# Optimizing Hydrolysis/Acidogenesis Anaerobic Reactor with the Application of Microbial Reaction Kinetics

## A. Paramsothy, B.F.A. Basnayake<sup>1</sup>, R.M. Wimalaweera and D.T.N. Wijesinghe

Postgraduate Institute of Agriculture<sup>1</sup> University of Peradeniya Peradeniya, Sri Lanka.

**ABSTRACT.** Among the various options available as treatment, a combined system of anaerobic/aerobic digestion is a promising technique for treating Municipal Solid Waste (MSW). The maximum extractions of elute in the first reactor of two-stage digesters reduce the required volume of reactors while benefiting from the production of biogas and aerobic compost. This study was undertaken to determine which of the configurations, up or downward flow of liquid in a hydrolytic phase anaerobic reactor, is best and to optimize feeding of reactor for maximum elute extractions. Two pilot scale (500-L) anaerobic digesters were used in this study. Daily feeding was done with presorted raw MSW.

The classical 'logistical growth' kinetics was used in the analysis. It was found that there exists two distinct phases of microbial growth. The phase change seems to take place when Volatile Suspended Solids (VSS) reach the peak value of  $\alpha/\beta$ . However at the time of this change, the cumulative Volatile Solids (VS) had not reached the peak due to high concentrations of raw wastes, transformed substrate and microbial cellular materials in the upward flow experimentation. In the case of downward flow, again, VS were not allowed to reach the peak due to limitations on diffusion of substrate and product. The rates of transformations in analyzing VS and VSS in the upward direction were much higher than those downward. It could be further improved by feeding the reactor 7.5 days after operating the digester and subsequent feeding every 3.3 days while extracting the elute everyday.

### **INTRODUCTION**

Growing urbanization and industrialization have led to the generation of large quantities of wastes, which can be broadly classified as Municipal Solid Waste (MSW), hazardous wastes and Industrial wastes. In Sri Lanka, the daily per capita solid waste generation from households is about 0.3-0.65 kg/day and the total amount of MSW generated is around 6400 tonnes/day (UNEP, 2001). Since the organic fraction makes up 65% of the total amount of MSW, it produces 4100 tonnes of biodegradable waste per day in Sri Lanka. Therefore, treatment of these wastes is an important component of an integrated solid waste management strategy to reduce both the toxicity and volume of the MSW for final disposal in landfill.

Among the various options available as pre-treatment, anaerobic digestion is a promising method of treating MSW because it has more advantages over other methods. Mainly, it gives useful products such as compost and biogas, which can be used as an

<sup>&</sup>lt;sup>1</sup> Department of Agricultural Engineering, University of Peradeniya, Sri Lanka.

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energy source in developing countries. Also it needs comparatively less space and reduces the amount of greenhouse gas emissions when compared to combustion/incineration, aerobic composting and land-filling (Environment Canada, 1995). Further, it reduces pathogens of MSW and could obtain hygienic compost from the remaining fibrous sludge.

Anaerobic digestion proceeds through a series of parallel and sequential processes by varieties of consortia. In a well-balanced anaerobic digestion process, all products of a previous metabolic stage are converted into the next one without significant build up of intermediary products. The overall result is a nearly complete conversion of the anaerobic biodegradable organic material into end products like methane, carbon dioxide, hydrogen sulfide, and ammonia.

When considering the particulate substrate like solid waste, hydrolysis is the rate-limiting step since the accessibility of hydrolytic microorganisms to the solid matter and hydrolysis of complex polymeric components are not at an optimum level (Delgenes *et al.*, 2002). The rate of hydrolysis is a function of factors such as pH, temperature, composition and particle size of the substrate (Veeken *et al.*, 2000).

MSW anaerobic research is focusing on optimizing the process conditions of the first phase, which is responsible for the breakdown of complex organics except lignified materials. Reducing the raw MSW to lignified materials is one object of the Sustainable Solid Waste Landfill Management Project so that elute formed in the first phase of hydrolysis is separated from the composting of lignified materials. Thus the present systems of composting could continue with the added advantage of energy generation. However, the present two stage anaerobic systems are very expensive and require better process conditions to handle large quantities of waste, particularly to address the controversial issue of dry and wet or solid and slurry phase digestion.

Kinetic analysis is more helpful to understand the conditions in the reactors and it can be used to modify and optimize the microbial dynamics of the reactors. This study is an attempt to compare two pilot scale experimentations (up flow and down flow reactor) of the hydrolytic phase digesters and to optimize feeding of reactor. This will determine the design criteria for landfill bioreactors and optimization of enzymatic reactions for rapid degradation of MSW.

### METHODOLOGY

### **Reactor design**

The Experiments were carried out at Meewathura University Farm, Faculty of Agriculture, University of Peradeniya. Two reactor systems were used with downward (P1) and upward (P2) leachate circulation system and the system mainly consists of a hydrolytic reactor (500-L) and two leachate tanks (200-L each), See annex I, II. The MSW was introduced to the middle compartment from the top feeding hopper and the elute fraction was filtered out from the system to be sent for the second phase digestion. The remaining fibrous sludge was removed periodically from the bottom valve of the reactor.

Elute of this slurry phase was circulated periodically in downward direction for P1 and upward direction for P2 with the use of a one hp centrifugal pump. Filtering plates

inside the reactor facilitate the process of filtering out elute from large or fibrous particles in both reactors.

### Feeding the reactor

The MSW collected from Local Authorities were used for the study. MSW were hand-sorted to obtain biodegradable fraction, then mixed, shredded and chopped to particles of less than 2.5 cm before feeding into the reactor. To understand the composition of MSW, random samples were analyzed. The quantity of water to be added was based on the average moisture content (10-15% DM) of the raw waste so that adequate water content was maintained in the influent to facilitate elute circulation and extraction. The feedings were done everyday for a period of more than 15 days.

## Samples for analysis

Samples were taken from the extracted elute and analyzed for Volatile Solids (VS) and Volatile Suspended Solids (VSS). All experimental analyses were carried out with standard methods (AOAC, 1992). The sample analysis was done on a daily basis.

## Analysis

It has been assumed that all of the parameters that depend on microbial growth follow the logistical growth curve;

$$X_{t} = \frac{\alpha X}{\beta X_{,t} e^{i\omega} + \alpha - \beta X_{0}}$$
(1)

where,

 $X_t$  = Biological transformation mass of microbes at time t.

 $X_a$  = Initial value of reactive of microbes.

 $\alpha$  = Transformation or growth coefficient.

 $\beta$  = Retardation coefficient, and

 $X = X_0 e^{\alpha t}$  = Biological transformation mass of microbes.

The first derivative

$$\frac{dX_i}{dt} = \alpha X_i - \beta X_i^2$$
(2)

A non-linear computer program based on Math Lab was developed to obtain the above coefficients and  $X_o$ 

The program parameters were  $a = \alpha$ ,  $m = \frac{\alpha}{\beta} X_0$ , and  $c = X_0$ 

The regression analysis was conducted to obtain coefficient of determination ( $R^2$ ). The program optimized the value of a, m and c to give the optimum  $R^2$  value.

When the first derivative 
$$\frac{dX_i}{dt}$$
 equated to transformation rate  $(Tr)$  and differentiated  
with respect to  $X_i$ :  $\frac{dTr}{dX_i} = \alpha - 2\beta X_i$  (3)

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and at the maximum value of the transformation rate (slope equal to zero), the maximum concentrate or utilization of biomass is;

$$X_{i} = \frac{\alpha}{2\beta} \tag{4}$$

Substituting  $\frac{\alpha}{2\beta}$  in equation (1), the time for maximum substrate utilization rate could be found

be found,

$$\frac{\alpha}{2\beta} = \frac{\alpha X_0 e^{\alpha t}}{\beta X_0 e^{\alpha t} + \alpha - \beta X_0}$$
  
$$\therefore \alpha \beta X_0 e^{\alpha t} = \alpha^2 - \alpha \beta X_0$$
  
$$e^{\alpha t} = \frac{\alpha^2 - \alpha \beta X_0}{\alpha \beta X_0}$$
  
$$t = \frac{1}{\alpha} \ln \left(\frac{\alpha}{\beta X_0} - 1\right)$$
(5)

### **RESULTS AND DISCUSSION**

### **Composition study**

Table 1 shows the composition of raw MSW and digester feed which were used for the study. MSW used for the study was found to be rich in organic materials such as food and vegetable refuse, yard wastes, and papers, which are mostly biodegradable (71%). The moisture content of samples was 62% and had an average biodegradable perishable content of about 65%. After manual sorting of MSW the biodegradable portion of digester feed has increased to 90% and other parts such as plastic and polythene, metal, glass and soil were reduced. Therefore, the sorted waste is highly suitable for biological treatments like composting and anaerobic digestion (Madugethika *et al.*, 2002). The composition of the MSW assumed to be consistent throughout the experiment periods since collection route and sources were the same.

### Single and two-phase reactions

The enzyme activity depends on the physical and biochemical changes. VS and VSS in elute are indicative parameters, which can be used to express microbial growth dynamics in bioreactors. The VS loss of the organic substrate is accumulated in elute and is proportional to microbial activity and, therefore, the microbial growth  $X_t$  can be expressed as a proportional percentage of VS or VSS accumulation in elute.

Waste component	Raw MSW%	Digester Feed% (w/w)	
	(w/w)		
Perishables (food refuse and	65.0	90.0	
vegetables)	6.0	5.0	
Cardboard/paper	15.0	1.0	
Plastic/polythene	1.0	0.0	
Metal	0.5	0.0	
Glass	0.7	2.0	
Soil/sand	11.9	2.0	
Other	100.0	100.0	
Total	62.3	78.6	
Moisture (%)			

## Table 1. Characteristics of raw MSW and digester feed materials.



# Fig. 1 Experimental and predicted microbial dynamics based on variation of VSS-elute from P1.

The results of increase in VSS of elutes with time follow the classical logistic growth curve shown in figure 1 and the same pattern was observed for most of the reactors. A sigmoid growth curve (predicted) also referred to as 'logistic law' can be fitted to the experimental data.



## Fig. 2 Logistical growth curves of single and two phases fitted for Volatile Solids (VS) and two phases for Volatile Suspended Solids (VSS) of elutes from down flow reactor (P1).

There are slight deviations from the logistic curve in some experiments. These deviations are prominent at the beginning and in the latter part of the curve. However as mentioned by several authors (Loehr, 1984, Hutchinson, 1978; Rehm and Reed *et al.*, 1981) closer examination of the results indicates that there are two microbial growth curves. Although hydrolysis has been described by first order kinetics, Vavlin *et al.*, (1996) compared two-phase, Contois, Monod and first order and found that two phase and Contois were equivalent and best simulated the data. But Contois kinetics has a single parameter representing substrate and biomass saturation levels. Separate analysis for two curves gives more accurate predictions for smaller number of data points, where  $R^2$  of single phase cannot be compared with two-phase reaction. Figure 2 and 3 show the fitted curves for P1 and P2 reactors and table 2 and 3 give the logistic growth curve coefficients. Growth curve coefficients explain the microbial reactions and hence different reactor configurations could be compared.

### Comparison of reactor configurations - up and downward flow of elute

In the upward flow (P2),  $\alpha$  value for VS, which is the growth coefficient, is greater than downward (P1) but the  $\beta$  value, which is the retarding coefficient, is also relatively greater for P2 than P1, thus, the peak value of  $\alpha/\beta$  in the downward (P1) being higher than P2. However, the phase changes take place before reaching the peak value, particularly in the P1 reactor. These phase changes seem to occur when VSS reach the peak values and the peak value in the case of P2 is higher than that in P1, although  $\alpha$ value of P1 is slightly elevated than that of P2, while  $\beta$  of P2 was less than that of P1. VSS is a close measure of microbial population densities (Loehr, 1984) and substrate excess or limitations as well as saturation of products could be related to VS concentrations.

According to Garcia-Heras, (2003) hydrolysis is the first step of converting complex waste into soluble products by enzymatic activities. The microorganisms secrete intracellular enzymes as catalysts for hydrolysis and it undergoes a lysis process in which the cell membranes are broken down to release the organic matter to the bulk substrate.



Fig. 3 Logistical growth curves of single and two phases fitted for Volatile Solids (VS) and two phases for Volatile Suspended Solids (VSS) of elutes from up flow reactor (P2).

Parameter		VS	. <u></u>	VSS			
	Phase-1	Phase-2	Single	Phase-1	Phase-2	Single	
α	0.3472	0.2509	0.2481	1.0300	0.2500	0.6543	
β	0.0060	0.0024	0.0022	0.1397	0.0138	0.0436	
Хо	5.4000	6.3000	6.0000	0.0050	1.2000	0.0400	
α/β	57.0000	104.000	110.0000	7.4000	18.0000	15.0000	
R <sup>2</sup>	0.9980	0.9915	0.9972	0.9952	0.9692	0.9826	
X at Max	28.9333	52.2708	56.3863	3.6864	9.0579	7.5034	
$\frac{dX_{i}}{dt}$	5.0228	6.5573	6.9947	1.8985	1.1322	2.4547	
Tm	6.5	18.9	11.6	7.1	18.6	9.1	

 Table 2.
 Logistical growth parameters for Down flow reactor (P1).

Tm - time for getting maximum value of the transformation rate Down reactor (P1)

	VS			VSS			
		¥ 5			V 33		
	Phase-1	Phase-2	Single	Phase-1	Phase-2	Single	
α	0.7887	0.2604	0.3533	0.9129	0.5094	0.4471	
β	0.0152	0.0022	0.0033	0.0953	0.0164	0.0139	
Xo	3.5388	47.7725	8.6782	0.4477	9.6740	3.5388	
α/β	51.8947	118.8484	106.8503	9.5778	31.0584	51. <b>8947</b>	
R <sup>2</sup>	0.9889	0.9988	0.9947	0.9935	0.9952	0.9963	
X at Max	25.9440	59.1818	53.5303	4.7896	15.5304	16.0827	
$\frac{dX_{t}}{dt}$	10.2310	7.7054	9.4561	2.1862	3.9556	3.5952	
Τm	3.3	7.5	6.9	3.3	7.6	4.7	

 Table 3.
 Logistical growth parameters for Up flow reactor (P2).

Tm - time for getting maximum value of the transformation rate Up flow reactor (P2)

The retardation  $\beta$  of VS could be attributed to excess of soluble substrate causing organisms to stop producing enzymes (Ramsay, 1997). Enzymes are normally produced at a rate proportional to the production (addition) of biomass (Humphrey, 1979; Jain, *et al.*, 1992). Before substrate diffusion rate becomes rate limiting, the concentration of the product probably inhibits enzymatic degradation (Gonzalez et al., 1989). The X<sub>0</sub> of microbial concentrations in VS and VSS in the upward flow (P2) are much higher in the phase two reactions than those in P1, signifying the effect of transformations to cellular materials, being the saturation of product. It could then be deduced that the retardation coefficient  $\beta$  would increase if there were excess of both substrate and product. Thus feeding of reactor should be reduced to increase hydrolytic reaction rate in the first phase.

## Effect of surface area

The solubility and suspended materials from the wastes are more in an upward direction of flow, particularly in a slurry phase concentrations and it is much more efficient than in a downward direction of flow since it has been shown that the surface area has a strong effect on the rate of enzymatic hydrolysis of cellulose (Walker and Wilson, 1991), lipids (Martinelle and Hult, 1994) and proteins (Ramsay, 1997). Mechanical size reduction further facilitates this process by providing homogenized substrate and increases the surface area of substrate for enzymatic reactions (Chang, 1993). Also shredding reduces the volume and makes it easy to handle. Buivid *et al.*, (1981) has observed that the particle size reduction inhibits methanogenesis and enhances acid generation. According to Veeken *et al.* (2000), the optimal hydrolysis method depends on reactor configuration, liquid velocities, solid concentrations and retention time. It could be deduced that the ratio of solid: water in the slurry phase would be optimum with increased specific surfaces of active sites for adsorption reactions and diffusion of hydrolytic products.

In the up flow reactor (P2) the substrate is mixed frequently due to upward pumping and the microbes secrete enzymes to the bulk liquid where it absorbs into a particle or reacts with a soluble substrate (Jain *et al.*, 1992) and diffusion is not limiting. But in the case of P1, the surface area exposed is reduced and diffusion becomes the constraining factor, lowering both  $\alpha$  and  $\beta$ . Because as reported by Vavilin *et al.* (1996), the attached organism secretes enzymes into the vicinity of the particle and benefits from the soluble substrates being released.

### **Optimization of feeding**

Logistic growth curve coefficients (tables: 2 and 3) give a better understanding of the reactions and it is clearly illustrated in rate of change in VS in figure 3. The transformation rate of VS (dVS/dt) can be plotted with respect to time as shown in figure 3 and the transformation rates give similar trends for both reactors. The maximum transformation rate occurs after 3.3 days and approximately 7.5 to 7.6 days for both VS and VSS for first and second phases of reactions and X<sub>t</sub> at maximum corresponds the same trend for both VS and VSS, (tables 2 and 3). However, the values for the maximum transformation rate (dVS/dt) for VS and VSS are higher for upward than downward flow, which explains why the time taken for maximum transformation rate for both first and second phases is much longer in P1 than that in P2.

In order to further increase the rate of transformation, the available nitrogen should be released to stabilize the reactor. The release of nitrogen commences at the end of the carbonaceous demand (Loehr, 1984) and the first feeding after loading the reactor could be at the maximum transformation rate of the second phase and then subsequent feeding once every 3.3 days while the elute is removed everyday.



Fig.4 Experimental and predicted rates of change of VS (dVS/dt) with time for the 1<sup>st</sup> and 2<sup>nd</sup> phases of hydrolytic and acidogenesis in P1 and P2. Acidogenesis/fermentation reactions

It is very likely that the second phase that has been identified could be acidogenesis where organic acids and alcohols are formed (Jain *et al.*, 1992). The peak value of VS in the second phase is almost the same in P1 and P2. However, the time taken to reach the peak was much less and all other kinetic parameters are higher for VS and VSS in the upward than in the downward flow (table 2 and 3).

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## CONCLUSIONS

The composition of MSW used in the experiments as feed was suitable and consistent for anaerobic digestion. The increases in VS and VSS follow the classical logistic growth curves for the two configurations of up and downward flow in the hydrolytic phase digester. Although the growth curves show a single-phase digestion, two distinct phases could be identified. The phase change takes place when VSS reaches the peak in the first phase reactions.

The growth coefficient  $\alpha$ , and the retarding coefficient  $\beta$  of the upward flow experimentation is higher than in downward flow experiments, resulting in a lower peak value for  $\alpha/\beta$ . The phase change of VSS takes place before VS reaches the peak value since excess concentrations of substrate, organic materials and microbial cellular materials retard the transformations in the upward flow experimentation. Mass transfer through diffusion is the limiting factor in the downward direction of flow. Although the upward flow is better than the downward in breaking down the solids, it could be more effective if the feeding of reactor is performed once the reactor has been stabilized at the maximum transformation rate of the second phase and subsequent feeding every third day while elute is extracted everyday.

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# ANNEX -1





## ANNEX II

Hydrolysis phase reactor



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