ANAEROBIC DIGESTION OF CELLULOSIC WASTES

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Summary

Anaerobic digestion is a potentially attractive technology for volume reduction of low-level radioactive cellulosic wastes. A substantial fraction of the waste is converted to off-gas and a relatively small volume of biologically stabilized sludge is produced. Process development work has been completed using a 75-L digester to verify rates and conversions obtained at the bench scale. Start-up and operating procedures have been developed, and effluent was generated for characterization and disposal studies.

Three runs using batch and fed-batch conditions were made lasting 36, 90, and 423 d. Solids solubilization rates and gas production rates averaged approximately 1.8 g cellulose per L of reactor per d and 1.2 L of off-gas per L reactor per d. Greater than 80% destruction of the volatile suspended solids was obtained. A simple dynamic process model was constructed to aid in process design and for use in process monitoring and control of a large-scale digester.
INTRODUCTION

Disposal of solid low-level radioactive waste is an increasing problem for the nuclear industry. The Oak Ridge National Laboratory (ORNL) generates about 2300 m$^3$ of low-level waste each year, of which about 350 m$^3$ is cellulosic and readily amenable to biological degradation. This waste is currently placed in trenches in the burial grounds after a portion is compacted. In the trenches, it is subject to natural biological decomposition, which leads to instability and subsidence in the burial grounds. One alternative disposal technology is incineration. However, incineration suffers from substantial off-gas cleanup requirements and the poor economics of small incinerators that handle relatively small volumes of material.

Another alternative is anaerobic digestion of the cellulosic fraction of the solids. Anaerobic digestion offers the attractive potential to reduce the volume of wastes by converting a substantial fraction of the solids to methane and carbon dioxide and producing a biologically stabilized sludge that is better suited for burial than is the original waste.

Feasibility studies, preliminary process design, and a cost estimate were carried out for an anaerobic digestion plant to treat actual wastes at ORNL [1-3]. The proposed process flowsheet (Fig. 1) includes separation of the solids remaining after digestion and liquid treatment in the ORNL low-level waste evaporator system. The solids can be mixed with a cement grout for landfill. A total volume reduction of 80-90% appears to be possible with this process.
Process development work was initiated to provide scale-up data and operating experience for the design and operation of the full-scale digester at ORNL. Goals of the work included the development of dependable start-up techniques for the digester, determination of the viability of the proposed batch feeding method, and determination of digester operating conditions. The latter included consideration of solids concentration, pH, alkalinity, liquid recycle, supplemental municipal anaerobic sludge, long-term operating stability and solids destruction, and the need for supplementation with a mineral and vitamin solution.

This report discusses a 423-d run with a 75-L digester. A mathematical model of the digestion process [4] was developed for use in guiding process development work and eventual process control. The verification of the model with experimental data and the experimental results of the run are presented.

MATERIALS AND METHODS

Substrates, Nutrients, and Inoculum

The digester was operated on simulated nonradioactive low-level solid waste composed of 90% blotter paper, 7% cotton/polyester (35/65) labcoats, and 3% other absorbents. This composition is representative of the actual radioactive waste that is proposed for biotreatment at ORNL. The feed was wet-shredded by American Delphi, Inc., Westminster, CA, to a 1-cm particle size, and stored at 4°C as a 10% slurry. During the feeding procedure, a predetermined volume was removed from the digester, then an equal amount of feed was measured and added. Solka-floc was also
used for several weeks when simulated mixed waste was unavailable. The nutrients, inocula, and start-up methods were described earlier [3].

Analytical Procedures

The samples of digester contents, seed sludge, and feed were prepared and analyzed according to Standard Methods [5] for total and volatile suspended solids (TSS and VSS), alkalinity, pH, and filtered and unfiltered chemical oxygen demand (COD) using Hach COD vials. Total volatile acids (TVA) and several individual volatile acids (acetic, propionic, isobutyric, butyric, isovaleric, and valeric) were analyzed using a Varian 3700 gas chromatograph with a 6.4-mm x 2-m glass column containing 60/80 Carbopak/0.3% Carbowax 20 M/0.1% H$_3$PO$_4$ at 120°C with a helium carrier and a flame ionization detector. Gas production was measured with a wet test meter. Gas compositions were measured with a Perkin-Elmer Sigma II gas chromatograph with a 3.2 mm x 2-m stainless steel Poropak-Q column operated at 30°C with a helium carrier.

The digester contents were sampled daily (except on weekends and holidays), and the quantity of gas produced was recorded each day. The sampling procedure for the digester involved taking two 200-mL samples, which were each analyzed for TSS and VSS and the results averaged. The remaining analyses (COD on filtered and unfiltered samples, individual volatile acids and TVA, pH, and alkalinity) were performed on pooled samples. The volume removed, the volume and content of the material fed to the digester (if any), and the time of sampling and feeding were all recorded.
Operating Procedures

Start-up was initiated by adding a seed culture to the feed mixture of 0.1% cellulose, methanol, and nutrients. The seed sludge was obtained from the Oak Ridge West End Sewage Treatment Plant and was added to obtain a 3 vol % sludge concentration in the digester. The digester was fed twice a week for several months and the biological activity gradually increased [3,4].

Thereafter the digester was operated in the fed-batch mode. The feeding schedule varied according to the type of experiment and ranged from no feeding for up to 2 weeks to feeding daily for several weeks. Usually, the digester was fed twice per week. In addition, the cellulose content was varied from less than 200 g per feeding to 500 g per feeding, with one feeding of 1500 g of cellulose.

During much of the operation with Solka-floc, the digester was operated to simulate recycle of supernatant from a solids settling step. The supernatant recycle is desirable in treatment of actual radioactive wastes to minimize the radioactive liquid effluent that must be further treated. All of the extra digester effluent withdrawn daily was saved and allowed to settle at 4°C. New feed for each day was prepared using the settled effluent supernatant as the liquid to suspend the cellulose.

Description of Process Model

A dynamic simulation model has been developed to aid in process development work [3,4]. It is a three-culture model corresponding to the three simplified bioconversion steps shown in Fig. 2. The cellulose hydrolyzers convert cellulose to sugars, the acetogens convert sugars to
acetic acid and a small amount of other products, and the methanogens convert acetic acid to methane and CO₂. In addition, each culture generates cell mass from its own substrate and produces CO₂ as a metabolic by-product.

This representation is a simplification of the overall conversion of complex substrates to methane and CO₂ [6,7]. The "acetogens" in Fig. 2 include fermentative bacteria. The H₂ + CO₂ route to methane is incorporated in the acetogenic and methanogenic steps. Although this pathway accounts for approximately 30% of the methane production, combining it with the acetate pathway gives a tractable yet reasonable model of this complex process. Separate representation of the two pathways to methane is straightforward, but would introduce yet more kinetic parameters to be specified a priori or obtained by curve-fitting.

Each mixed culture is assumed to grow according to Monod-type kinetics,

\[
\frac{dX}{dt} = X(\mu - k_d), \tag{1}
\]

where \( X \) is the cell concentration and

\[
\mu = \mu_{\text{max}} \left( \frac{S}{S + K_S + (S^2/K_i)} \right), \tag{2}
\]

where \( \mu \) is the specific growth rate, \( S \) is the substrate concentration, \( K_S \) is the usual half-saturation constant, \( K_i \) is the substrate inhibition constant, and \( k_d \) is the specific death rate.
Mass balance equations are written for the substrates and products in the reaction scheme shown in Fig. 2. For example, the rate of change of acetic acid (HAc) concentration in the digester is

\[
\frac{dC_{\text{HAc}}}{dt} = \mu_A X_A \Phi_{\text{HAc}} - \mu_M X_M (\Phi_M + \Phi_{\text{CH}_4} + \Phi_{\text{CO}_2}) .
\]

Subscripts A and M refer to the acetogenic and methanogenic cultures, respectively, in Fig. 2. Substrate and product kinetic rates are proportional to organism growth rates through the \( \Phi \) coefficients, which are calculated from conventional yield factors and carbon stoichiometry. For example, \( \Phi_{\text{HAc}} \) is the quantity of acetic acid produced by acetogens per unit of acetogens produced, and has units of g HAc/g acetogens. Similarly \( \Phi_M \) is the quantity of acetic acid converted to methanogens per unit of methanogens produced, and has units of g HAc/g methanogens. The \( \Phi \)s are obtained from the relationships in Table I [6-11], along with stoichiometric factors when necessary for dimensional consistency.

Equations analogous to Eqs. (1)-(3) were formulated for the three cultures, cellulose, sugar, acetic acid, methane, CO\(_2\), and other soluble carbon species that are not substrates for methane and carbon dioxide and may accumulate. The set of nine simultaneous differential equations comprise an initial value problem that was solved using the ODE library routine on the DEC 10 system at ORNL. To simulate fed-batch operation, the problem was reinitialized at each feeding point to account for material fed and withdrawn. No particular effort was made to adjust parameters in the model to fit the experimental data with the exception
of the fraction of sugar converted to "other" soluble carbon, which was set at 0.095 based on experimental observations. All kinetic and yield parameters in Table I were held constant throughout the simulation.

The experimental feed solids content, volume, and frequency were used in the simulation as the feed input and the corresponding effluent was calculated in the simulation just prior to feeding. For graphical representations, the simulation data were printed out at the same frequency as the experimental data were taken. For example, the gas production was totaled for a period and divided by the length of the period to give an average rate for the interval, analogous to the experimental data. The rates are therefore integrated averages and not instantaneous rates at a given time. This method causes considerable smoothing of the simulation data.

RESULTS AND DISCUSSION

Operation of Digester

Digestion of simulated low-level waste was carried out for the first 215 d. Operation with effluent supernatant recycle began on day 216 and ended on day 341. Solka-floc was used as the feed cellulose starting on day 238 and continued through day 359. During the final phase of operation, a starvation test (day 385 through day 401) and a large batch feed test (day 414 through day 423) were completed.

Table II describes the carbon balance on the digester for the duration of the run. The total amount of carbon fed was calculated based on the known amount of feed and its carbon content. The gas produced was measured by the wet-test meter, converted to standard temperature, pressure,
and dry gas, and divided by 22.4 L/mol to obtain the mols of carbon (CH$_4$ + CO$_2$) produced. The mols of solid and soluble carbon removed by sampling were calculated based on the volume of the sample removed and the experimental VSS and soluble COD determinations for that day. For the entire run, 93.6% of the carbon fed was accounted for by the carbon out as gas, solids, and soluble carbon. The remaining 6% can be allocated in part to loss of material during several equipment failures. Over 70% of the carbon fed was converted to off-gas, and over 80% of the solids fed were solubilized.

Figures 3-6 give an overall picture of the 423-d experimental run. The experimental data are shown as points and the simulation results are the solid lines. Figure 3 shows the digester VSS concentrations. Considerable scatter occurred in the data, primarily because of the difficulty in obtaining a representative sample of the contents after the digester had been fed. The problem is caused by large clumps of solids in the digester. For this reason, there is more variation in the experimental data than is seen in the simulation. When the feed rate was increased, the minimum VSS values gradually increased. As the digester became acclimated to the higher feed rates, the VSS values decreased and tended to stabilize.

The solids degradation rates and off-gas rates are shown in Figs. 4 and 5. The solids degradation rates are more erratic than the gas rates, because they are calculated from the experimentally measured values of VSS. The experimental VSS rates are computed by subtracting the VSS value for the current day from the VSS for the previous day (after adding
the feed and subtracting the sample from the previous day), then dividing
by the elapsed time. The rates varied from about 0.8 to 2.0 g/L•d during
the first 300 days of the run, and from 2.0 to 6.5 g/L•d from day 300 to
day 400. Figure 5 shows the gas production rate; a peak of almost 6
L/L•d was reached, but typically the rates varied from 0.5 to 4.0 L/L•d.
Figures 3, 4, and 5 show the cyclical nature of the fed-batch operation
in the fine structure on the plots. After feeding, the gas and solids
rates and the VSS concentration increase and then decrease until the next
feeding.

Figure 6 is a plot of the TVA during the run, and shows peaks at
days 50-150, again near day 300, and also at day 360. The latter two
peaks occurred during changes in the feeding rates and coincided with
peaks in the TVA/ALK ratio. When the peaks occurred in the TVA/ALK
ratio, the pH was raised to 7.5 using sodium hydroxide to increase the
alkalinity. Over the course of the run, the pH was fairly stable between
6.5 and 6.9, depending on the time since feeding, and no regular pH
control was necessary.

The liquid recycle experiment was conducted during days 216 through
341 (125 days). During this time, a total of 23.8 kg of cellulose solids
was fed. This included 1.7 kg of prepared simulated waste and 22.1 kg of
Solka-floc. No inhibitory effects were seen. Total liquid recycle
operation can be compared to a hypothetical batch reactor which is fed an
equivalent amount of cellulose. In this comparison, the batch digester
would require an initial solids concentration of 41.6% w/v (23.8 kg in
58.7 L of digester volume) to use the same quantity of liquid as the fed-
batch, liquid-recycle digester.
The digester was deliberately starved for a period of 17 days. Near the end of the run, when samples were withdrawn, an equal volume of water was added and on two days, a mineral-nutrient solution was added. The digester was fed twice during the following two weeks and then it was fed 150 g of Solka-floc at one time. The gas and solids degradation rates were monitored over the next several days until the digester was shut down. The gas rate results for these tests are shown in Fig. 7. The solid line in Fig. 7 is the model simulation. The digester was responsive to the feedings and produced high gas rates after the 1500 g feeding.

Modeling Results

Experimental data and simulation results are compared in Figs. 3, 4, 5, and 7. The agreement between the experimental data and the simulation is semi quantitative in both frequency and amplitude and is generally satisfactory, considering the approximate nature of the model.

Figure 4 shows the comparison of the experimental and simulated solids degradation rates. There is more scatter and deviation between the experimental and simulation results for the VSS rate because of the problems mentioned previously in obtaining representative samples of the VSS each day. The VSS for the simulation was calculated by adding the biomass for the cellulose, inerts, and organisms provided by the simulation for each day and then proceeding as for the experimental data at the same time intervals, with the same volumes of feed and effluent and the same feed cellulose content.

Figure 7 shows the gas production rate data for the experiment and simulation for a 70-d period during which the digester was starved and
then fed a single large batch of cellulose. The simulation follows the experimental data semi quantitatively, although the peaks and valleys are more exaggerated. The gas rate in the simulation fell to zero about a week after the starvation period began, while the experimental rate never fell all the way to zero. The simulation also predicts a higher peak for the gas rate after feeding. In general the simulation predicts a faster response to perturbations than is produced in the digester. This anomaly could not be significantly reduced by changes in the parameter values (Table I). Separate representations of the acetate and the $\text{H}_2 + \text{CO}_2$ pathways might provide additional flexibility in the model.

CONCLUSIONS

This process development work verified earlier studies. Start-up procedures were developed using methanol supplementation to avoid inhibition by reaction intermediates and promote establishment of the proper organisms. Operation was stable for an extended period of time under fed-batch conditions with widely varied feed composition and feeding schedule, including starvation and overfeeding. The digester also was operated for four months on nearly total recycle of liquid effluent with no noticeable loss of efficiency. A simple dynamic process model was developed that simulated the experimental dynamic behavior under stable fed-batch operating conditions and also under some process upset conditions. The value of this model lies in its utility for process control and operational guidance for a full-scale fed-batch digester.
ACKNOWLEDGMENTS

S. N. Lewis performed many of the analyses on the digester contents and assisted in the operation of the digester. G. W. Strandberg frequently provided valuable technical advice. The cellulosic feedstock was wet-shredded free of charge by American Delphi, Ind., Westminster, CA.

References


<table>
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<th>Parameters for simulation model</th>
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<tbody>
<tr>
<td><strong>Maximum specific growth rate, day⁻¹</strong></td>
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<tr>
<td>cellulose hydrolyzers</td>
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<tr>
<td>acetogens</td>
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<td>methanogens</td>
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<td><strong>Specific death rate, day⁻¹</strong></td>
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<td>methanogens</td>
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<td><strong>Substrate half-saturation constant, g/L</strong></td>
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<td>CO₂ from acetic acid, via methanogens</td>
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<td><strong>Cell yield factor, g cells/g substrate</strong></td>
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<td>cellulose hydrolyzers from cellulose</td>
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<td>methanogens from acetic acid</td>
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<td><strong>Initial concentrations, g/L</strong></td>
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*Initial concentrations of species not shown were set equal to zero. Concentrations of microorganisms were estimated to give the desired start-up time. Simulation results at longer times were relatively insensitive to these initial conditions.*
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<td>Total</td>
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\(a\)Includes periodic effluent and contents of digester at termination of run.
Figures

Fig. 1. Process flowsheet for anaerobic digestion of low-level cellulosic waste.

Fig. 2. Comparison of experimental and simulated VSS. Legend: □ = experimental data; —— = simulation.

Fig. 3. Comparison of the experimental and simulated solids degradation rates. Legend: X = data; —— = simulation.

Fig. 4. Comparison of the experimental and simulated gas production rates. Legend: □ = data; —— = simulation.

Fig. 5. Total volatile acids (TVA) in the digester for Run 3.

Fig. 6. Comparison of experimental and simulated gas production rates during starvation and overfeeding. Legend: + = data; —— = simulation.