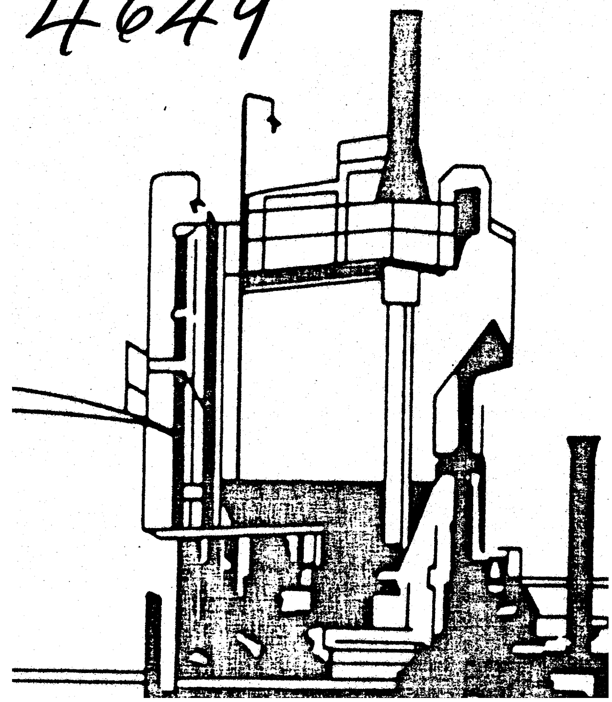
4649



INDUSTRIAL WASTE

Proceedings of the Thirteenth Mid-Atlantic Conference

INDUSTRIAL WASTE

Proceedings of the Thirteenth Mid-Atlantic Conference

June 29–30, 1981

The Mid-Atlantic Industrial Waste Conference is sponsored by

University of Delaware
Department of Civil Engineering
Division of Continuing Education
Newark, Delaware

In cooperation with

Bucknell University
Drexel University
The Johns Hopkins University
Villanova University
Delaware Department of Natural Resources
  and Environmental Control
Maryland Department of Natural Resources
Pennsylvania Department of Environmental Resources
U.S. Environmental Protection Agency, Region III

Session III
Case Studies

TREATMENT OF TANNERY BEAMHOUSE WASTE WITH A BENCH-SCALE ANAEROBIC REACTOR

M. H. Tunick, A. A. Friedman[1], D. G. Bailey, Eastern Regional Research Center, Agricultural Research, Science and Education Administration, U.S. Department of Agriculture, Philadelphia, Pennsylvania.

INTRODUCTION

Effluent streams from the leather tanning and finishing industry present a difficult challenge for economical waste treatment. These wastewaters contain large quantities of BOD consisting primarily of dissolved and suspended hair proteins from the unhairing step in which the hides are prepared for tanning. The suspended and dissolved solids are high due to the use of large quantities of salt and lime in various steps of leather manufacture. Sodium sulfide, used in the unhairing process, adds to the chemical oxygen demand (COD) and is a potential toxicant in a biological treatment system.

Conventional aerobic treatment, even after dilution and high rates of aeration, has not been shown to achieve the proposed standards set for the tanning industry [1]. Further treatment, particularly for direct discharge, is necessary. Several aerobic systems for tanning wastes have been described [2,3]. It is possible to acclimate activated sludge to this waste but the cost of energy for aeration remains high [3].

Anaerobic treatment of a variety of industrial wastes has demonstrated the potential of this method for treating difficult wastes. Pharmaceutical [4] and polymer synthesis byproduct [5] are two of many examples. A. A. Friedman et al. presented work last year at this conference on the use of a bench-scale anaerobic filter (AF) to treat tannery beamhouse waste [6]. Pretreatment, in which the pH was lowered, liberated sulfide as a gas and removed part of the dissolved protein by precipitation. Removal of up to 70% of

[1]Department of Civil Engineering, Syracuse University, Syracuse, N.Y. 13210.

the remaining COD was then achieved by the AF. A combination of the AF plus a rotating biological contactor removed over 98% of the 5-day BOD applied to the dual system.

This paper describes a 35 l bench-scale suspended anaerobic system which has treated beamhouse waste and achieved COD removal comparable to that of the AF. In this work, the only pretreatment was dilution. Aerobic followup treatment was not included in this study but would be necessary following an anaerobic treatment process. The unexpected finding of methane generation as well as COD reductions—in spite of sulfide levels in excess of 1000 mg/l—improves considerably the potential for practical application of this process for removing COD from tannery effluent.

MATERIALS AND METHODS

Reactor

The bench-scale anaerobic reactor consists of two cylindrical tanks (Figure 1). The anaerobic reactor is 12 inches ID and 18 inches high. It has an airtight cover of plexiglass, through which provision is made for stirring, heating, feeding, and sampling. A horizontal tube 1/2 inches ID and 15 inches from the bottom connects the reactor to the second cylinder which is 6 inches ID and 18 inches high. This serves as a settling tank from which settled sludge is constantly recirculated to the reactor and effluent leaves the system through an overflow port.

Suspension of the anaerobic sludge is maintained by a stainless steel stirrer, driven at 60 RPM by a 0.05 HP electric motor. The impeller consists of two 2-inch square blades pitched at 45° and suspended 4-1/2 inches from the bottom of the reactor. The mother liquor is maintained at 37 C by a hotfinger located in a silicone-filled test tube suspended from the lid. Two similarly held test tubes in the lid are used for monitoring temperature and for a thermistor providing feedback for the temperature control. Gas produced in the reactor and the settling tank is collected, and volume is measured by water displacement. Samples for determination of gas composition are obtained by a hypodermic syringe through a septum mounted in the top of the reactor. Two stainless steel tubes extending 12 inches are mounted in the lid. One of these is used for feeding and the other for withdrawing liquid samples.

As the effluent leaves the reactor it flows into the settling tank and down through a stainless steel tube to within 4 inches of the bottom. The bottom is cone-shaped to collect settleable sludge which is recirculated at 70 ml/min back to the reactor. The final settled effluent exits through an opening opposite the entrance port and passes through an inverted siphon to prevent escape of gas.

The tannery influent consisted of beamhouse unhairing waste diluted to the desired COD. The feed was continuously added to the reactor with a peristaltic pump at a rate of 10-15 l/day.

Chemical Analyses

Representative samples of feed, mother liquor, and effluent were taken each work day. Total chemical oxygen demand (TCOD) was measured by the culture tube method of Knechtel [7]. Correction for sulfide was made by taking twice the sulfide concentration and subtracting this number from the TCOD concentration. Gas composition was measured with a Hewlitt-Packard model 5734A gas chromatograph, with a 6 ft. x 3/16 inch aluminum molecular sieve column and a thermal conductivity detector (carrier: 20 ml He/min; sample volume: 0.5 ml; temperature programming: 85 to 200 C at 32 C/min). A typical chromatogram is shown in Figure 2. Volatile fatty acids (VFA) were analyzed on the same instrument with flame ionization detection and a 6 ft. x 1/4 inch stainless steel column consisting of 15% SP-1220/1% H_3PO_3 on Chromosorb W [8] (carrier: 20 ml He/min; sample: 10 µl; temperature: 150 C). A chromatogram of this type is shown in Figure 3. Suspended solids (SS) and volatile suspended solids (VSS) were determined by procedures in Standard Methods, 14th edition [9]. Sulfide ($S^=$) was analyzed titrimetrically by oxidation with $K_3Fe(CN)_6$ [10]. Total Kjeldahl nitrogen (TKN) and ammonia levels were measured on a Technicon Auto Analyzer [11].

Start-up

The reactor vessel was filled with sludge from an existing anaerobic pilot plant and fed with diluted tannery waste at a rate of up to 72 g TCOD/day. After 16 weeks of operation, reactor supernate was removed and additional anaerobic sludge was added. Sludge was never wasted during the course of the experiment. Four weeks later the VFA concentration in the reactor was increased by the addition of glucose to the feed. The glucose loading was maintained at 35 g/day for 2 weeks; after that time, the feed was again made up to consist solely of diluted tannery waste. Monitoring of gas production began 7 weeks after glucose addition was stopped. At this time the experiments and data collection reported below were begun.

RESULTS AND DISCUSSION

TCOD Removals

An average reduction in influent TCOD during the 4-month period reported was 62% after correction for sulfide (Figure 4). This average was maintained over a volumetric TCOD loading range of from 0.92 to 4.92 kg/m^3/day, and a feed concentration of 2000 to 15,000 mg/l COD. At the highest levels of TCOD applied there seemed to be a small decrease in efficiency. Sulfide increased in the reactor and contributed a significant portion of the TCOD measured. Since this would be rapidly removed by subsequent aerobic treatment, the corrected TCOD is a more accurate means of evaluating the effectiveness of the anaerobic treatment.

The VSS content of the anaerobic reactor varied between 500 to 2000 mg/l over the test period. It fluctuated widely but did not appear to be increasing. When the TCOD removed was plotted vs the TCOD applied per gram of VSS, a graph similar to Figure 4, suggesting a removal of about 60%, resulted. However, in this case the scatter of data points around the line was greater. VSS ranged from 30 to 70% of the total solids in the feed. Hydraulic detention time of the reactor was generally 60 hr.

The TCOD applied/day and TCOD in the effluent/day are shown in Figure 5. Accurate sampling of the feed and the effluent from these experiments is difficult, as indicated by the scatter. However, the distinct changes in level of feed loading rates are apparent. The average removal efficiency over the period from January 8 to February 11 was 62% at a loading rate of 1.27 kg TCOD/m^3/day. During the rest of the period in February and March it was 62% while the applied TCOD averaged 3.89 kg TCOD/m^3/day.

Other Parameters

The pH of the reactor varied from 7.4 to 8.2 but changed very slowly. The system rapidly developed a level of 600 mg/l of VFA; although it ranged up to 1800 mg/l, it never dropped below 600 mg/l. This is an indication that the microorganism population was always changing but never fell below a certain level. The stability of the pH, in spite of VFA variability, is probably due to the high alkalinity of the feed from the unhairing waste.

Kjeldahl nitrogen and ammonia analyses were performed on samples from the feed, reactor, and effluent. TKN across the system remained constant. However, 32% was converted to free ammonia which appeared in the effluent.

Gas Production

Perhaps the most interesting finding of the research deals with methane production in this system. Figure 6 shows the concentrations of sulfide ions and volatile fatty acids in the reactor and the volume of methane produced each day. It is generally accepted that sulfide, which reached levels as high as 1000 mg/l in the reactor, inhibits methane generation. As expected, the reactor initially did not produce gas, but shortly after start-up gas was generated at a rate of 4-5 l/day. This is equivalent to nearly 0.2 l CH_4/g COD destroyed/day. Even at this level, however, roughly 30 times less gas was generated per unit of COD removed than normally produced in municipal digesters. Over the period of these experiments, gas production slowed to low levels on two occasions. In both cases the decrease corresponded to a rapid increase in TCOD loading on the reactor. The pH of the reactor, as indicated before, was quite stable and changes in gas production did not correlate with a change in pH.

It appears from Figure 6 that concentration of VFA, concentration of sulfide, and methane generation all reacted to the TCOD change shown in Figure 5 rather than to each other. The gas production reacted most dramatically and was the slowest to recover. At precisely the point where feed concentrations were increased all of these parameters dropped and all ultimately recovered.

Figure 7 shows the percent of TCOD removed daily. Comparison of this with the loading pattern shown in Figure 5 clearly shows that the TCOD removal was not affected by a rapid change in TCOD applied. On one occasion, a return sludge line broke and the sludge in the system spilled onto the laboratory bench. In the morning it was scooped back into the settling tank, and by the next sampling time the TCOD removal had completely recovered. This indicates that the system is not acutely poisoned by oxygen and is quite stable under anaerobic conditions.

A second feature on this figure demonstrates how rapidly the system recovers from a spill. These interactions are consistent with the generally accepted thesis that TCOD removal and methane formation are two different systems in the anaerobic process. Since the volatile fatty acids reacted and recovered at different rates than the methane production, perhaps there are even three systems.

Scale Up

The practicality of an anaerobic system for tannery waste depends on the size of the system required and the energy costs associated primarily with maintaining the necessary temperature.

The size of the system depends on the concentration of waste which can be treated, the removal reaction rate, the mean cell retention time, and the hydraulic detention time. The bench-scale system would permit treatment of waste with COD as high as 15,000 mg/l. The hydraulic retention time required is 60 hr. Equalized waste from the entire tannery has a much lower COD (approx. 3-4000 mg/l). The ability of this system to treat very concentrated waste might not be used to full advantage on the total effluent.

In addition, the anaerobic system must be run at a temperature of 37 C. In a municipal digestor the methane generated can be burned to produce sufficient energy to maintain that temperature. The yields of gas in this reacto have not been nearly that good. In part, this is due to the fact that this waste is largely proteinaceous. Through the use of heat exchange between the treated effluent and the influent, a significant gain in efficiency could be obtained.

Anaerobic treatment of tannery waste might be efficient only for specific concentrated streams; the smaller amount of liquid would require less heat and reactor size. The effluent from this reactor would then be combined with the rest of the streams for further aerobic treatment.

CONCLUSIONS

Experimental results obtained on the treatment of tanning unhairing effluent with a bench scale anaerobic reactor can be summarized as follows: TCOD reductions of over 60% were achieved on this waste with loadings as high as 4.92 Kg/m^3/day (15,000 mg/l), with only a 60-hr hydraulic retention time. In this series of experiments, the removal appeared to be independent of the loading over the range tested. Production of methane, sulfide, and volatile fatty acids was strongly affected by a rapid change in the feed concentration. Concentration of each dropped quickly when TCOD increased. Recovery of sulfide and VFA was much more rapid than that of methane generation. Methane was generated in this system in spite of the presence of sulfide at levels greater than 1000 mg/l. Sulfide levels continually increased during the test period. It was presumably formed from the disulfide linkages present in the dissolved hair protein, keratin. Approximately 32% of the Kjeldahl nitrogen in the feed was converted to ammonia over the same time period. Periodic tubing connector problems resulted in spills of sludge from the reactor, which, however, recovered rapidly.

REFERENCES

1. U.S. Environmental Protection Agency, "Leather Tanning and Finishing Point Source Category Effluent Limitations

Guidelines, Pretreatment Standards, and New Source Performance Standards," Federal Register, 44, 38746 (July 2, 1979).

2. Bailey, D. G., Tunick, M. H., Cooper, J. E., Friedman, A. A. and Chang, I. L., "Aerobic Suspended Fixed Film Treatment of High-Strength Tannery Beamhouse Waste," 12th Mid-Atlantic Industrial Waste Conference Proceedings, Bucknell University, Lewisburg, Pa., 142 (1980).

3. Cooper, J. E., Happich, W. F., Mellon, E. F. and Naghski, J., "Acclimatization of Activated Sludge to Lime-Sulfide Unhairing Effluents," JALCA, 71, 1 (1976).

4. Jennett, J. C. and Dennis, N. D., "Anaerobic Filter Treatment of Pharmaceutical Waste," JWPCF, 47, 104 (1975).

5. Witt, E. R., Humphrey, W. J. and Roberts, T. E, "Full-Scale Anaerobic Filter Treats High Strength Wastes," 34th Industrial Waste Conference Proceedings, Purdue University, Lafayette, Indiana, 229 (1979).

6. Young, K. S., Friedman, A. A. and Bailey, D. G., "Pretreatment of Tannery Beamhouse Wastewater Using an Anaerobic Filter: Preliminary Results," 12th Mid-Atlantic Industrial Waste Conference Proceedings, Bucknell University, Lewisburg, Pa., 102 (1980).

7. Knechtel, J. R., "A More Economical Determination of Chemical Oxygen Demands," Water and Poll. Control, (May-June 1978), 25.

8. Supelco, Inc., Analysis of VFAs from Anaerobic Fermentation, Bulletin 748E, Bellefonte, Pa. (1975).

9. Standard Methods for the Examination of Water and Wastewater (Washington, DC: APHA, 1976), 14th edition.

0. Booth, H., "Atmospheric Oxidation of Alkali Sulphide Solutions," J. Soc. Leather Trades Chemists, 40, 238 (1956).

1. Technicon Industrial Systems, Industrial Method No. 34474 W/B, Tarrytown, N.Y. (1977).

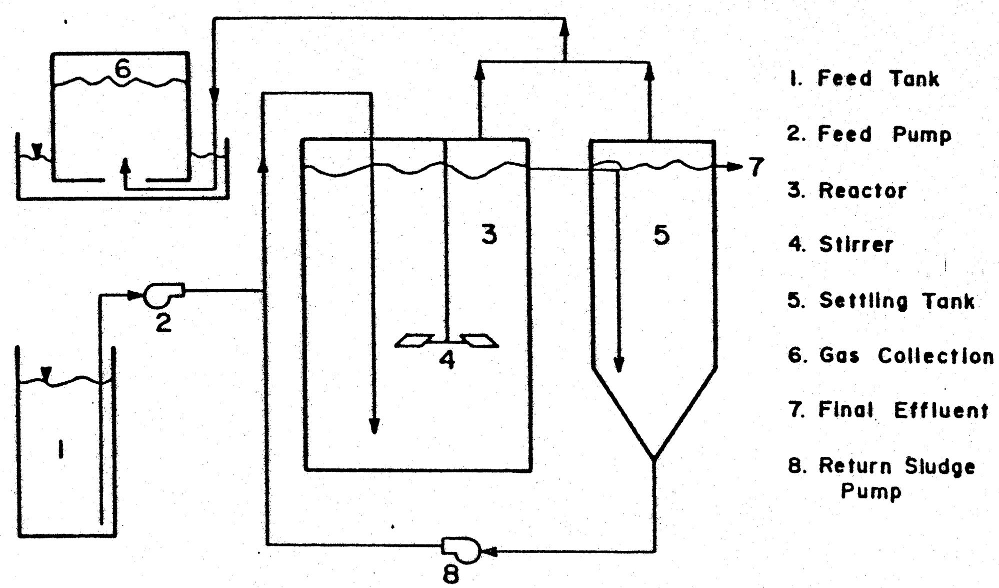


Figure 1. Schematic diagram of bench-scale reactor.

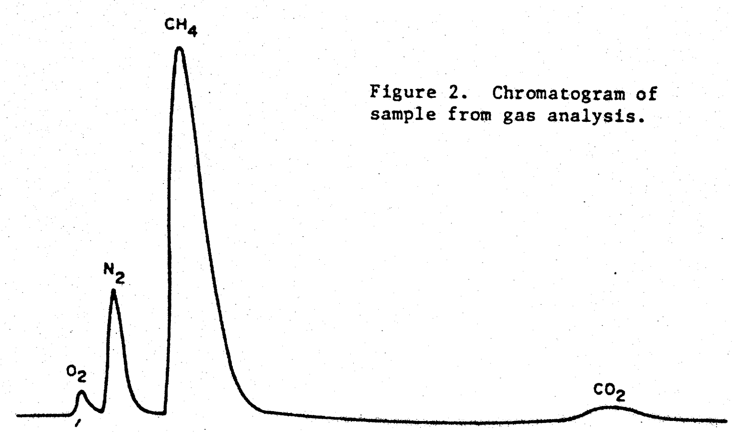


Figure 2. Chromatogram of sample from gas analysis.

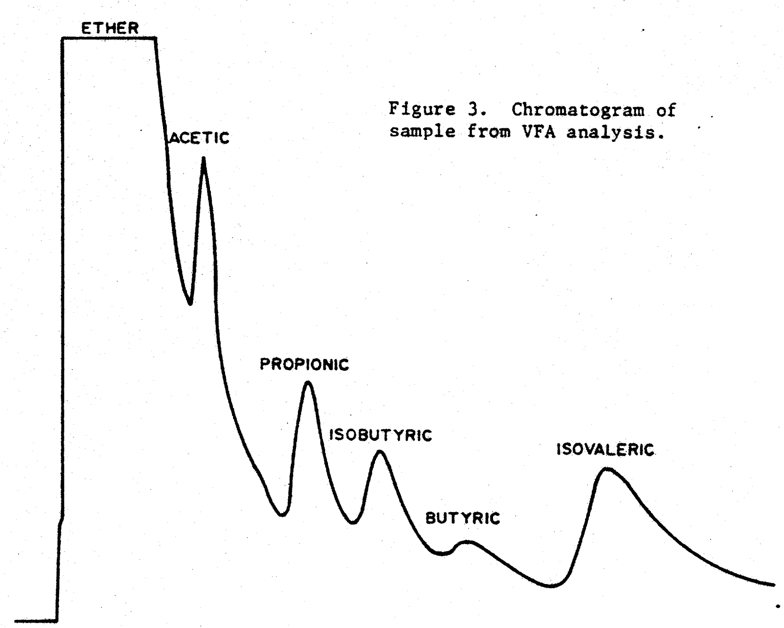


Figure 3. Chromatogram of sample from VFA analysis.

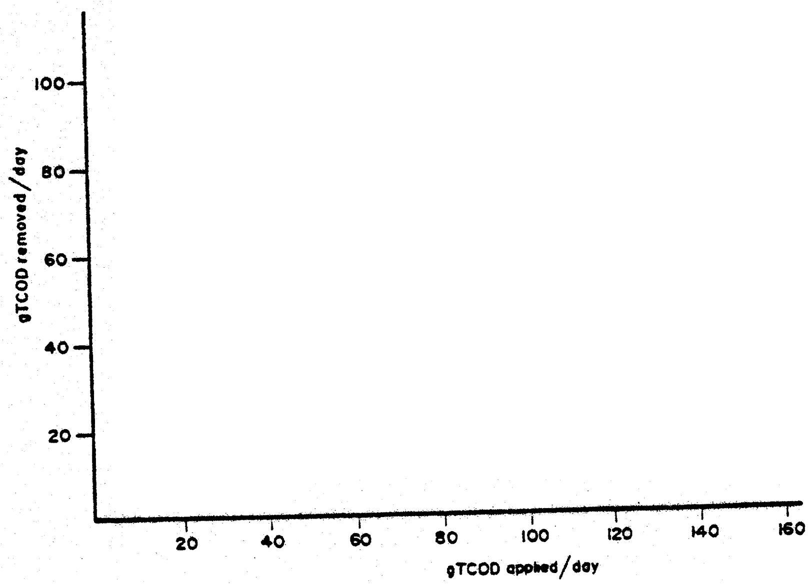


Figure 4. Application and removal of tannery beamhouse waste

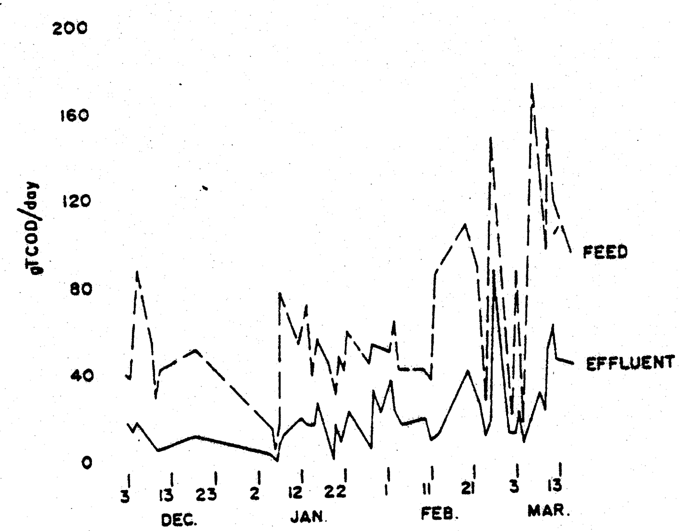


Figure 5. Chronological variation of TCOD in feed and effluent

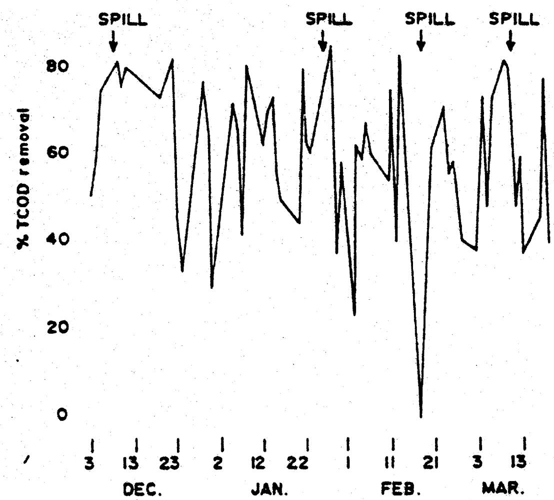


Figure 6. Chronological variation of TCOD removal

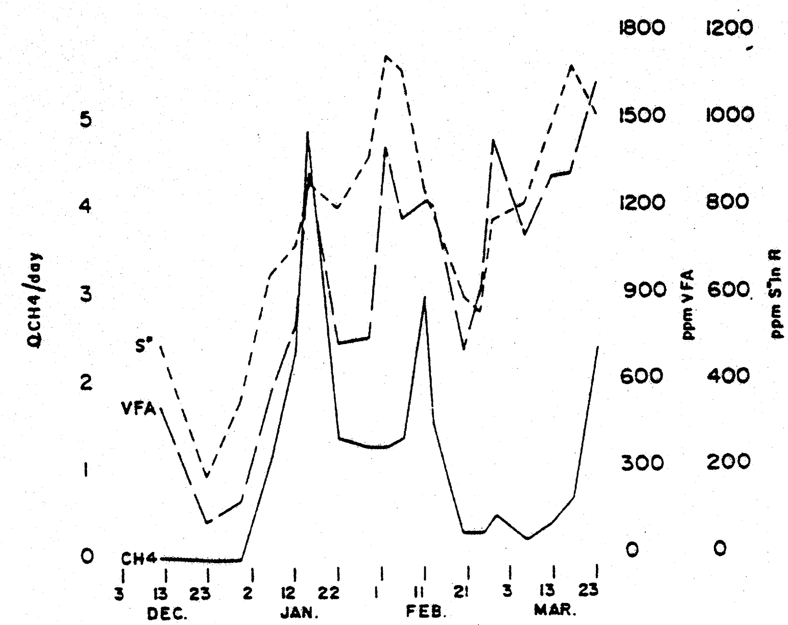


Figure 7. Comparison of reactor CH_4 production, VFA, and $S^=$