ENERGY AND PROTEIN PRODUCTION
FROM PULP MILL WASTES

Annual Report
for the Period September 15, 1978-December 15, 1978

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June 15, 1978

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Prepared For
THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT E(11-1)-2983

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ABSTRACT

Effort was concentrated during the past quarter to define the extent of biological control necessary to achieve high production rates of methane. Although sustained production rates in excess of 100 cc/hr were consistently obtained in the previous quarter, the fermentation activity decreased with respect to productivity. All efforts during the past quarter proved ineffective in arresting the decline in productivity. Methane production now averaging 20 cc/hr is no better than productivity previously obtained on ozonated SSL with no supplemental methyl alcohol addition being added. Although it is still evident that supplemental methyl alcohol enhances methane production, the rate is now below the satisfactory or expected level. The fundamental conclusion one must draw from this quarter's results is that methane fermentation of simple oxygenated molecules is more efficient and produces a richer off-gas in terms of energy content than the same fermentation conducted on low molecular weight fragments obtained by the ozonation of SSL.

During the quarter two papers were prepared and accepted for publication in the Journal of Process Biochemistry and the Tappi Journal. These publications complement the papers presented previously at national meetings of American Institute of Chemical Engineers and the American Chemical Society.

BACKGROUND

Nearly three million tons of lignin derivatives and other soluble organic compounds are generated a waste by-product annually by the sulfite pulping process.

Conventional mechanical treatment of the waste liquor to prevent pollution consists of evaporation of the water and burning of the dried solids. Although some cooking chemicals are recovered and energy is generated by the combustion, the evaporation consumes 20 to 50 percent of the heat generated, the burning creates air pollution, and the evaporate has an objectionably high BOD due to the presence of volatile organic compounds.

Conventional biological treatments such as the activated sludge process, storage oxidation and aerated stabilization seek to avoid water removal. Although these methods effectively remove the low molecular weight organics, thus lowering the BOD, the levels of lignosulfonates and sulfur are not significantly reduced.

A newer biological treatment is fermentation by Torula yeast for protein production. Although this consumes the pentose and hexose sugars the levels of lignosulfonates and sulfur are not affected.

Research conducted at Michigan Technological University has attempted to degrade the lignosulfonates by continuous digestion with a mixed microbial culture containing the sulfur-reducing anaerobe Desulfovibrio Desulfuricans. This research indicated that the lignosulfonate molecule or its sulfur component is not readily metabolized.

The general lack of success with biodegradation of lignosulfonates suggests that a chemical pretreatment may be desirable. Stern and Gasner showed that ozonation of kraft mill waste liquor degraded its lignin derivatives and increased their susceptibility to fermentation. The Barber-Colman Company has shown that wet oxidation of sulfite paper-pulp waste also produces lower molecular weight compounds.

Both yeast growth and fermentation with Desulfovibrio should be

aided by chemical pretreatment. In addition, methane-producing anaerobes seem ideally suited for subsequent fermentation. Benson and Partansky have estimated that is 25% of the carbon in desugared spent sulfite liquor (DSSL) could be converted by methanogenesis, the caloric value of the annual production would be equivalent to that of forty billion cubic feet of natural gas. Many anaerobic bacteria (i.e. Methanobacterium ruminantium, methanococcus, Methanosarcina, Methanosperillum hungatii, Methanobacterium omelianskii) are methanogenes. Since 1975 work in this laboratory on the development of a process for converting the pollutants present in sulfite pulp mill waste to useful fuels and protein has been supported by a grant from the Energy Research and Development Administration (now the Department of Energy. The process as currently visualized is shown in Diagram 1. The primary yeast fermenter converts wood sugars and other assimilable organics into protein and CO₂. The ozonator modifies sulfur bonds and breaks down high molecular weight organics. The ozonated fragments are fed to the anaerobic digester where a mixed bacterial culture is employed because only a few specific organics can be utilized by methane bacteria and therefore other organisms (i.e. Desulfovibrio) are needed to develop the substrate for methane synthesis. A secondary yeast fermentation is included to permit digestion of any unassimilated ozonated fragments that can be utilized by Torula yeast. Any BOD remaining is removed by standard treating processes such as the activated sludge process or soil infiltration. During the anaerobic digestion some organic sludge, biological solids and lignin will be produced. The solids are recovered in a thickener and can, after dewatering, be burned as fuel if no higher value alternative is available. By virtue of the work thus far completed, we believe the following conclusions are justified:

1. Desugared spent sulfite liquor reacts readily with ozone to produce lower molecular weight organic fragments which can be metabolized by a variety of microorganisms. Ozonation removes color bodies and increases BOD.

2. Production of protein through growth of Torula yeast on DSSL is enhanced by ozonation. Longer ozonation times reduce this effect.

3. Production of methane by anaerobic fermentation is enhanced by ozonation. Longer ozonation times increase this effect.

STAFFING

During this quarter major project direction was furnished by Dr. E. T. Williams replacing principle investigator Dr. J. T. Patton, who is now Professor and Head, Department of Chemical Engineering, New Mexico State University. The co-principle investigator, Dr. M. F. Jurgensen, contributed approximately 5 percent of his time to project direction on the microbiological aspects of the research. Dr. Patton, also contributed 3 days to the project as a consultant. During the quarter it was necessary to replace Mr. Craig Bremmon, technologist in charge of microbiological research, and Mr. Sushil Dugar, Ph.D. candidate. Mr. Bremmon resigned to accept a position with Gulf Petroleum Corporation and Mr. Dugar, having completed the research necessary for his degree, left the University. Ms. Kathy Blue, a student in microbiology, was hired to replace Mr. Bremmon and a search is currently in progress for additional graduate students to fill the void left by Mr. Dugar.

RESULTS AND DISCUSSION

The most significant result, negative one, obtained this quarter was a steady decline in methane production over a period of 6 weeks. Gas rates which peaked at over 100 cc/hr during the past quarter steadily

declined to a steady-state value of 11 cc/hr for a substrate consisting of ozonated SSL supplemented by 0.5% methyl alcohol. Efforts to reverse this trend were unsuccessful. Addition of special growth supplements such as vitamins and minerals produced no response. Increases and decreases in dilution rate were similarly futile and even placing the fermenter on batch operation failed to achieve significant improvement. In fact, batch fermentation accelerated the decline in methane production. Plans to study techniques of producing fragmentation by ozonation were suspended until the fermentation problem had been resolved.

SUMMARY AND CONCLUSION

The results obtained this past quarter provide the stimulus and direction for work to be conducted during the next period. Past experience in the operation of anaerobic digesters for waste treatment indicates wide fluctuations in productivity is to be expected. Although the factors responsible for this are not fully indentified or well understood, it is possible that our research fermenters are behaving similarly. It is hoped that subsequent work will identify the factors responsible for the poor performance. This would be a valuable contribution to the design and operation of methane fermentaters in the waste treatment field.

The unexpected decrease in productivity and the added emphasis on defining the problem have caused the project to fall behind the progress projected in the milestone status chart. At this time the project has been successfully restaffed with the exception of one additional graduate student. This new staffing will allow the progress to be accelerated to bring the project back into phase

with the milestone chart projections.

PLANS FOR THE FUTURE

During the next quarter work will concentrate on identifying the factors responsible for the decline in productivity from the methane fermenters. Possibilities under study will be the question of viruses which may have attacked a key bacterium in the mixed population, the washout of a key specie or some chemical change in the nature of the substrate caused by variations in ozonation procedures. As soon as the productivity problem has been resolved work will again be expanded to include other areas of interest such as the effect of ozonation or ozonation catalyst on productivity. Additional work is also planned to confirm the production of acetate during the methane fermentation and evaluation of its use as a substrate in the protein production phase of this study. Trial runs are also planned of Kraft mill and Semi-chemical mill effluents to evaluate the applicability of the process to these waste streams.