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ANAEROBIC DIGESTION OF CELLULOSIC WASTES

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ABSTRACT

Anaerobic digestion is a potentially attractive technology for volume reduction of 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 is underway using a 75-L digester to verify rates and conversions obtained at the bench scale, to develop start-up and operating procedures, and to generate effluent for characterization and disposal studies.

Three runs using batch and batch-fed conditions have been made lasting 36, 90, and over 200 days. Solids solubilization and gas production rates and total solids destruction have met or exceeded the target values of 0.6 g cellulose per L of reactor per day, 0.5 L off-gas per L of reactor per day, and 80% destruction of solids, respectively. Successful start-up procedures have been developed, and preliminary effluent characterization and disposal studies have been done. A simple dynamic process model has been constructed to aid in further process development 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 2300 m³ of low-level waste each year, of which ~350 m³ is cellulosic and amenable to biological degradation. This waste is currently placed in trenches in the burial grounds, where it is subject to natural biological decomposition, which leads to instability and subsidence in the burial grounds. An alternative disposal technology is incineration; however, incineration is widely viewed as undesirable because of substantial off-gas cleanup requirements and the poor economics of small incinerators to handle relatively small volumes of material.

Anaerobic digestion offers the 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. The anaerobic digestion process is similar to a residential septic tank and stabilization of sludge as practiced in the municipal wastewater treatment industry. The major biochemical reactions are illustrated in Fig. 1. Feasibility studies, a preliminary process design, and a cost estimate have been carried out for implementation of an anaerobic digestion plant to treat actual wastes at ORNL.^{1,2}

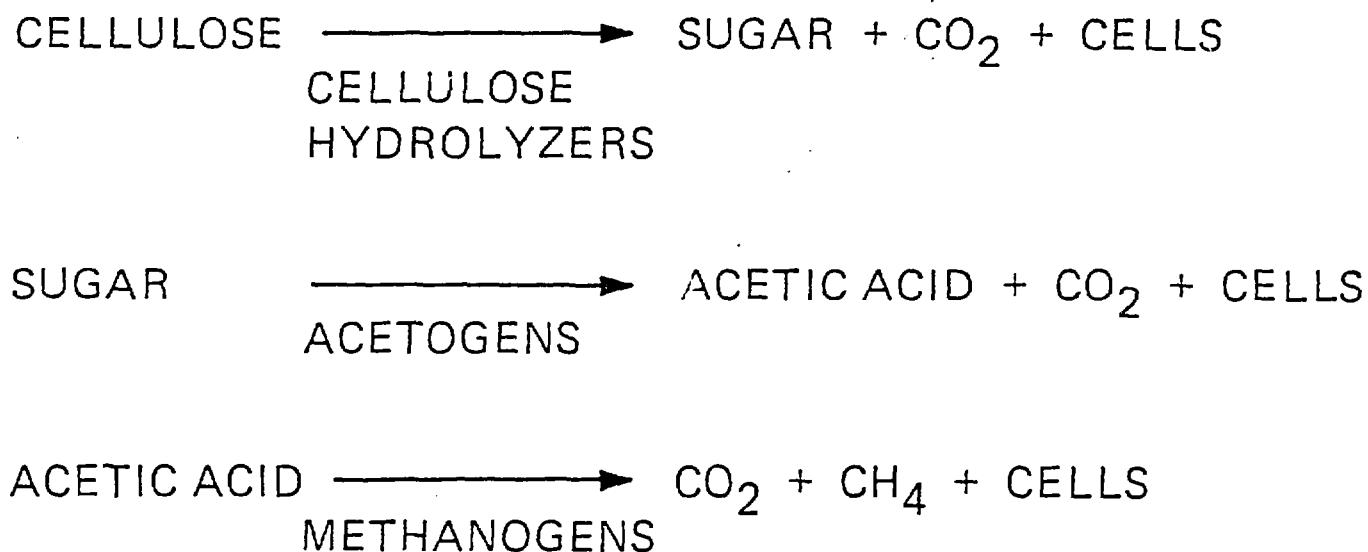


Figure 1. Major biochemical conversion steps in the anaerobic digestion of cellulose.

The initial feasibility study¹ explored the rates and extent of microbial digestion of blotter paper, cloth, sanitary napkins, and pine sawdust in shake flasks, batch stirred reactors, and fed-batch stirred reactors. From these results, a cellulose degradation rate of 0.6 g/L·d and a gas production rate of 0.5 L/L·d were chosen for process design purposes.

The preliminary process design and cost estimate² were based on anaerobic digestion of a wet-pulped cellulosic materials mixture that is batch-fed to the digester. A 94.5-m³ (25,000-gal.) digester would be needed to digest the ORNL waste at a solids concentration of 1-2%. The flowsheet for the process (Fig. 2) includes separation of the solids remaining after digestion from the water that will be treated in the ORNL low level waste evaporator system. The solids will be mixed with a cement grout for landfill. It appears that a total volume reduction of ~80-90% will be possible with this process. Disposal of the effluents via hydrofracture was considered

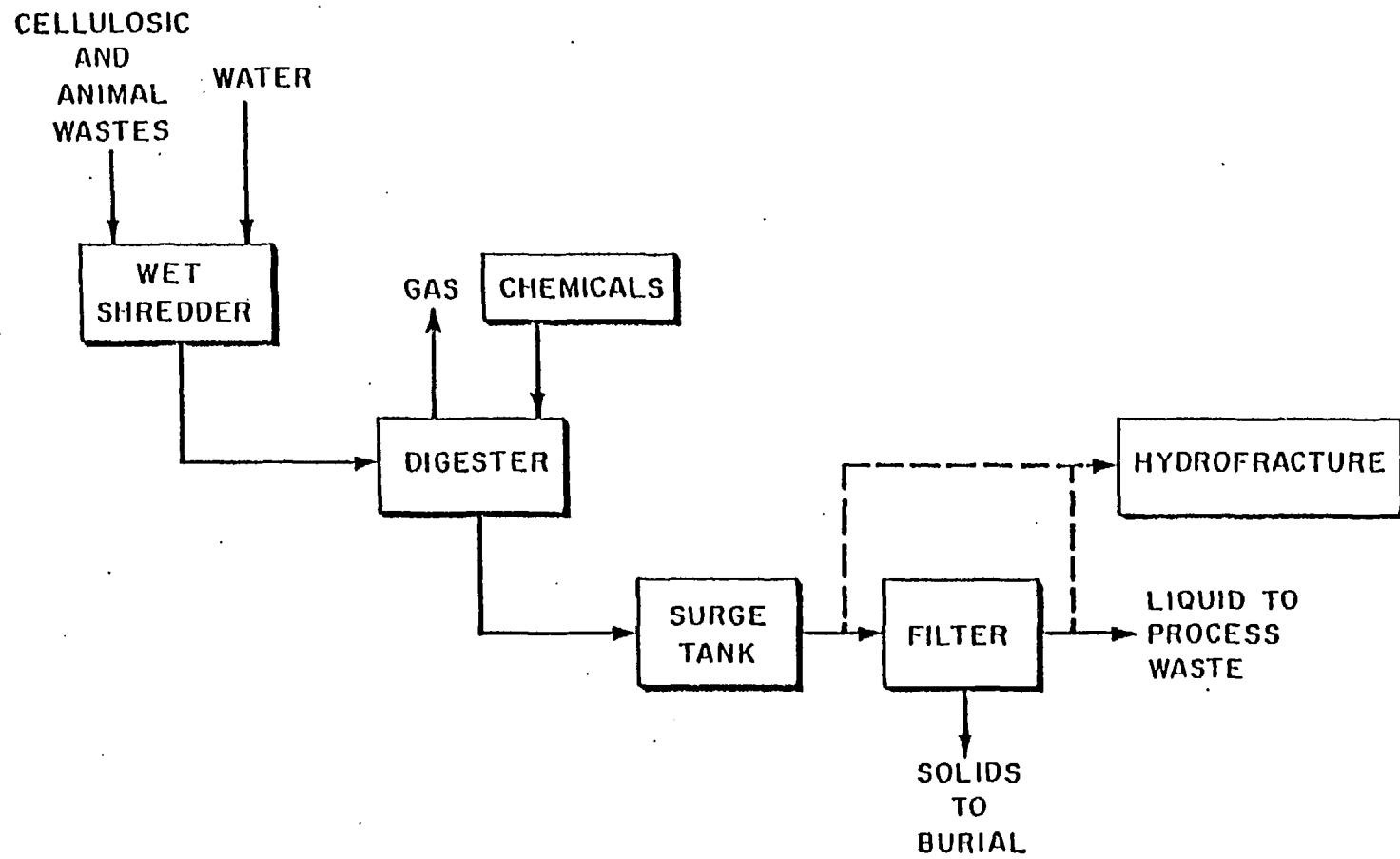


Figure 2. FLOWSHEET FOR ANAEROBIC DIGESTION OF LOW-LEVEL CELLULOSIC WASTE



initially, but is not now being pursued. Total capital costs are estimated to be $\sim \$2000/m^3$ of uncompacted waste, and annual operating costs are estimated to be $\sim \$270/m^3$ of uncompacted waste.

Process development work has been initiated to provide scaleup data and operating experience for the design and operation of the full-scale digester at ORNL. The experimental work is being carried out in a 75-L digester using a feed material that simulates the cellulose materials found in the ORNL low-level solid waste. Goals of this work include 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 includes consideration of solids concentration, pH, alkalinity, liquid recycle, supplemental municipal anaerobic sludge, long-term operation stability, and solids destruction. A mathematical model of the digestion process is ~~be developed for~~ use in guiding process development work and eventual process control.

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EXPERIMENTAL PROCEDURES

Feed Material and Inoculum

The 75-L digester is operated on simulated low-level radioactive solid waste composed of 90% blotter paper, 7% cotton/polyester (35/65) lab coats, and 3% sanitary napkins. The feed was shipped to American Delphi, Inc., Westminster, California, for wet-shredding and then shipped back to ORNL as a $\sim 10\%$ slurry of about a 1-cm particle size, and stored at 4°C .

The inocula used to seed the digester, and also added to the digester occasionally to increase gas rates, were obtained from several local municipal wastewater treatment plants. A portion of the sludge was added to the digester the same day as obtained, if possible, and the remainder was stored at 4°C for later addition, but was not stored for more than two weeks.

Analytical Procedures

Samples of digester contents, seed sludge, and feed are analyzed periodically for total and volatile suspended solids (TSS and VSS), alkalinity, pH, and filtered and unfiltered chemical oxygen demand (COD) (using Hach COD vials) according to Standard Methods.³ Total volatile acids (TVA) and several individual volatile acids (acetic, propionic, isobutyric, butyric, isovaleric, and valeric) are analyzed using a Varian 3700 gas chromatograph with a 3.2-mm 2-m column containing 60/80 Carbopak C/0.3% Carbowax 20 M/0.1% H_3PO_4 at 120°C with a helium carrier and a flame ionization detector. Gas production in the digester is measured with a wet test meter.

Digester Description and Operation

The 75-L digester is a standard industrial fermenter with associated instrumentation and piping that was purchased from New Brunswick Scientific Company. Its working volume is ~65 L. The digester is made of 316 stainless steel and is jacketed for temperature control. It is also equipped with pH control and agitation speed adjustment. The fermenter was modified for operation as an anaerobic digester by removing the gas sparger and the internal baffles. The three turbine impellers on the agitator shaft were replaced by a single 7-in.-propeller type agitator (Lightnin A310, Mixing Equipment Co.), which provides better pumping action to suspend the larger particulates with less violent mixing action. An additional sampling system was also added to the digester to obtain more uniform samples of the contents. The sampler consists of a top-entering 1/2-in.-OD stainless steel tube that can be raised or lowered to any vertical position to sample the digester contents. The sampler is operated by pressurizing the digester with nitrogen and then opening the sample valve.

Operation is initiated by adding a seed culture to an initial feed mixture of cellulose and nutrients. Various start-up procedures have been investigated, and the following protocol has been adopted. The solids concentration is initially set at 0.1% cellulose and methanol is added as a carbon source specifically for the methanogenic bacteria. The methanol concentration is set equivalent to the carbon content of the cellulose added. The seed is added to obtain a 3 vol % concentration in the digester. The pH is maintained at ~7.0, the temperature is maintained at ~35°C, and the agitation speed is ~80 rpm.

During start-up, the concentration of cellulose is gradually increased over a period of ~40 d while methanol is fed periodically as the population of methanogens gradually builds up in the digester. After the first week, 1 L of municipal digester sludge is added daily during the week for a period of two months. The TVA concentration and pH are closely monitored to prevent a build up of inhibitory acids, which occurs when cellulose is solubilized faster than the acids are converted to gas.

The digester is operated in the batch-fed mode; the volume of feed to be added is calculated, that volume of material is withdrawn from the digester, and the same volume of fresh feed is added. The material added may include nutrient solution and additional sludge in addition to the cellulose slurry. The usual feed mixture contains ~200 g dry wt cellulose in a total volume of 4.0 L. The usual criteria for feeding is a slowing of the gas production rate and a significant decrease in the TVA concentration in the digester. These criteria result in a feeding schedule of two or three times per week. During some of the tests, feeding was conducted on a daily schedule, while other tests required a weekly schedule. Also, the feed cellulose content was varied, and the feed volume was changed to obtain different hydraulic residence times and solids loadings.

Process Modeling

A dynamic simulation model is being developed to aid in process development work. It is a three-culture model corresponding to the three major bioconversion steps shown in Fig. 1. 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 CO_2 .^{4,5}

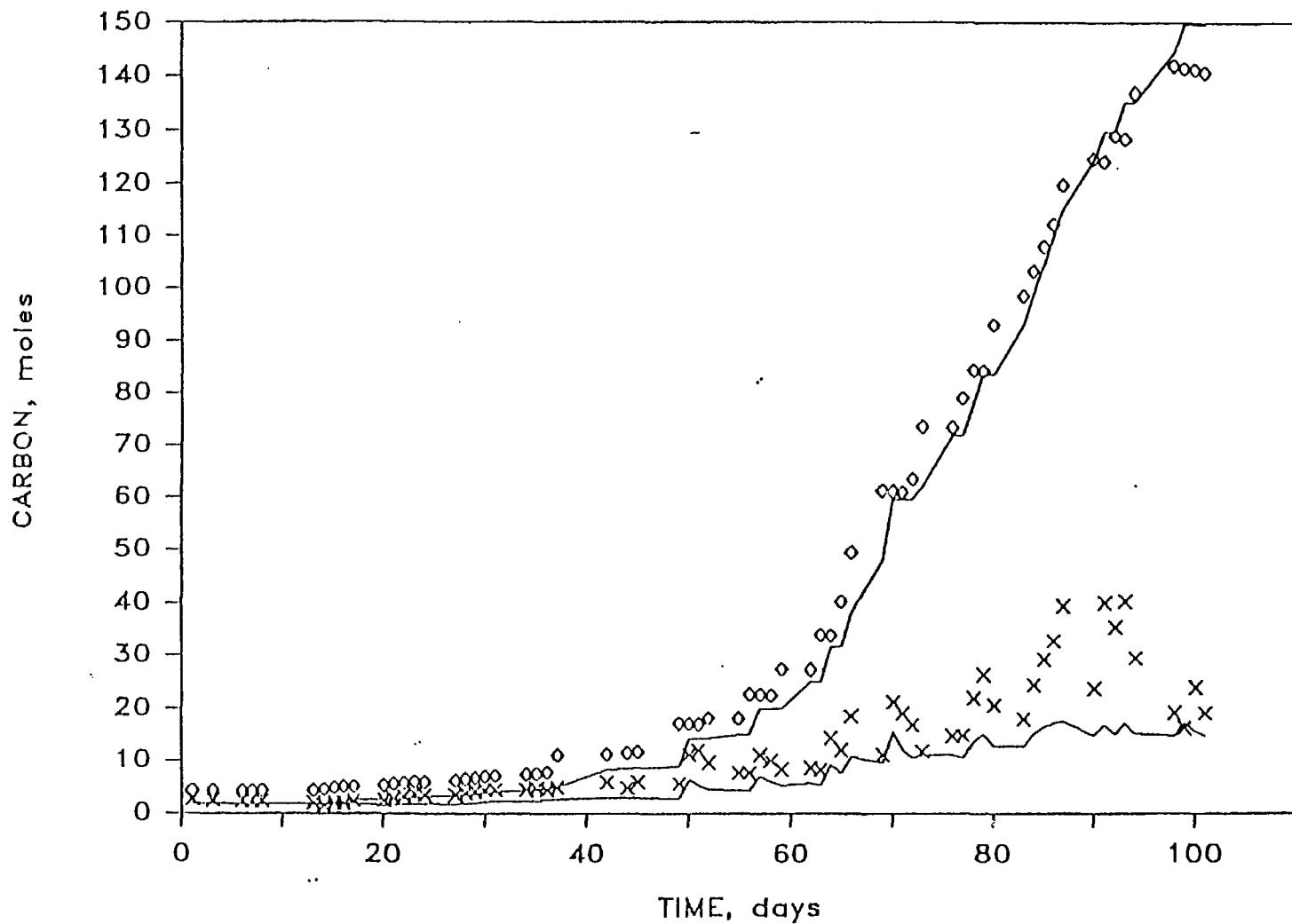
In addition, each culture generates cell mass from its own substrate and produces CO_2 as a metabolic by-product. Note that the $\text{H}_2 + \text{CO}_2$ route to methane is not included. We have found it unnecessary to include the latter process in order to simulate our data in a satisfactory manner. Substrate and product kinetic rates are proportional to organism growth rates through coefficients which are calculated from conventional yield factors and carbon stoichiometry.

The resulting 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 batch-fed operation, the problem ~~was~~ is reinitialized at each feeding point to account for material fed and withdrawn. Details of the model and parameter values may be found in refs. 6 and 7.

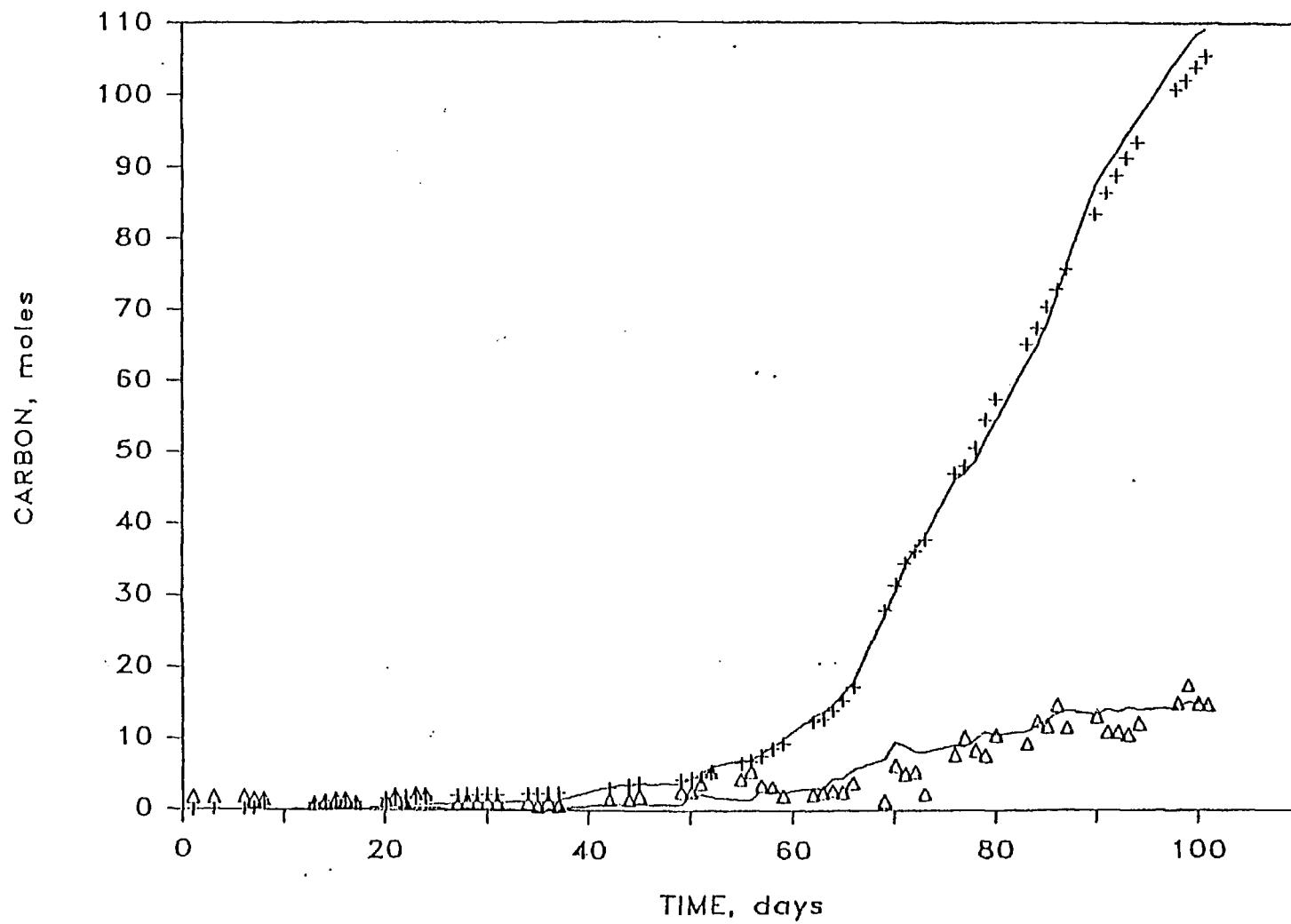
RESULTS AND DISCUSSION

Results from the most recent experiment are shown in Figs. 3-5. The experimental data are represented by symbols and the simulation is represented by continuous curves. The experiment was started with 0.1% cellulose and 300 mg/L methanol. The concentration of cellulose was gradually increased and the TVA concentration was closely monitored to prevent the rapid buildup that caused inhibition in earlier batches. The first 40 d were a start-up period; gas production averaged ~ 0.02 - 0.05 L/L·d (1-2 L/d) as the solids concentration was increased to ~ 3000 mg/L (0.3%). After 70 d, the solids concentration had reached $\sim 0.65\%$, the gas production dramatically increased up to 1.2 L/L·d, and the solids degradation rate increased to 1.45 g/L·d. At this point, the rates exceeded the design rates of 0.6 g cellulose/L·d and 0.5 L gas/L·d at a hydraulic retention time (HRT) of ~ 35 d.

During the next 30 d, the feeding interval was decreased and the amount of cellulose in the feed was increased. As a result, the solids in the digester were increased to $>1.5\%$. During one 5-d period, the digester was fed daily at an HRT of 16 d. The gas production was >0.5 L/L·d during this period, but the propionic and butyric acid components of the TVA began to slowly increase, causing an increase in the ratio of TVA to alkalinity. This ratio, when >0.4 - 0.5 , is indicative of impending problems in the digester and should stay <0.3 in a healthy digester. At times, the ratio was >0.6 - 0.8 , a very unhealthy condition.



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Fig. 2. Experimental and simulated carbon inventories for 75-L digester showing cellulose feed and volatile solids. \diamond = experimental net carbon feed; \times = experimental volatile solids; — = simulated values.



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Fig. 2. Experimental and simulated carbon inventories for 75-L digester showing gas and soluble carbon. + = experimental gas; Δ = experimental soluble carbon; — = simulated values.

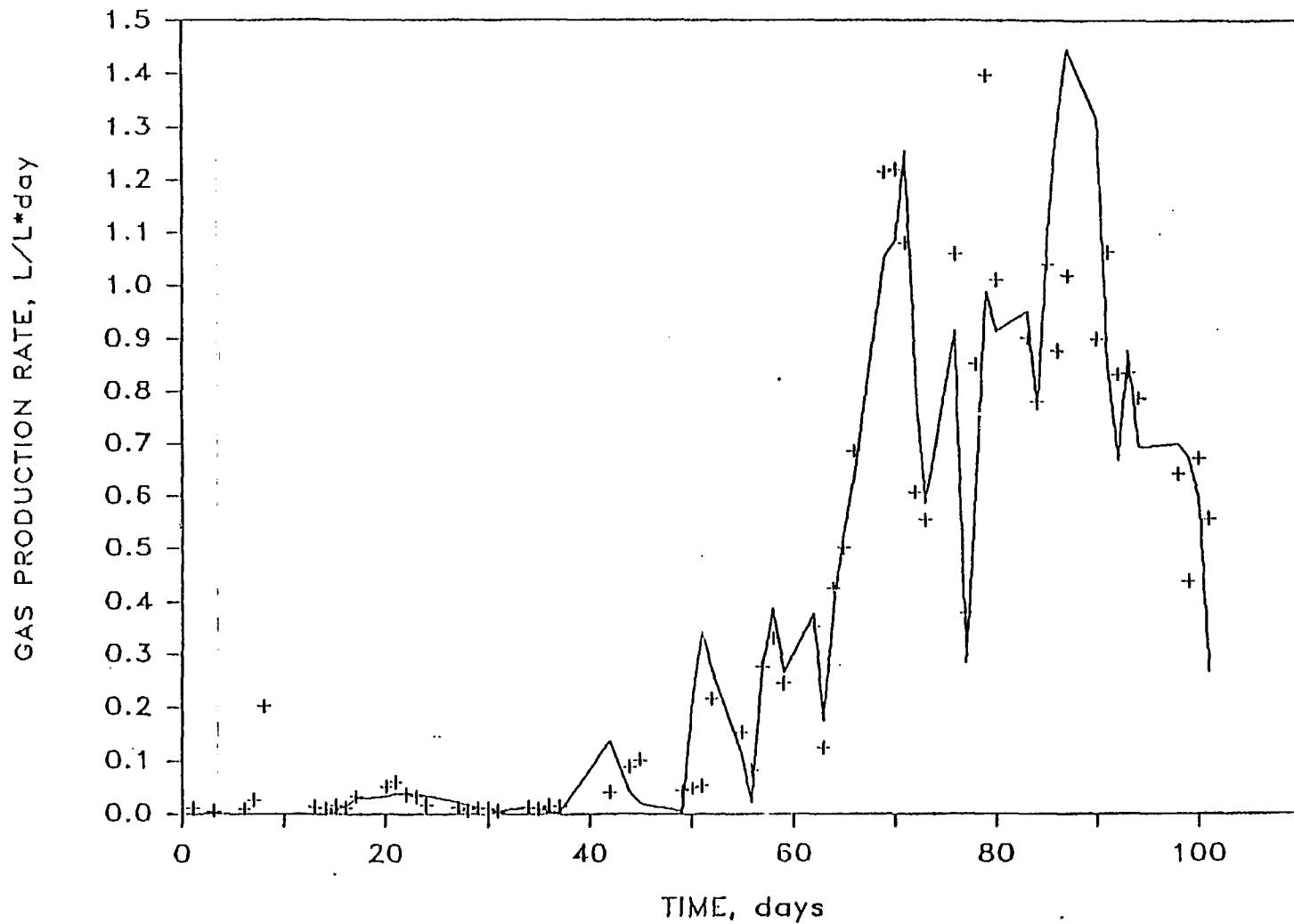


Fig. 5. Experimental and simulated gas production rates for start-up through 102 days of operation. + = experimental values; — = simulated values.

X Several methods were employed to lower the TVA concentration and the ratio of TVA to alkalinity. One method was to let the digester itself bring the TVA level down by decreasing the amount of cellulose in the feed and increasing the feeding interval to an HRT of 50 d. The TVA did not decrease, but the gas rate and the solids degradation remained relatively stable. Next, a short HRT and low solids concentration in the feed were used to dilute the TVA by washing it out. The HRT was reduced to 22 d and the feed concentration was reduced to ~2% solids (5% was normally used). The TVA was reduced by 60% in ~2 weeks and the TVA to alkalinity ratio was reduced from >0.5 to <0.3. As the TVA came down, the feed rate and concentration were gradually built up at an HRT of 25 d. The digester organisms then appear to have developed the ability to rapidly degrade the propionic and butyric acids. This resulted in TVA to alkalinity ratios of <0.1 and TVA ~~values~~ of 100-300 mg/L. X Concentrations

The solids concentration in the digester has ranged from 0.5 to 1.5% (depending upon the length of time after feeding) and the solids degradation rate and gas production rate have averaged 1.34 g/L·d and 0.71 L/L·d, respectively. One important point that is apparent from Figs. 3 and 4 is that the inventories of VSS and soluble carbon have not built up unduly over the course of the run, and the cellulose that is broken down and solubilized is converted to gas. For the 100-d period, the overall solids degradation has been ~75%, with ~83% of the solubilized carbon going to off-gas. These integrated performance parameters will improve with additional operating time.

It can be seen in Figs. 3-5 that the agreement between the experimental data and the simulation is satisfactory. No particular effort was made to adjust parameters in the model to fit the data with the exception of the fractions of sugar converted to acetic acid and to "other" soluble carbon.

← ^{no ft} The volatile solids parameter shown in Fig. 3 is a combination of micro-organisms, undigestibles, and cellulose. This parameter is difficult to measure accurately in the digester due to the difficulty in obtaining a representative sample of the larger suspended solids. For this reason, there is more variation in the experimental data than is seen in the simulation.

Gas production rates are shown in Fig. 5. The agreement between experiment and simulation is semiquantitative in both frequency and amplitude. The experimental rates are daily averages during the week and 3-d averages over weekends. Some smoothing of the simulated gas rate was introduced by printing the rates at the same intervals as the experimental data were taken.

The experimental run shown in Figs. 3-5 is continuing and is >300 d. Recent work has focused on recycle of the liquid effluent, after removal of residual solids, in order to minimize the liquid effluent for ultimate disposal. For a period of three months the HRT has been infinite — that is, no fresh water has been added. Approximately 2 L of clarified effluent has

been used to slurry 300 g of dried feed twice per week, and an equal volume of material removed from the digester at each occasion. The gas rate has averaged 1.3 L/L·d and the solids degradation rate has averaged 1.45 g/L·d. These rates are comparable to those in Figs. 3-5 with no liquid recycle, and indicate no inhibition of performance. The TVA concentration and the TVA/alkalinity ratio have remained low and stable, as desired. These results have important practical implications for operation of the larger digester to be built at ORNL, and for effluent disposal.

Work is also underway to assess performance of the digester at higher solids loading rates. Preliminary results indicate that a 2-3-fold increase in the loading rate is easily achievable, and gas rates increase proportionally without undue accumulation of solids and acids in the digester.

EFFLUENT DISPOSAL STUDIES

The plan for effluent disposal at ORNL is fixation of the sludge in concrete for burial and treatment of the liquid effluent in existing low-level waste evaporator system. A solids-liquid separation will be carried out to give a sludge with satisfactory water content for cement formation and a liquid with satisfactory properties for the evaporator system. Studies to characterize these liquid and solid fractions have been initiated.

Issues to be addressed for treatment of the liquid by evaporation include the physical behavior during evaporation (e.g., foaming), carry-over of organics to the condensate, and nature of the residual concentrate. Studies to date have shown that the pH of the digester effluent is ~7, and there is a concentration of ~0.15 N of weak organic acids. The acid concentration may be reduced through improved operation of the digester. After neutralization to pH 10, the liquid foams excessively at the boiling point, but the foaming can be controlled with antifoam. In the waste evaporator system, the digester effluent would be diluted with other wastes, which should minimize foaming.

Measurements of pH, COD, total and inorganic carbon, and TVA in an original effluent sample, the concentrate, and several condensate fractions are shown in Table 1. It can be seen that the majority of the COD and acids remain in the concentrate residue, although some lighter acids do go to the condensate.

Studies on fixation of the solids in concrete have been initiated, but no definitive results are available yet. However, personnel experienced in this area have indicated that no unusual problems are expected. Principal variables to be investigated include water content of the sludge, and physical and chemical stabilities of the cement.

Table 1. Characterization of effluent fractions following evaporation and concentration

Sample	pH	Chemical oxygen demand (mg/L)	Total carbon (mg/L)	Inorganic carbon (mg/L)	Volatile acids ^a as acetic acid (mg/L)
Original effluent	6.43	13,200 ^b	9470		1060
Concentrate	10.21	16,500	4735		
1st condensate fraction (20 mL)	9.95	460	4090	4000	24
2nd condensate fraction (250 mL)	9.05	140	420	400	18
3rd condensate fraction (250 mL)	8.10	90	120	100	14

^aThe 1st and 2nd condensate samples contained some lower boiling organics, such as formic acid, that were not resolved.

^bThis sample contained solids that were included in the chemical oxygen demand. The others were clear liquids. Similar samples with no solids contained 7000-8000 mg/L of chemical oxygen demand.

SUMMARY

Process development work to date has led to the following accomplishments, observations, and conclusions:

1. Rates and yields obtained in earlier scouting studies have been verified at a nominal 75-L scale. The solids destruction rate, the gas production rate, and the extent of solids degradation have met or exceeded the design values used in the preliminary design of the ORNL facility. Substantial liquid recycle appears to be a feasible mode of operation.

2. Start-up procedures have been developed and tested for the case of sewage sludge inocula. A relatively low concentration of cellulosics (~0.1%) and supplementation with methanol are desirable to avoid inhibition by reaction intermediates and promote establishment of the proper organisms. The time required for start-up appears to be 1-2 months. While the time could probably be reduced with more development work, this start-up period is probably satisfactory from a practical standpoint.

3. A significant quantity of effluent has been produced for further characterization and disposal studies, and is stored at 4°C. Additional biological activity will be negligible at this temperature. It is probable that process effluent will be held in tankage for short periods of time before disposal in any case.

4. A simple dynamic process model has been developed that satisfactorily simulates the experimental behavior under stable operating conditions. The value of this model lies in its utility to guide further process development work, especially with respect to operation under stress and various feeding schedules, and in potential utility for process control and operational guidance for a full-scale digester.

Additional process development work is planned and/or is underway. This work includes additional liquid recycle studies, operation under various stressed conditions and higher solids loading, and disposal of solids. Completion of these activities will further enhance the prospects for implementation of anaerobic digestion of cellulosic wastes as a volume reduction technology.

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