andrew S. 1991. Doctoral Dissertation, Michigan State University, East Lansing, MI

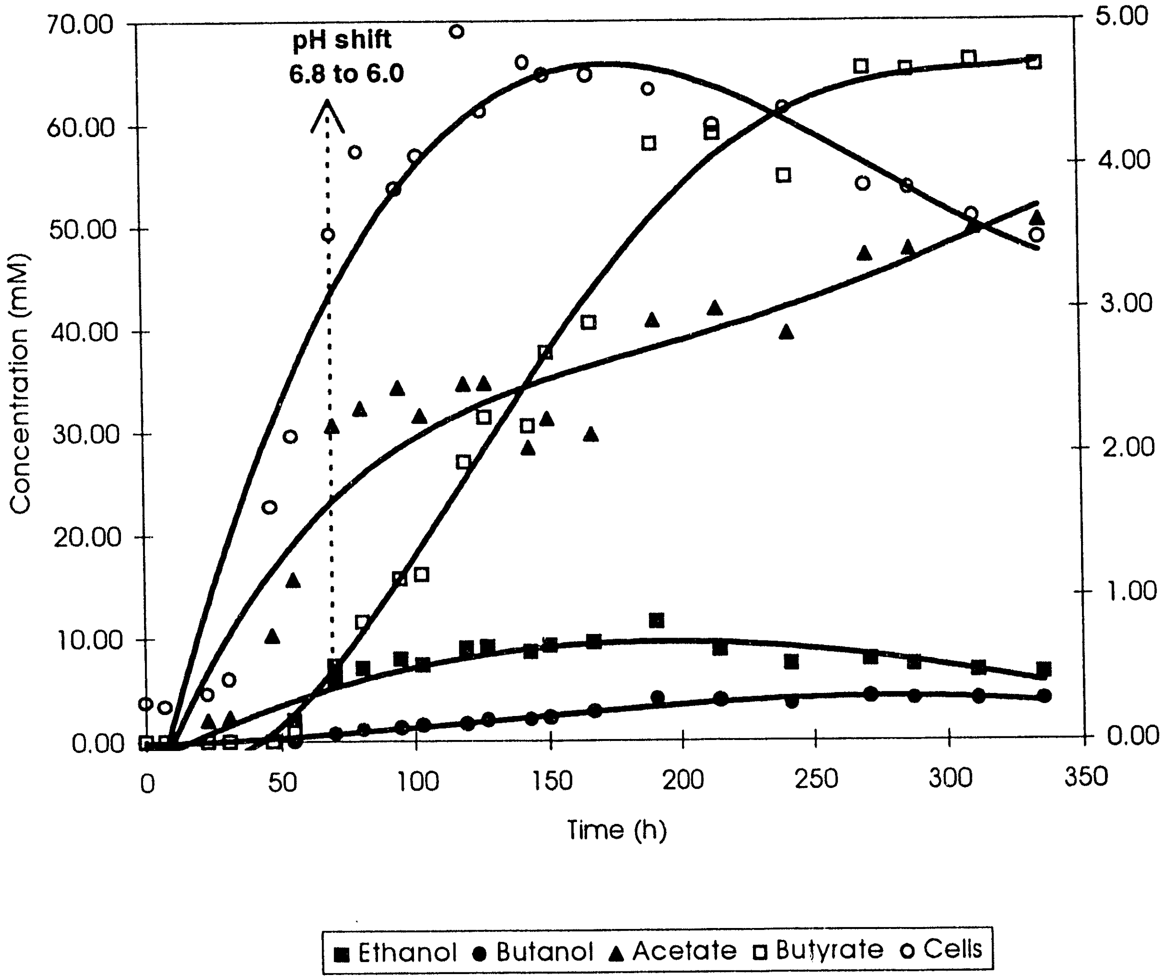

Figure 1. Growth and product profiles during fermentation of synthesis gas by *B. methylotrophicum*.

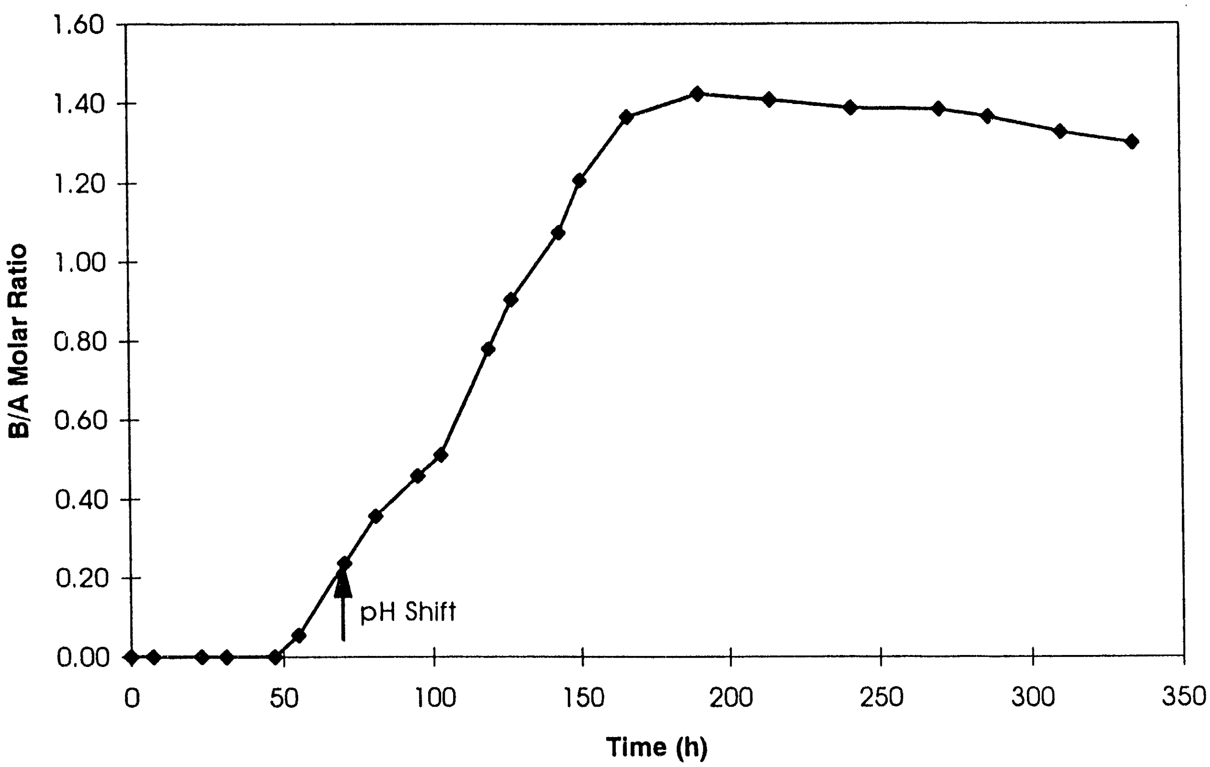

Figure 2. Effect of late log phase pH shift on butyrate to acetate (B/A) ratio during synthesis gas fermentation.

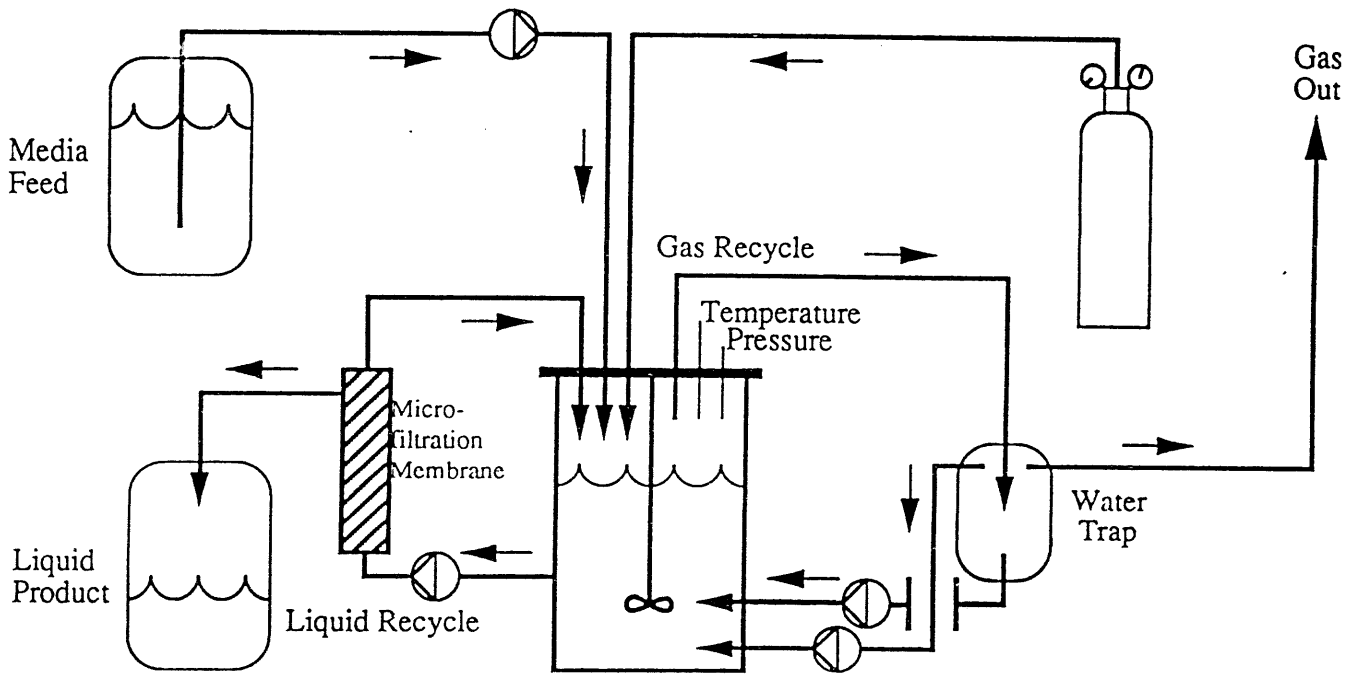

Figure 3. **Schematic diagram of continuous, cell recycle synthesis gas fermentation system.**

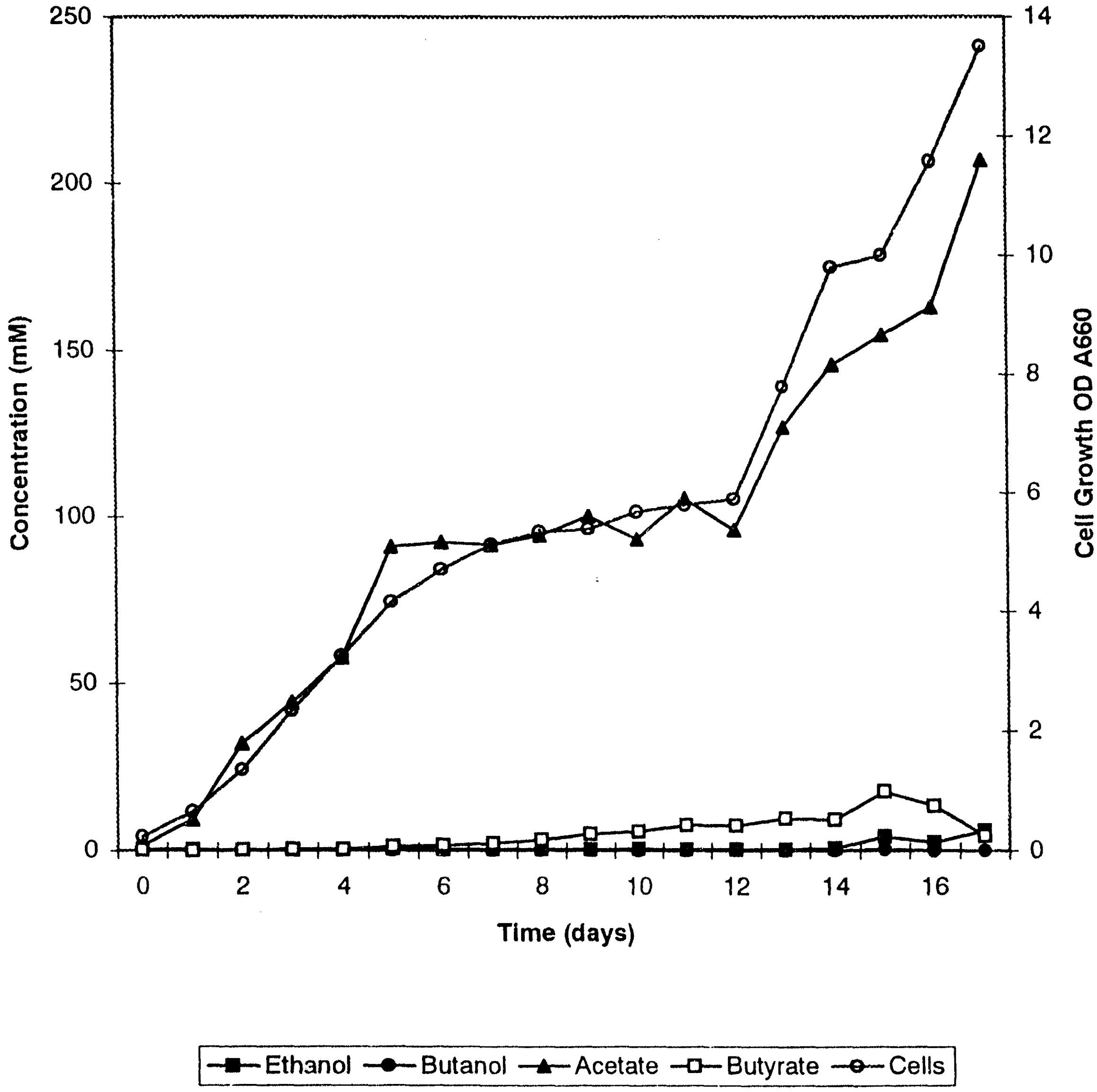

Figure 4. Initial fermentation product profile during a cell recycle *B. methylotrophicum* synthesis gas fermentation.

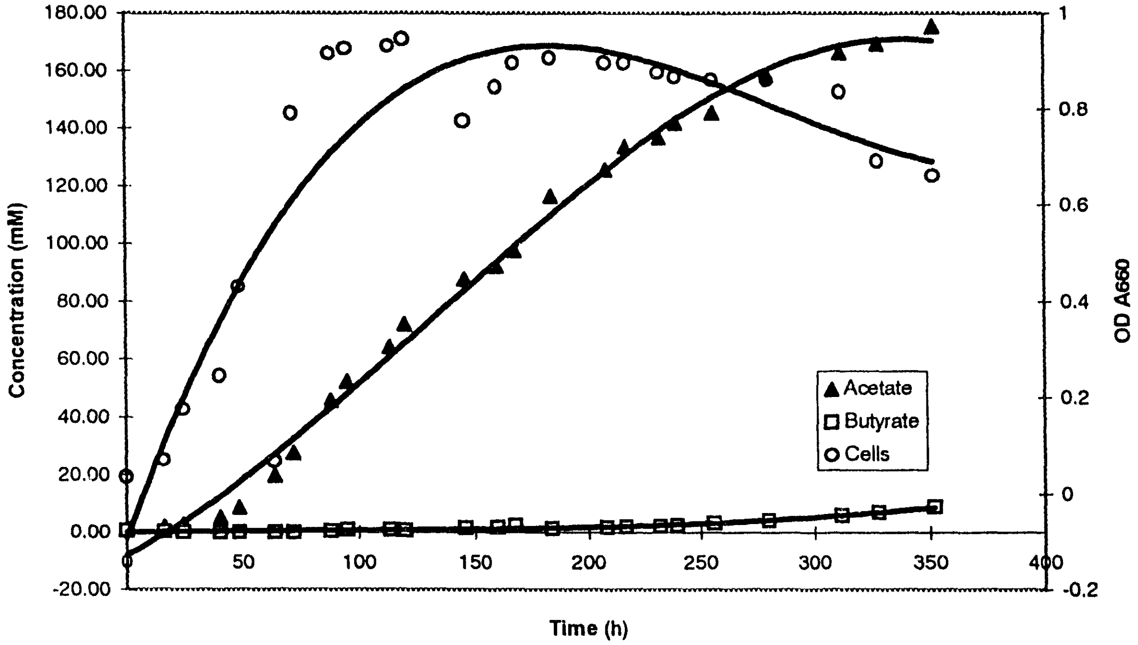

Figure 5. **Fermentation profile of *B. methylotrophicum* on 50/50 H_2-CO_2 at pH 6.8.**

DATE
FILMED
9/21/94

END