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ENERGY AND PROTEIN PRODUCTION FROM PULP MILL WASTES

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DISCLAIMER

ABSTRACT

The effect of ozone treatment on spent sulfite liquor yeast plant effluent was studied. A 500 ml capacity packed column was constructed to efficiently react ozone with spent sulfite liquor (SSL) on a continuous flow basis. The SSL was reacted at pH 3.0 for 3 hours averaging an ozone consumption of 12.8 gm/l. It was found that pH tended to decrease during ozonation indicative of the formation of oxalic and other organic acids. Chemical oxygen demand (COD) decreased 13% form 101,000 to 88,000 mg/l. The SSL was rendered more biologically metabolizable as indicated by the biological oxygen demand (BOD) increase of 10.5% from 10,500 to 11,600 mg/l.

The ozonated SSL was then fed to an anaerobic fermenter for conversion to fuel gas. The average gas production was 423 ml/day from 700 ml size fermenter at a retention time of 2.8 days. The fermenter effluent gas contained approximately 65% CH_4 and 35% CO_2. Total bacterial populations were found in excess of 147×10^7 counts/ml and approximately 70% of the bacteria present was methane bacteria while 30% proved to be Desulfovibrio. The fermenter liquid effluent exhibited a drop in BOD of 3,200 mg/l corresponding to the amount of COD in the CH_4 produced.

Torula yeast were observed to grow on ozonated SSL in contrast to no growth on raw SSL thus indicating a potential for protein production.

INTRODUCTION

Lignin and other soluble organic compounds of wood are the major waste products from the pulp and paper industry. The amount of pulp mill waste effluent produced each year is enormous. For example, the sulfite pulping industry alone accounts for nearly three million tons of organic waste material annually.[1] The disposal of this spent sulfite liquor (SSL) is a significant source of water pollution. Mueller and Walden[2] estimate that 2,100 gallons of spent sulfite liquor are produced for every ton of sulfite pulp manufactured.

Various techniques have been developed to dispose of this enormous quantity of waste product. Originally the bulk of this material was discharged into the streams and lakes convenient to the pulping operations.[3] The rivers and bodies of water which currently receive the spent sulfite liquor are overtaxed and cannot continue to accept even the current level of discharge without detrimental environmental effects. The expansion of this segment of the pulping industry has been curtailed because of the pollution problems and the operation of many existing plants is now threatened.

Methods of treating pulping waste liquor to eliminate the pollution hazard can be generally classified as mechanical or biological. Mechanical methods generally separate the water, usually by vaporization, and dispose of the solids by burning, burying, or sales. The conventional treatment is the evaporation of the water followed by the burning of the organic solids. Besides eliminating stream pollution, this process recovers some of the cooking chemicals and considerable energy is generated during the combustion of the solids. Nevertheless, the treatment does have its disadvantages. The burning of the organic solids creates air pollution. The evaporated water contains all the volatile organics originally present in the effluent and thus, the condensate has an

objectionably high BOD content. In addition, 20-50 percent of the energy recovered by burning the organic solids is consumed by the evaporation process which detracts from the overall thermal efficiency of the operation. Growing demand for SSL solids as roadbinders, clay modifiers, etc. has allowed some mills to sell the residues rather than burn it.

Biological treatment seeks to avoid the expensive water removal step by enzymatic conversion of the waste effluent to a form which can be more efficiently removed. The activated sludge process, storage oxidation and aerated stabilization have been extensively studied.[4] In general, these treatments remove only the low molecular weight soluble organic fractions which effectively lowers the BOD_5 of the SSL. The high levels of lignosulfonates and sulfur are not significantly reduced,[5] and the energy potential of this organic resource is sacrificed.

It is the object of this research to convert the sulfur and organics now classified as pollutants in spent sulfite liquor by means of a combination chemical - biological process into synthetic methane and proteins. The process is self sufficient with respect to energy requirements and could make a significant contribution toward relieving the projected shortages in the energy and food supplies.

The general lack of success with biodegradation of lignonsulfonates suggests that some pretreatment must be required to degrade the SSL, or transform it into a state which could be metabolized. One such possibility is to break the lignosulfonate moiety into smaller molecular weight fractions through ozone treatments. Stern and Gasner[6] have shown that such processing of kraft mill waste liquor did cause a shift in the molecular weight distribution of lignins to lower weight fractions. Ozonation also increased the susceptability of the waste liquor to biological decomposition. The lignosulfonate present in SSL

would likely be affected in a similar manner. This technique could be used prior to a yeast fermentation to increase protein yields, or after to facilitate the removal of residual BOD and COD. The sulfur fraction of the lignosulfonate released by ozonation could be removed by stripping and/or bioreduction.

The BOD remaining after yeast fermentation or ozonation is amenable to subsequent biological treatment. The methane-producing anaerobes seem ideally suited for such a role. These organisms use fatty acids, alcohols, and carbon dioxide as substrates which are the readily available organic materials remaining in the SSL after yeast fermentation.[7] Methane bacteria have also been reported to fix atmospheric nitrogen.[8] If confirmed, this could alleviate the requirement of adding a supplemental inorganic nitrogen source during the fermentation process. Methane produced from SSL would then be used as a supplemental energy source in the processing plant.

Production of methane from organic residue by anaerobic digestion is well known. A variety of substrates ranging from activated sludge to cultured algae have been converted to methane by this process.[9,10] Considerable interest has recently developed on obtaining methane from animal wastes.[11]

Methane fuel production from SSL was earlier considered as a promising fermentation possibility due to the ease with which the gaseous product could be recovered. Calculations by Benson and Partansky[12] based on incubation studies gave a heating value of 1,430,000 BTU/ton of pulp, assuming a 25 percent carbon removal, and incubation at 36°C. Cultures acclimatized to SSL by successive batch transfers or continuous fermentation were not used. Bannik and Muller[13] also found significant production of methane from SSL, and Wiley[14] patented a process for use in sulfite pulp plants. The calorie value of the organic waste present in SSL amounts to approximately 40 trillion BTU's annually, equivalent to 40 billion cubic feet of natural gas.[15] However, the relatively low cost of other fuels at that time discouraged subsequent research on methanogenesis using pulp mill substrates. This situation would now appear to have changed.

Process Description

Conceptual design work has resulted in the development of a multistage process which has the potential for converting the pollutants present in sulfite pulp mill waste, SSL, to useful fuels and protein. The process utilizes three fermentation stages coupled with the chemical and physical operations, ozone cracking, steam stripping, and centrifugation to synthesize and harvest useful products derived from the SSL. This process is shown in the accompanying flow diagram, Figure 1.

Waste liquor from the pulp mill enters the process in the primary yeast fermenter where all assimilated organics are converted to protein and CO_2. Effluent from the primary fermenter passes through a centrifuge to harvest the protein. It then passes to the ozonator where it is treated to modify the sulfur bonds and break down the high molecular weight organics. Ozone cracked effluent is cooled and fed to the anaerobic digestor. Here a mixed bacterial culture is used to convert the remaining organics to synthetic methane. Only a few specific organics can be utilized by methane bacteria. For this reason a mixture of other organisms, largely Desulfovibrio, are needed to transform the ozonated fragments into substrate for methane synthesis.

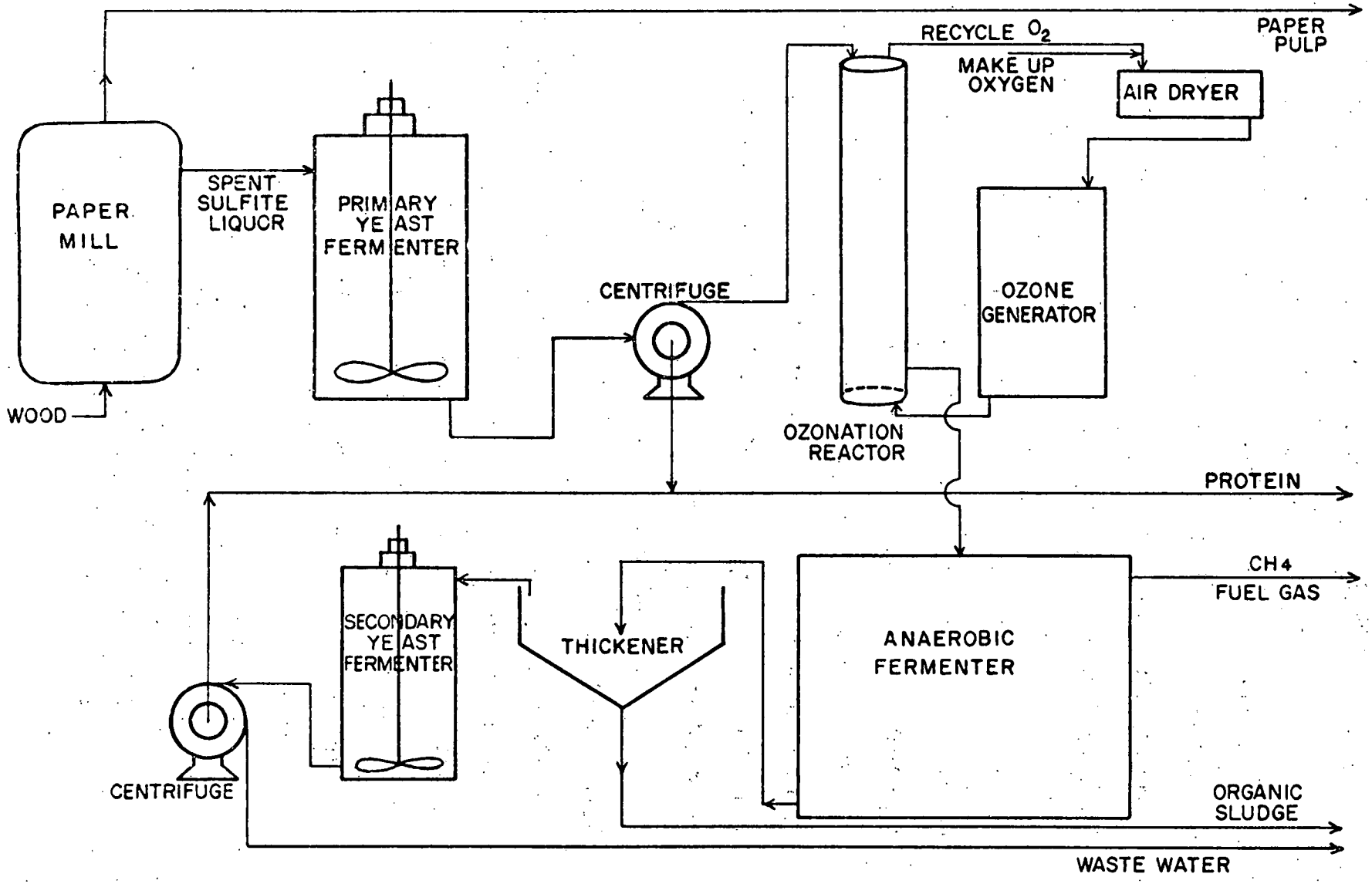
The effluent from the anaerobic digestor may still contain unassimilated ozonated fragments which can be utilized by Torula yeast. The effluent from the methane fermenter can, therefore, be fed to secondary yeast fermenters, and then to a centrifuge for protein removal. Any BOD_5 still remaining is removed by standard treating processes such as activated sludge or soil infiltration.

During the anaerobic digestion some organic sludge, biological solids and lignin, will be produced. The effluent from the anaerobic digestor is fed to a conventional thickener for the recovery of the precipitated organics. The sludge, after dewatering, can be utilized as fuel by burning directly if no higher value alternate is available.

FIGURE I.

PROCESS FLOW SHEET

CONVERSION OF PULP MILL WASTE TO PROTEIN AND FUEL GAS



PROGRAM PLAN

This project seeks to explore the possibility of converting organic waste materials available from sulfite pulp mill operation to protein and fuel gas. Past research has demonstrated that this objective cannot be met by only biological means. Lignosulfonates, the major organic present in the pulp mill effluent are not easily metabolized. Prior data suggests that either the presence of sulfur in the molecule or the high molecular weight is the problem. The objective of this work is to desulfonate and breakdown the lignosulfonates by ozonation. The effect of this chemical treatment on biological utilization will then be assessed.

Three types of microorganisms will be utilized to produce energy and protein. Protein production will be accomplished with yeast. Organic fractions not converted by yeast will be desulfonated and gasified simultaneously using a mixed culture containing methane and sulfur reducing bacteria.

The significant program milestones together with the estimated completion dates are given below:

Milestones	Completion dates
1. Order and install major experimental apparatus.	Dec. 1, 1976
2. Obtain multiple cultures from various sources representative of the three types of micro-organisms to be used in the bio-synthesis experiments.	Jan. 15, 1977
3. Screen biological cultures for ability to effect desired chemical transformations.	June 15, 1977
4. Characterize pulp mill waste stream with respect to chemical types and molecular rate ranges.	June 15, 1977

Milestones	Completion dates
5. Establish effects of reaction time and temperature on the products obtained by ozonation of pulp mill waste stream.	June 15, 1977
6. Define effect of varying ozonation conditions on the ease with which selected microbes can metabolize the resultant chemical products.	June 15, 1977
7. Construct bench scale development unit utilizing the optimum microbial strains and reactor sequences defined in the first year of the program.	June 15, 1977
8. Optimize process conditions to maximize yield and operating costs.	Sept. 15, 1978
9. Conduct demonstration runs and then scale process equipment to obtain material balance and kinetic data for process design.	Mar. 15, 1979
10. Design and evaluate the commercial potential of the demonstrated process and prepare the final project report.	June 15, 1979

The above milestones and completion dates are preliminary estimates but every attempt is being made to obtain the required data by the time specified. This will allow each phase of work to proceed on schedule. Due to the challenging nature of this exploratory research it is also anticipated that subsequent work in each of the above areas may need to be continued past the target completion dates.

PROJECT INITIATION

Staffing

Upon being notified of the contract award steps were immediately taken to advertise for graduate students and a research technician in appropriate journals. From the many research technician applications received, Mr. Craig Bremmon, M. S. bacteriologist, South Dakota State University, was selected as being the most qualified. Mr. Bremmon has played a major role in the set-up of the laboratory and installation of the major pieces of equipment. It is largely through his efforts that the experimental work has progressed at such a rapid rate. Mr. Sushil Dugar, B. S. chemical engineering, Jadavpur University, M. S. chemical engineering, Michigan Technological University, was selected as a recipient of the graduate research fellowship. Mr. Dugar's strong background in chemical engineering complements the bacterialogical effort. This greatly expedites the design of experiments and interpretation of research results.

The efforts of these two senior researchers have been amplified through the efforts of five undergraduate research assistants. These students have been assigned various facets of the overall program. They have worked diligently to maintain progress in their respective areas in keeping with the program plan and objectives.

Overall direction for the project was provided by the principal investigators John T. Patton, chemical engineer, and Dr. Martin F. Jurgensen, microbiologist. Due to some unexpected needs by the U. S. Forest Service, Dr. Jurgensen was able to devote only about 10% of his time to this project during the past year. By shifting other responsibilities Dr. Patton was able to increase his participation to provide additional leadership. In addition, Dr. Yuan-Zong Lai, lignin chemist, was employed part time to enable the project to proceed with the required amount of professional supervision. It is anticipated that some of the

responsibilities will be shifted during the latter stages of the project to bring the total overall participation by each of the principal investigators into agreement with the original budget. Experimental design and data interpretation was supervised by Dr. J. P. Beckwith, statistician, who donated 10% of his time to the project in accordance with the budget.

Equipment

Several major pieces of equipment and lab installations were required to make the project operational. The first category includes the equipment required for ozonation of the raw spent sulfite liquor. A Welsbach Ozone Generator, Model T-816, was purchased and installed. During the past year it has performed in accordance with the specifications and has proved to be a most reliable piece of equipment. The ozone reaction is carried out in a 500 ml capacity, 1" ID Glass Column six-feet tall which is packed with ceramic berl saddles. SSL is fed to the ozonator and is circulated through the column by means of two Masterflex pumps. A mixing chamber is provided where the pH is automatically monitored and controlled with a Radiometer automatic titrating apparatus.

The second major equipment category includes fermentation apparatus and equipment required for the biological conversions and assay work. Four continuous stirred tank fermentors furnished by Michigan Technological University were adapted for anaerobic studies and installed. These were also equipped with Masterflex pumps to be operable in either the batch or continuous mode. Foot operated culture transfer and media preparation equipment developed at Virginia Polytechnic Institute was constructed in the chemical engineering shop and placed in operation. Each element is performing as expected and the results obtained are consistently high quality. The only major piece of equipment requred to be purchased was a BOD_5 incubator and associated glassware. This item was purchased from the VWR Scientific Company, was installed and is operating satisfactorily.

EXPERIMENTAL RESULTS

Ozonation

Upon installation of the ozone generator preliminary experiments were conducted to provide data useful for the design of a continuous ozonation reactor. These experiments were conducted by bubbling ozone through 300 ml of SSL contained in a 500 ml Erlenmeyer flask. Treating time was varied from 1.0 to 6.0 hours. At the end of six hours the rate of ozone consumption reached a minimum value and no further chemical change was noted. It appeared that samples treated at lower pH's reached equilibrium more quickly with respect to ozone consumption. Both the raw sulfite spent liquor and ozonated samples obatined after 6 hours of reaction time were characterized with an infra-red spectrophotometer. The spectra, presented in Figure 2, suggests that a significant transformation of aromatics to carboxylic acids has been effected during ozonation.

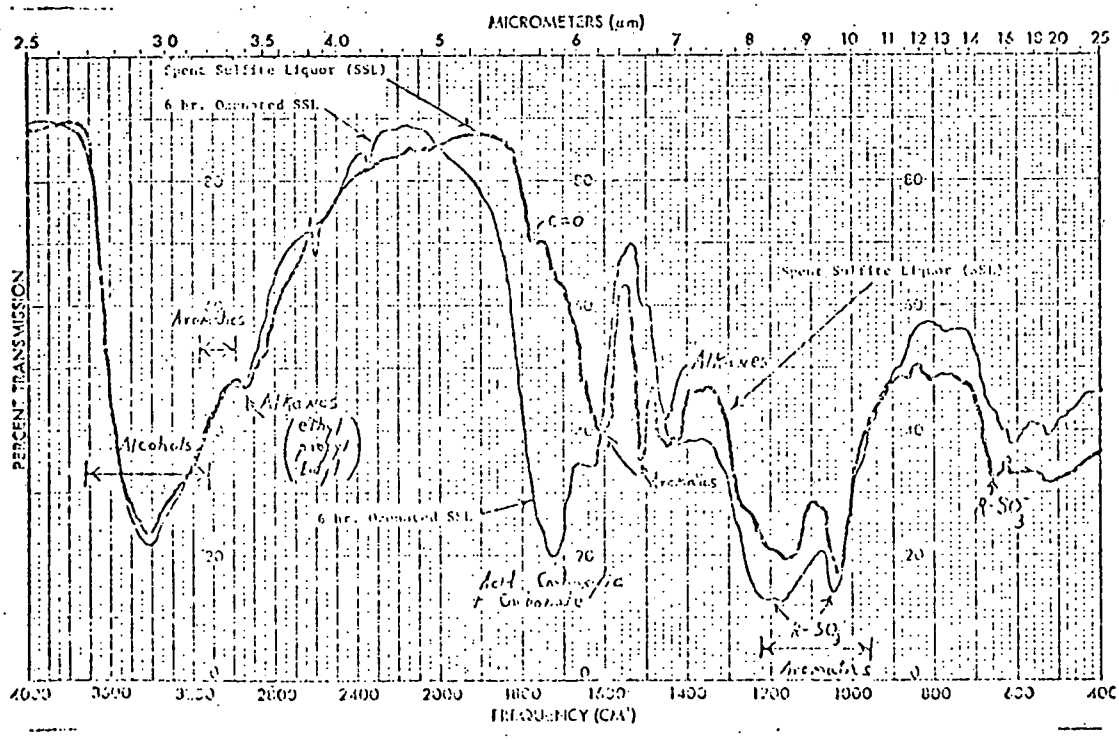


Figure 2

Infra-red Spectral Conparison 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 and compared with material precipitated from raw spent sulfite liquor by the addition of sodium hydroxide. These spectra, presented in Figure 3, show indications of structural change, however these have not been fully explained at this time.

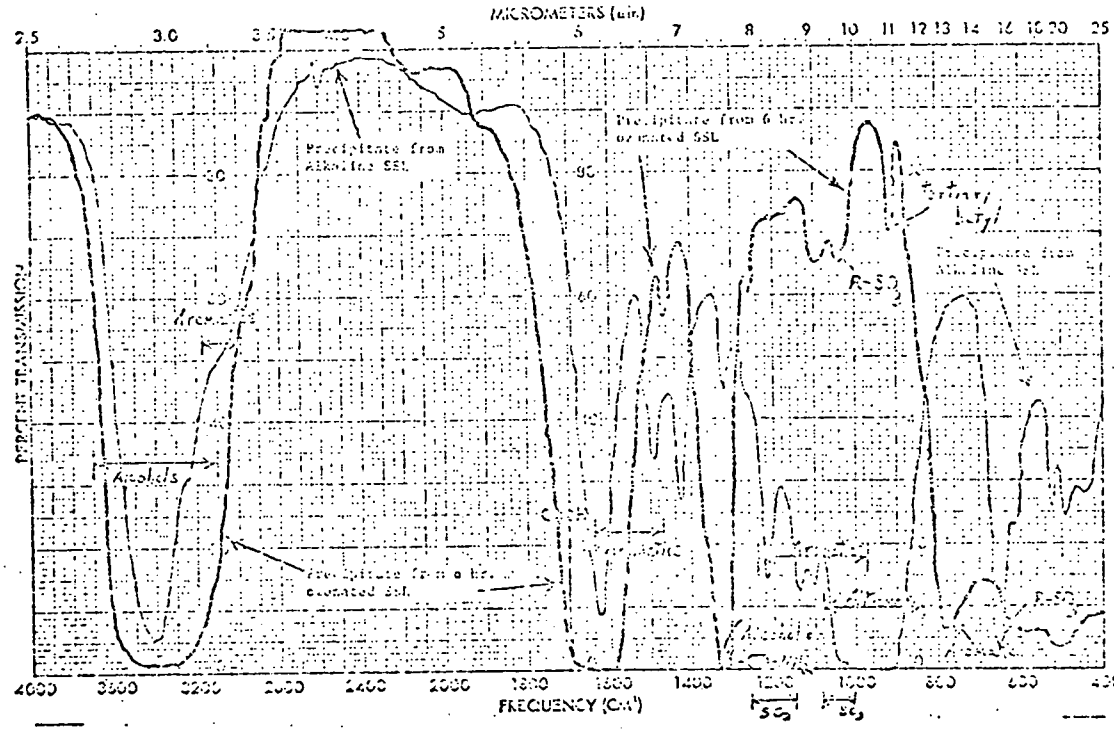


Figure 3

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

Figure 4 presents the spectra of both the total dissolved solids, TDS, originally present in spent sulfite liquor and 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 insoluble calcium salts of organic acids formed during ozonation.

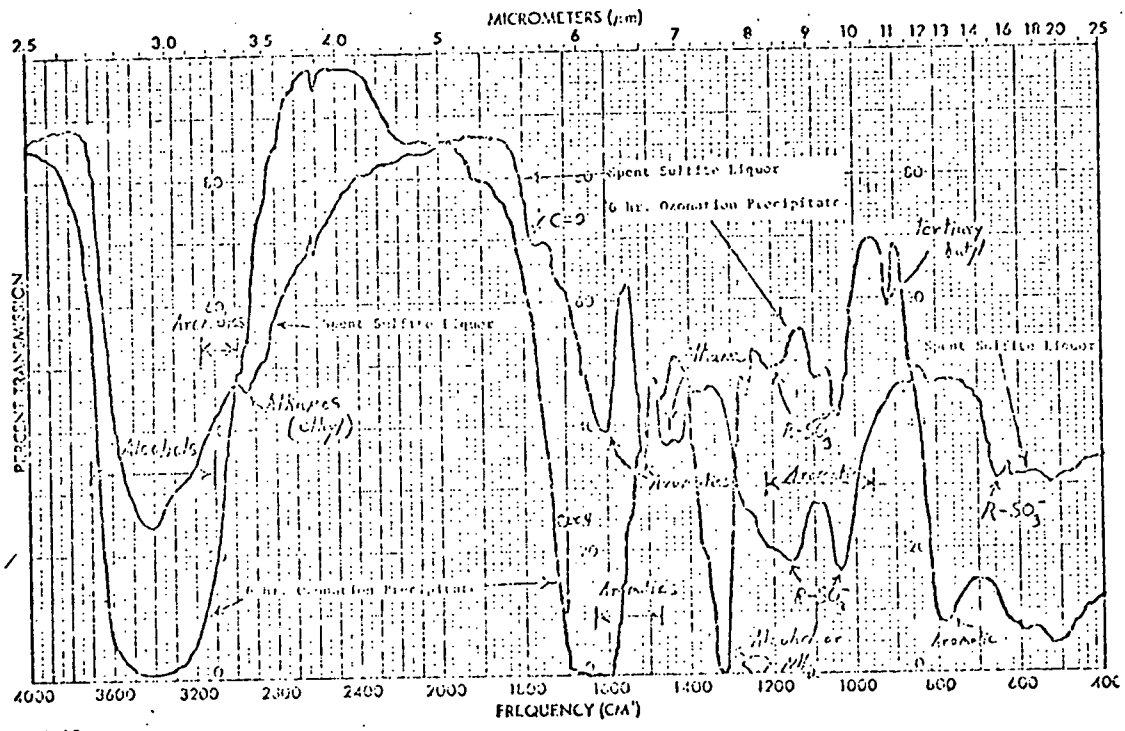


Figure 4

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

During the first year a major effort has been expended on the installation of equipment and the development of techniques required to perform the required anaerobic biological experiments. Until this phase of the experimental program became operational preliminary studies were conducted on the material transformed by ozone treatment. Samples of SSL 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 occured. 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.

The fact that pH continuously dropped during ozonation reaction coupled with

the yield of assimiable organics at both high and low pH was the dominant reason behind the selection of pH 3 as the reaction condition for the first series of runs in the continuous reactor. It was decided to initially carry the ozonation reaction to completion, to the point that ozone was just detectable in the off gas from the reactor. The period of time required for this degree of ozonation was 3.0 hours. The flow rate to the reactor is 650 cc/min oxygen containing 1.8% ozone. The characteristics of the treated SSL and spent sulfite liquor are given in Table 1.

Table 1
Analysis of Raw and Ozonated SSL

	Raw	3 hr. ozonated SSL
BOD , mg/l	10,500	11,600
COD mg/l	101,000	88,000
Sulfur gms/l	6.8	6.8
Total Organic Carbon	4.25%	3.75%
Total Dissolved Solids	9.5%	9.3%
a) organic 8.1%		a) organic 8.0%
b) inorganic 1.4%		b) inorganic 1.3%

Ozone consumption averaged 12.8 grams per liter of SSL treated, the quantity which theoretically should have reduced COD by 12,800 mg per liter. The COD reduction, 13,000 milligrams per liter, actually recorded is well within the range of experimental error associated with the analytical tests involved.

During ozonation a small quantity of white precipitate develops which is insoluble in organic solvents. This material has tentatively been identified as calcium oxalate. Although the quantity of precipitate is not great it does build up and at time can plug lines in the continuous reactor system as well as the fermentation equipment. The I.R. spectra of the precipitate is shown in Figure 3.

Fermentation

Communication with leading researchers in the field of methane fermentation yielded the unanimous suggestion that a conventional operating sludge digester is the best source of methane bacteria. There was also consensus that the microflora from one source was essentially the same as that present in any other municipal waste treatment plant. The initial culture was obtained from the anaerobic treating plant located at Brookings, South Dakota. The cultures were acclimated by successive transfers in flasks containing SSL diluted to 50% strength with distilled water and enriched with acetate, formate, lactate, alcohols, and potassium phosphate. Innoculum prepared by serial transfer in this medium was used to innoculate a 700 ml continuous fermenter containing the same medium. Methane productions slowly increased to approximately 30 cc/hr at which time continuous feed addition was initiated at a rate to provide a residence time in the fermenter of four days. Good growth and continuous gas production was achieved and this fermentation has provided the source for all subsequent innoculum.

After several weeks of operation only minor variations in gas production were observed indicating the process had reached steady state. The concentration of methane in gas produced during this period was surprisingly high, averaging better than 75% CH_4. Off gas was analyzed chromatographically as shown in Figure 5. In as much as future runs based solely on ozonated SSL showed lower methane concentrations it is presumed that the high methane concentration in run 1 was generated primarily from the substrate added to enrich the media, namely acetate or formate.

TABLE 2

Steady-State Continuous Fermentations

Date	Run No.	Days at Steady State	Feed Composition	Retention time (days)	Effluent COD	Effluent BOD_5	Gas Production cc/hr @°C, 1 atm.	Gas Composition CO_2%	Gas Composition CH_4%
1/2/77	1-A	2	5% SSL and prescribed synthetic	3.1	-	-	12.2	8.2	91.8
1/18/77	2-A	3	25% SSL and prescribed synthetic	3.0	-	-	13.2	11.7	88.2
2/17/77	3-B	3	50% SSL series fermentor effluent	2.9			3.1	20.2	79.8
2/17/77	4-C	8		3.0			5.6	15.2	84.8
5/10/77	5-A	4	75% SSL	3.6			7.8	33.5	66.5
5/16/77	6-A	5	75%	3.6	78655	8613	7.5	25.0	75.0
5/16/77	7-B	5	75%	3.4	84005	7533	22.3	41.7	58.3
5/22/77	8-A	10	75%	2.3	83458	8005	6.3		
5/23/77	9-B	6	75%	2.2	82745	5204	33.1		
5/27/77	10-A	4	75%	2.2	79513	7600	7.5	37.8	62.2
5/27/77	11-B	3	75%	1.7	87260	8647	23.6	49.6	50.3
5/27/77	12-C	10	75%	3.7	89215	9933	5.1	37.8	62.2

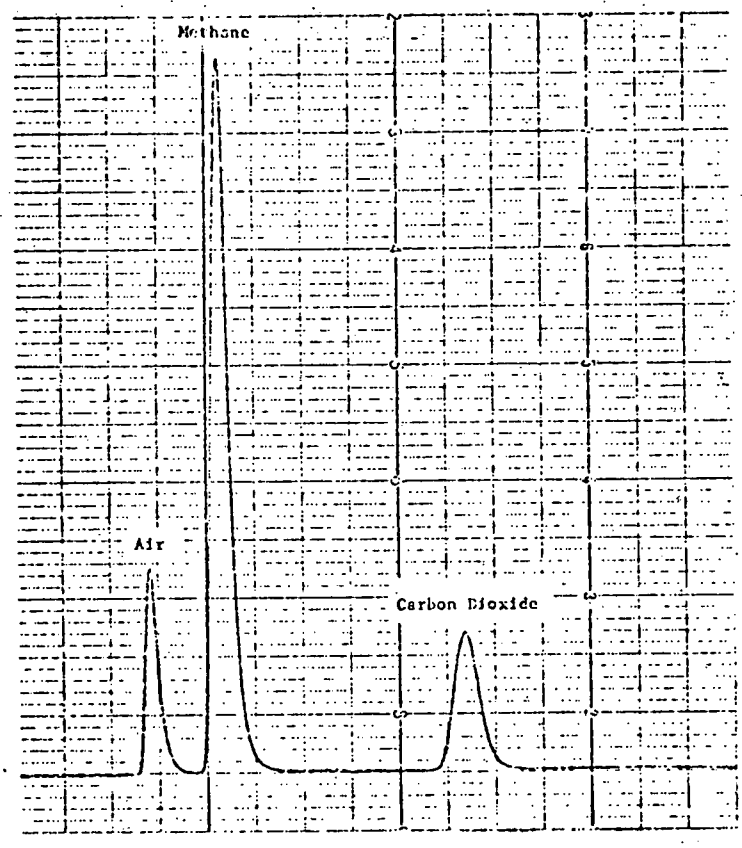


Figure 5. Gas chromatographic analysis of effluent gas from fermenter 2.

The addition of enrichment substrates was gradually diminished until fermentation proceeded with only ozonated SSL as a carbon source. During this period gas production gradually decreased. Analysis of the decline indicated that the fermentation might be substrate limited and therefore the amount of distilled water was reduced so that the feed consisted of 75% ozonated SSL. The representative steady state results of runs are summarized in Table 2.

Over the past two months there has been a gradual and as yet unexplained decline in the gas production rates. Future experiments are planned to define the factor responsible for the loss in methane synthesis activity.

Microbial Analysis

Periodically the fermentors have been assayed to determine the population of the various bacteria present in the system. For the past three months organisms of only three genena have been identified as shown in Table 3.

Table 3

Groups of Organisms Found in an Ozonated Spent Sulfite Liquor Anaerobic Fermenter

Percent Present	Group	Species	Energy Yielding Metabolism
30.7%	Gram negative curved to sigmoid or spirilloid rods	Desulfovibrio sp.	Lactate, pyruvate malate, SO_2, SO_3
69.3%	Methanogenic bacteria		

Percent Methane Bacterial Species Present	Group	Probable Species	Energy Yielding Metabolism
45.6%	Gram negative, short to long straight or slightly curved rods with rounded ends	Methanobacterium mobile Methanobacterium soehgenii Methanobacterium formicum	CO_2, formate H_2, acetate, butyrate
44.3%	Gram positive coccoids to short lancet-shaped rods	Methanobacterium ruminantium	CO_2, H_2, formate, acetate as carbon source
10.1%	Gram negative cocci occuring singly, in pairs, or clumps	Methanococcus mazei	acetate, butyrate

There has been gradual decrease in the number of methane bacteria present in the system however, all concentrations are in the 10^7-10^8 cfu per milliliter range. The variation between assays is not significantly conclusive at this time. A summary of these data is given in Table 4.

Table 4
Total Counts of Methane Bacteria and Desulfovibrio Growing on Ozonated SSL

Date of Sample	Methane Bacteria cfu/ml*	Desulfovibrio Methane Fermenter, cfu/ml*	Desulfovibrio DES Fermenter, cfu/ml*
2/10/77			87×10^3
3/9/77			1×10^3
3/23/77	155×10^7	38×10^7	
3/31/77			173×10^7
4/13/77	89.4×10^7	30.6×10^7	83×10^7
5/17/77	63.4×10^7	61.6×10^7	99×10^7

*cfu - colony forming units

It can be seen that during this same period the population of Desulfovibrio in the methane fermenter has more than doubled form a early value of 30.6×10^7 cfu per ml to 61.6×10^7 cfu per ml. The consistent upward trend in these data are a strong indication that the microbial population ratio are shifting which may partially explain the decrease in gas production.

Protein Fermentation

The work on protein fermentation was initiated late in the first year of the project and, hence, only preliminary results are available. Cultures of

Torula yeast were obtained from effluent samples supplied by Lake State Yeasts Company, Rhinelander, Wisconsin. Cultures of this yeast were used to innoculate raw SSL and substantial growth was observed. This was expected in as much as several commercial plants are utilizing raw SSL as a substrate for the production of yeast. Growth ceases when all the available wood sugars have been consumed. The effluent from the yeast fermentation was filtered and sterilized. The fact that the effluent was not capable of supporting further yeast growth was confirmed by innoculating a sterilized sample of this effluent and no growth occurred. The effluent was then subjected to ozonation for a period of three hours at pH 3. The ozonated product was then innoculated with the same Torula yeast culture and growth commenced immediately. Work during the coming year will quantify the degree of additional protein which can be produced due to the ozonation of the spent sulfite liquor.

DISCUSSION OF RESULTS

Exploratory experiments conducted during the first project year served to establish two facts. Reliable operability of the many pieces of equipment which were assembled to similate bench scale operation of the conversion process was achieved. The second fact, which represents the major significant accomplishment of the project to date, involves the feasibility of the processing scheme. Although the process looked promising on paper, experimental verification of the ability of methane bacteria to convert lignin or lignosulfonate fractions was an unknown. The fact that both methane and protein have been produced in measureable yields is extremely encouraging and will provide the impetus for future work on this project.

The preliminary data compare quite favorably with published results from other research on the biosynthesis of methane. The production of one standard

cubic foot of methane per day per cubic foot of fermenter volume is about the highest efficiency reported in the current literature. Methane yield on many of the runs with ozonated SSL equaled this value.

Methane production is consistent with the change in BOD_5 which occurs during the fermentation period. During fermentation BOD_5 is reduced approximately 3,200 milligrams per liter. Assuming that this decrease in BOD_5 resulted from the liberation of methane one calculates that approximately 17 milliliters of gas per hour should be generated. This result is consistent with the experimental data and sample calculations quantifying the conversion process are given in Appendix A. The fact that BOD_5 is quantitatively converted into equivalent methane production will allow some acceleration in the experimental design during the coming year. It is hypothesized that ozonation conditions which yield the highest value of BOD_5 should also provide the maximum amount of substrate for methane production. Hence, ozonation conditions can be screened with the BOD_5 test.

The data also indicate that the majority of the ozone utilized in breaking down the lignosulfonates was not effective in generating biodegradable fragments. Although ozonation reduced chemical oxygen demand, COD, by roughly 13,000 milligrams per liter biological oxygen demand, BOD_5, only increased 3,200 milligrams per liter or roughly 25% of what theoretically could have been obtained. It would appear that the bulk of the other 75% of the ozone was expended in the production of CO_2 from the organic fraction in SSL. This is a wasteful use of ozone and an expensive way to make carbon dioxide. A search for reaction conditions under which the ozone will be more effectively utilized to generate BOD_5 will be a prime objective of future research directed at converting pulp mill wastes to protein and synthetic fuel gas.

Appendix A

1) BOD_5 of ozonated liquor — 11,600 mg/liter

BOD_5 of fermenter effluent — 8,400 mg/liter

Difference in BOD_5 — 3,200 mg/liter

= 0.1 gm moles O /liter

Gas Analysis of Effluent gas from fermenter: 65% CH_4 and 35% CO_2

Since CO_2 came out of the fermenter the reduction of BOD_5 is reflected by the loss of CH_4, the only oxidizable component in the gas effluent.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Reduction in BOD_5 is 0.1 gm moles O /liter which is equivalent to 0.05 gm moles CH_4.

0.05 gm moles CH_4 ≃ 1.12 liter of CH_4 at 0°C and 1 atm. But this is only 65% of total gas

: Total gas production = 1.72 liter/liter SSL

2. Fermenter Volume = 700 ml

Average Residence Time = 2.84 days

Feed Rate = 246.5 ml/day

: Theoretical gas production = 423.9 ml/day

= 17.7 ml/hr.

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