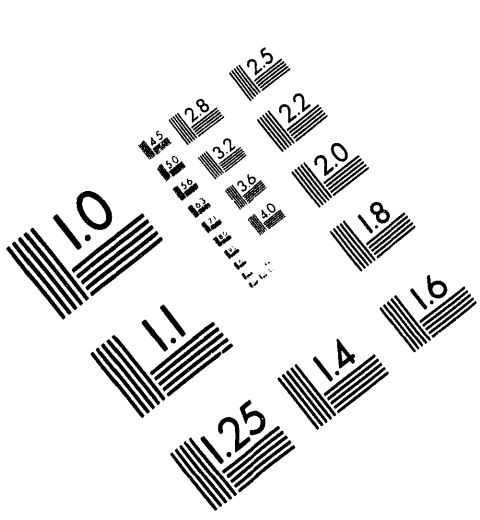

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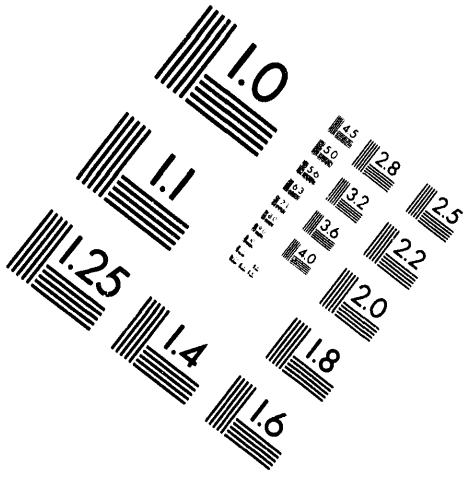

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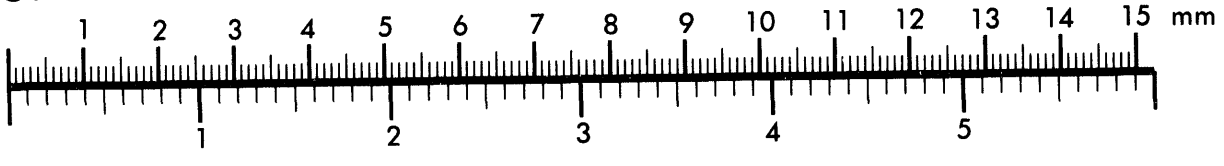

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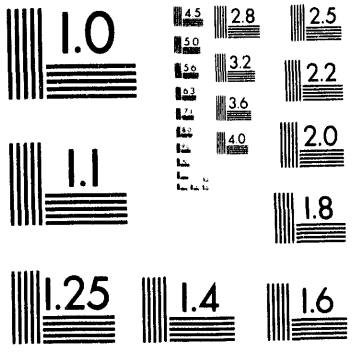

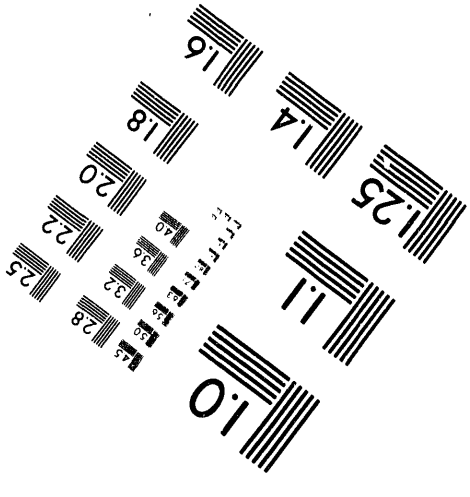

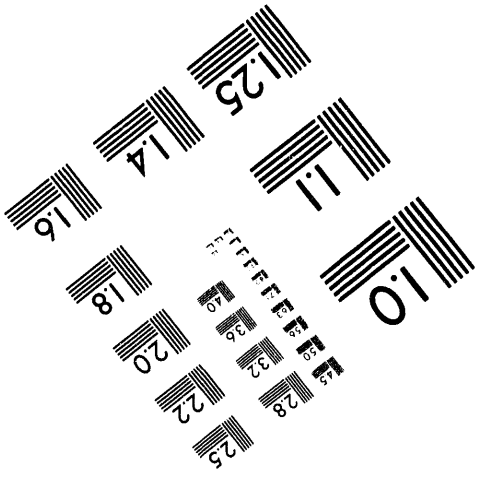

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DOE/PC/92117--T9

Report No. PETC-SYN 29-94

BIOCONVERSION OF COAL DERIVED SYNTHESIS GAS TO LIQUID FUELS

Contract No. DE-AC22-92PC92117

Quarterly Technical Progress Report
April 1, 1994 - June 30, 1994

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

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July 18, 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.
- Evaluation of bioreactor configuration for improved mass transfer of syngas.
- Recovery of carbon and electrons from H_2-CO_2.
- Initiation of pervaporation for recovery of solvents
- Selection of solid support material for trickle-bed fermentation

SUMMARY OF TECHNICAL PROGRESS

- Enhanced butyrate production during H_2/CO_2 (50/50) batch fermentation.
- Isolation of CO-utilizing anaerobic strains is in progress.
- Pressure (15 psig) fermentation evaluated as a means of increasing CO availability.
- Polyurethane foam packing material selected for trickle bed solid support.
- Cell recycle fermentation on syngas operated for 3 months. Acetate was the primary product at pH 6.8.
- Trickle bed and gas lift fermentor designs modified after initial water testing.
- Pervaporation system constructed. No alcohol selectivity shown with the existing membranes during initial start-up.

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

Pressure CO Fermentation

Recent work by Klasson et al. (1993) showed increased ethanol production by *Clostridium ljungdahlii* with increased CO pressure. An effort was undertaken to determine if a similar phenomenon was exhibited by *B. methylotrophicum*. Straight CO was chosen over synthesis gas due to the corrosive effects of syngas on our gasket materials and the subsequent potential for a leakage of large quantities of gas under elevated pressure.

Two fermentations of *B. methylotrophicum* on CO at 15 psig were conducted. The pH was shifted from 6.8 to 6.0 after log phase growth in the first batch and during log phase growth in the second batch. The profiles of the two batches are shown in Figure 1.

Neither batch resulted in a cell concentration approaching that seen on synthesis gas (DOE Report, PETC-SYN-25-94). Shifting the pH from 6.8 to 6.0 did not enhance selectivity for butyrate in either batch under pressure and appears to limit the growth when applied during the log phase of the second batch. Increased concentration of CO by raising the pressure to 15 psig did not seem to improve *B. methylotrophicum* fermentation.

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

The cell recycle system restarted on April 6, 1994 was still in operation as of June 30, 1994. The system was initially restarted on 100% CO to minimize the corrosive effects of the synthesis gas. After reaching an initial high cell density (OD A_{660} >13), the culture underwent some lysis. The system was switched to synthesis gas, but a low cell density steady-state (OD A_{660} =5) was reached. The culture was intentionally washed out to encourage new growth, but the re-established steady-state showed only low cell density. We were concerned that the culture was utilizing yeast extract as a carbon source, limiting the use of CO. To test this hypothesis, the yeast extract content of the feed was cut in half, to 0.1%. The culture responded by nearly doubling of cell density.

Acetate was formed as the primary fermentation product, with the exception of some butyrate production during the batching after the cell washout. The pH has been recently lowered to 6.0, but no results are available yet.

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

Initial water tests with the original design, utilizing the 3" diameter LH fermentor, required high liquid recirculation rates to fluidize the celite bed. Flow rates were in excess of 3 L/min. Given the previously observed effects of synthesis gas on the pump tubing, we concluded that such high flow rates is likely to result in a tubing failure. We have now obtained a 1" column designed as a fluid bed reactor which can be modified for gas lift operation. Water testing showed that a more reasonable flow rate of 200-300 ml/min was sufficient to fluidize the bed. A 2 L fermentor will be used as a flow through cell for pH control.

Trickle-Bed Fermentor Design and Operation

The LH fermentor has now been modified for use as the primary trickle bed reactor. A 2 L fermentor will be used as a flow through cell for pH control. Polyurethane packing foam was chosen as the solid support over other support materials such as pebbles and various rachig ring packing materials on the basis of visual *B. methylotrophicum* growth on the material in vials and recommendations from in-house trickle-bed experts. The foam is cut into 1 cm cubes.

7. Develop a Membrane-Based Pervaporation System for Continuous Removal of Alcohols from Fermentation Broth

The pervaporation system was constructed this quarter and testing of synthetic broth was initiated. No alcohol selectivity was observed using the experimental membranes obtained from Zenon. Efforts are underway to obtain other membranes and to improve the design and performance of the system.

8. Develop Process Conditions and Optimization of Fermentation of H_2-CO_2 by *B. methylotrophicum* 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 after fermentation would be closer to 50:50.

In the previous quarter a batch fermentation of H_2/CO_2 at pH 6.8 produced almost exclusively acetate (A). Figure 3 shows the fermentation profile of a batch run this quarter with a late log phase pH shift to pH 6.0. Selectivity for butyrate (B) was enhanced to a B/A molar ratio of 0.2. It demonstrates that *B. methylotrophicum* can ferment H_2-CO_2 to recover carbon and electrons from CO depleted synthesis gas to produce both C_2 and C_4 acids. These acids can be recycled to the synthesis gas fermentor or be converted to alcohols in the solventogenic fermentor.

D. DIFFICULTIES/PROBLEMS

We reported earlier (DOE Report No. PETC-SYN 25-94) that due to the nature of gaseous substrate (sulfur gases, components in syngas) we have been experiencing mechanical problems in operating and maintaining the reactor systems over a long period of time. We have been forced to keep resetting and repeating the same system in the hope of completing one good run to obtain meaningful and reliable results. Obviously, this has affected our progress and the schedule. We will continue to put in our best efforts to maintain these systems but it is hard to predict the forthcoming mechanical problems. Should we experience any additional problems it is likely that we will have to request for a no-cost extension to complete the on-going fermentation runs.

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

2. Klasson, K. T., M. D. Ackerson, E. C. Clausen and J. L. Gaddy. 1993. Biological Conversion of Coal and Coal-Derived Synthesis Gas. Fuel, 72(12): 1673-1678.

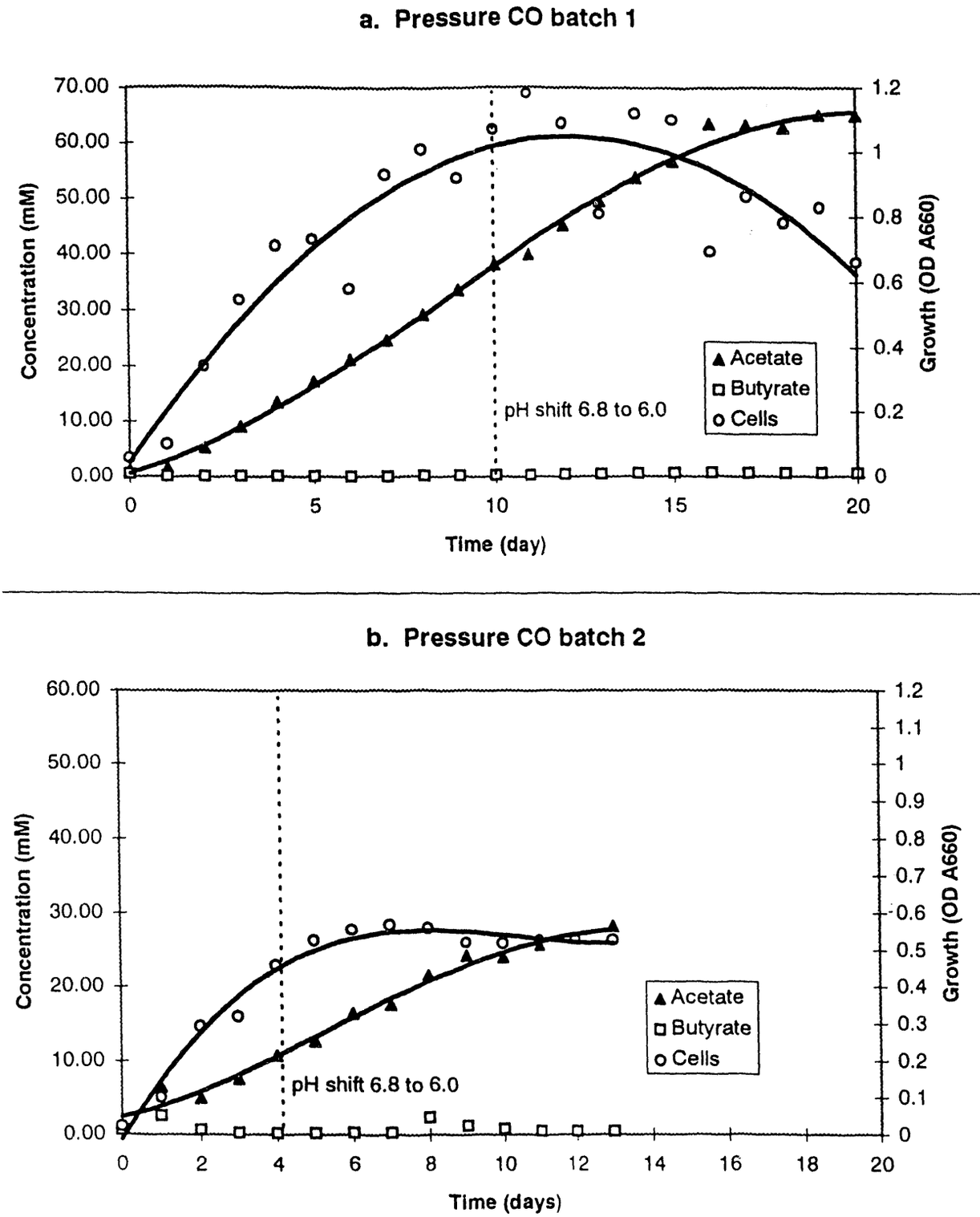

Figure 1. Profiles of batch fermentations of *B. methylotrophicum* on CO at elevated (15 psig) pressure.

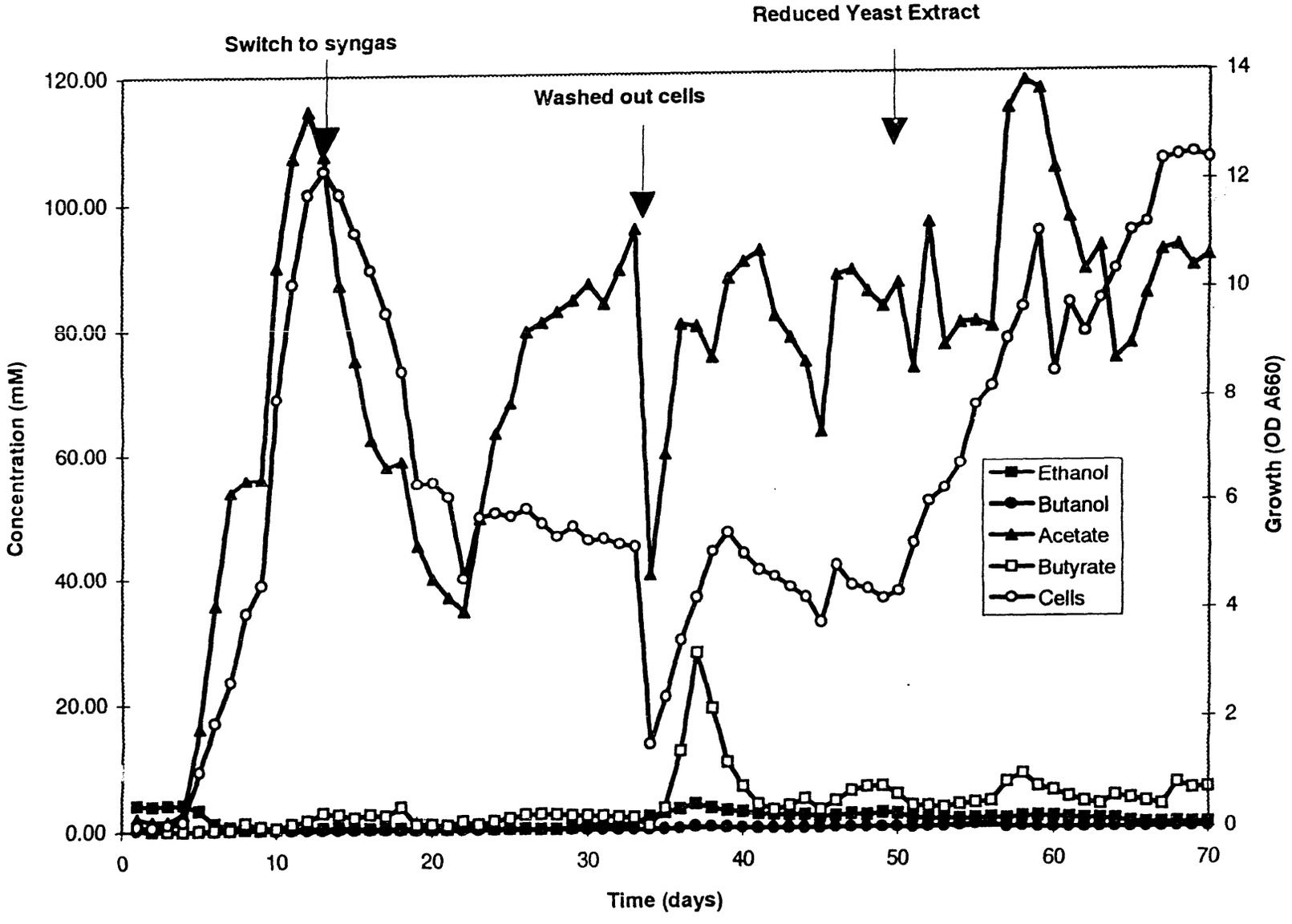

Figure 2. Fermentation profile of second *B. methylotrophicum* cell recycle on syngas.

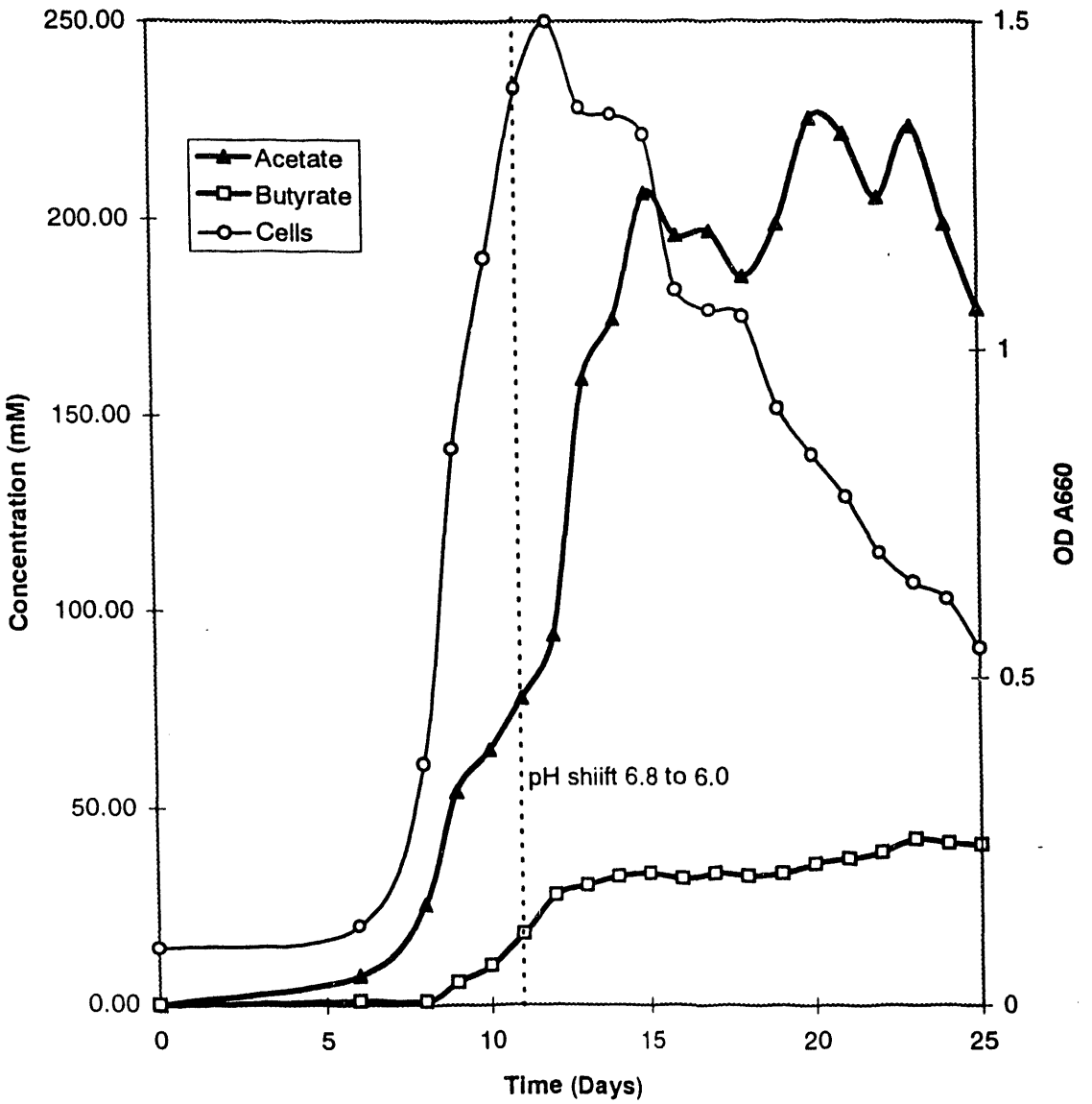

Figure 3. Fermentation profile of *B. methylotrophicum* on H_2/CO_2 (50:50) with late log phase pH shift.

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