COO-2983-2
Distribution Category UC-95e

ENERGY AND PROTEIN PRODUCTION FROM PULP MILL WASTES

Progress Report
for Period September 15, 1976-December 15, 1976

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December 15, 1976

Prepared For

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT E(11-1)-2983

DISCLAIMER

ABSTRACT

Significant progress was made during the past quarter in establishing the operability and reliability of major pieces of equipment needed for the production of protein and methane from spent sulfite liquor, SSL. Batch ozonations of SSL were conducted at times varying from 1 to 6 hours at pH's in the range of 10 to 2. These screening experiments consistently indicate that low pH's favor the breakdown of SSL into organic fragments which are more easily assimulated by micro-organisms. Approximately 23% of the organics are oxidized at all pH levels indicating that pH has no effect on the total oxidation of SSL. As was expected total sulfur content of SSL is not measurably altered by ozonation. The intense brown color of SSL is appreciably removed during ozonation. The contents of the reactor assume a light brownish-yellow hue during the course of a 4 hour ozonation treatment. Attempts to quantify the reduction have not been successful to date.

BACKGROUND

By the start of this quarter all of the experimental apparatus had been ordered and progress made in installing items received. Analysis of available supplies of nitrogen and oxygen indicated that both required minor processing before use in the experimental program. The oxygen was contaminated with a small quantity of moisture which was successfully removed by the installation of a silica gel drying column to treat the gas before it is fed to the ozone generator.

The nitrogen problem consisted of small quantities of oxygen making it unacceptable for establishing an anaerobic environment in the biological reactor. The problem was resolved by passing the nitrogen

over a heated bed of copper shavings. This system is regenerated by passing pure hydrogen over the copper shavings once the surfaces have become oxidized. A piece of equipment to effect this gas treatment was constructed in the university shop and tests show it to operate effectively. Twenty-five gallons of calcium base spent sulfite liquor was obtained from the St. Regis Paper Company in Rhinelander, Wisconsin to provide the raw material for the experimental program. Cultures of both yeast and methane producing bacteria were requested from several sources.

STAFFING

The project is fully staffed and operating as a team. This includes the two principal co-investigators, one post graduate research assistant and one Ph.D. graduate student. Since the beginning of the current term Dr. Jurgensen has devoted ten percent of his time and Dr. Patton thirty-five percent. For the remainer of this term Dr. Jurgensen will devote fifty percent of his time to the project while Dr. Patton reduces his contribution to ten percent. This will bring the annual manpower total into agreement with the budget. Performance under this contract is in strict compliance with the terms and requirements specified by ERDA.

EXPERIMENTAL PROCEDURES AND RESULTS

A packed column reactor was designed for the ozonation study and the materials required for its construction ordered. Installation of the ozone generator was completed and preliminary exploratory experiments conducted by bubbling ozone through a flask containing spent sulfite liquor. Data from these experiments are useful for designing experiments

in the packed tower reactor. Ozonation treating times of 0 to 6 hrs. were studied with significant changes in the sulfite spent liquor being noted. Both the raw sulfite spent liquor and ozonated samples obtained after 6 hours of reaction time were characterized using an infra-red spectrophotometer. The spectra suggests that a significant transformation of aromatics to carboxylic acids has been caused by ozonation. This can be seen in the spectra presented in Figure 1.

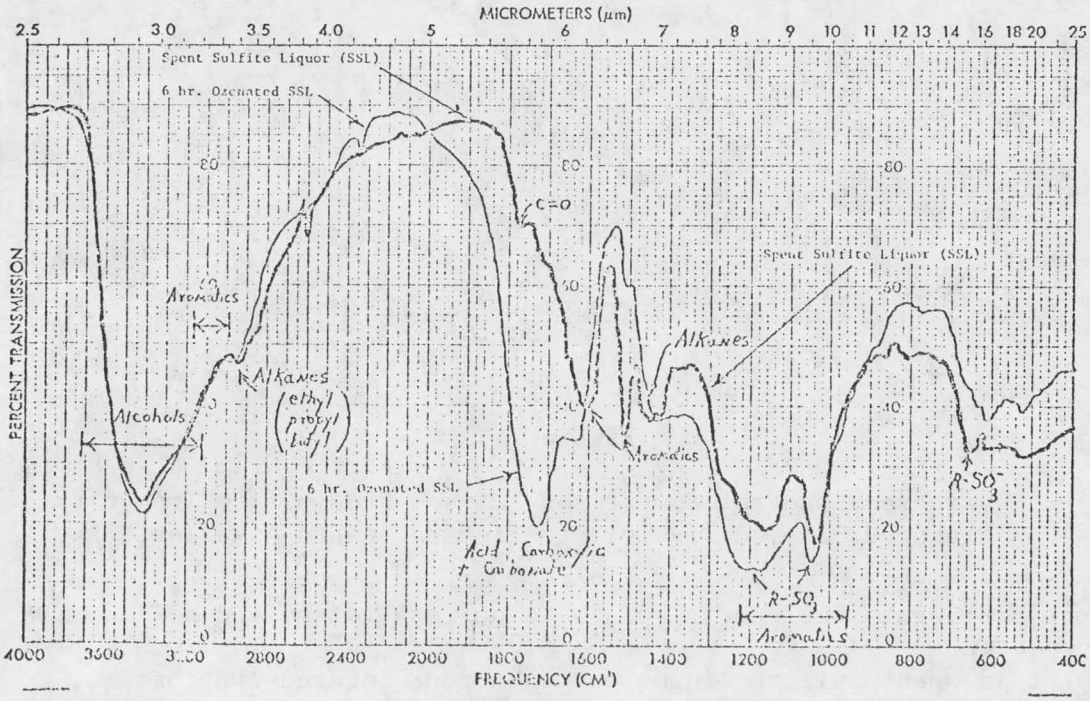

Figure 1

Infra-red Spectral Comparison between Spent Sulfite Liquor (SSL) and 6 hr. Ozonated SSL.

During ozonation a small quantity of precipitate is formed. This precipitate was also characterized by infra-red absorption analysis and compared with material precipitated from raw spent sulfite liquor by the

addition of sodium hydroxide. These spectra are presented in Figure 2 and, as before, certain differences are evident. These differences are not conclusively understood at this time.

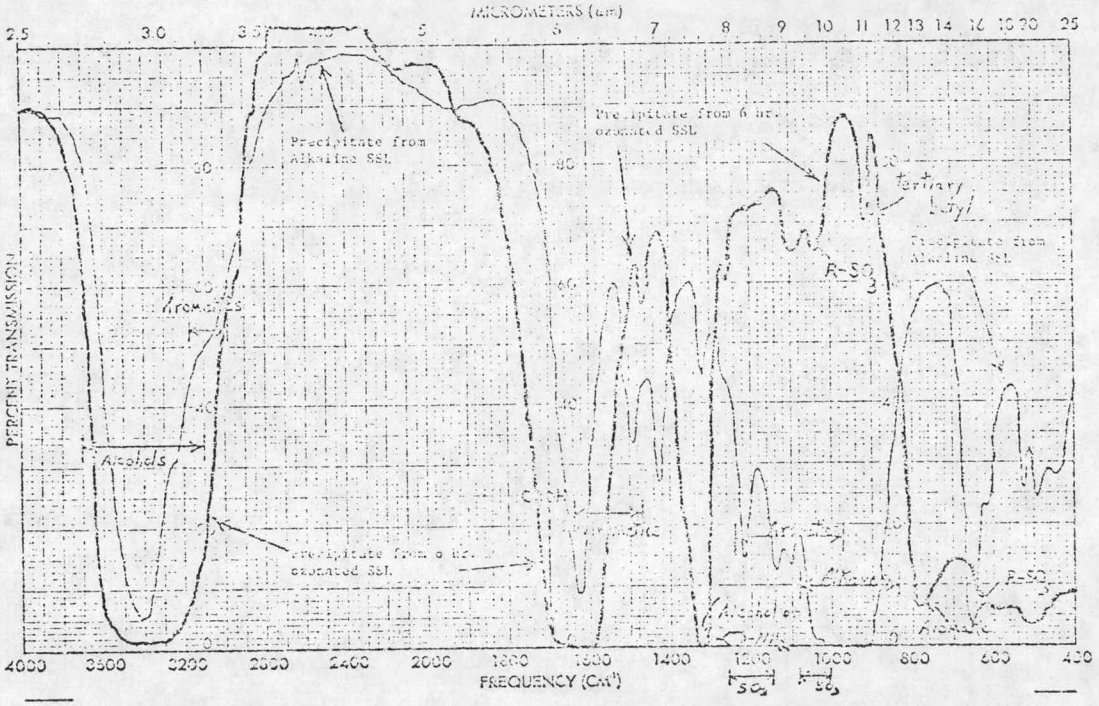

Figure 2

Infra-red Spectral Comparison between Precipitate from 6 hr. Ozonated SSL and Precipitate from Untreated Alkaline SSL.

Figure 3 presents the spectra of both the total dissolved solids, TDS, present in spent sulfite liquor and the ozone induced precipitate. The differences noted in this figure are much better defined indicating a shift to higher concentration of oxygenated compounds. At this time there appears to be a strong possibility that this precipitate is an insoluble calcium salt of some high molecular weight acids formed during ozonation.

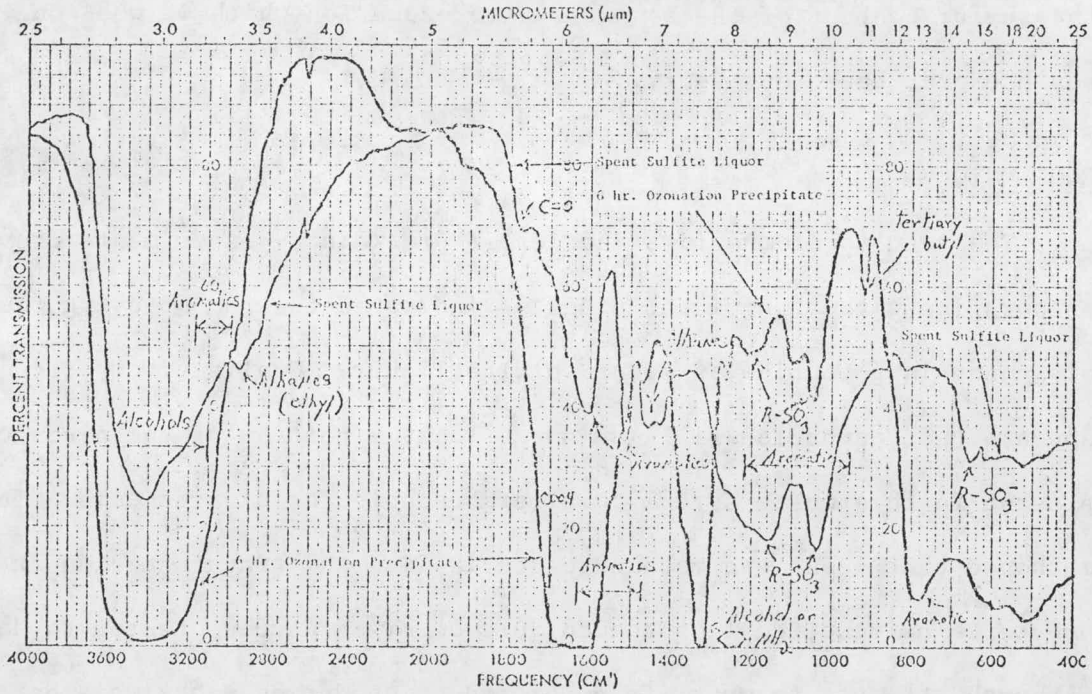

Figure 3

Infra-red Spectral Comparison between Spent Sulfite Liquor TDS and 6 hr. Ozonation Precipitate

During this quarter a major effort has been expended on the installation of equipment and the development of techniques required to perform the required anaerobic bioliogical experiments. Until this phase of the experimental program becomes operational preliminary studies have been conducted on the material transformed by ozone treatment. Samples of spent sulfite liquor ozonated for 6 hours were evaluated using standard BOD, COD and sulfur analytical tests. The concentration of metabolizable organics increased 100% when ozonation was conducted at a pH of 3.0. In contrast when ozonation was conducted at an alkaline pH very little increase in BOD content occurred. Surprisingly though at both acid and alkaline pH's the COD of the ozonated sample was reduced

the same amount, 23%. Tests indicated that there was no change in the sulfur content of the sample due to ozonation which is what one would expect based on theory.

CONCLUSIONS

The results of the first series of preliminary experiments are encouraging with significant progress indicated toward improving the biosynthesis potential of spent sulfite liquor. Qualitatively it appears that ozonation will convert at least a portion of the organics present in this waste stream to a form useable for biosynthesis. It is hoped that yeast and methane bacteria find the transformation in substrate as beneficial as the culture of mixed aerobes tested to date. Although attempts to quantify color reduction during ozonolysis by spectrophotometer have been unsuccessful to date, the fact that the changes are visible to the eye suggest that future experiments will be more definitive.

PLANS FOR THE FUTURE

During the next quarter fermentation experiments will be instituted using both yeast and methane bacteria to evaluate ozonated products for biosynthesis of energy and protein. The results of these experements will be largely to identify and select those cultures which have the most promise for use in future experimental procedures. New sources of useful bacterial cultures will be sought in an effort to improve the probability of selecting an optimum strain for these experiments.

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