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Determination of Kinetic Parameters in Anaerobic Digestion Process Using Distillery Wastes – A Mathematical Approach

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Abstract- Biodegradation offers an eco-friendly option for disposal of waste coming from different breweries and wineries. A model-based analysis through rigorous experimentation has been accomplished to study different aspects of the biodegradation of distillery wastes. Using distillery waste as resource material, energy is derived in the form of biogas containing high percentage of methane which is produced by concerted action of various groups of anaerobic bacteria. The effect of process parameters such as B.O.D. loading, digestion temperature, stirrer speed and cell mass concentration are very much important for biomethanation process. On the other hand kinetic parameters such as maximum specific growth rate, kinetic constant and ultimate methane yield take the leading role in the production of biogas adopting biomethanation process.

By computer analysis of the experimental data model equations relating maximum specific growth rate with digestion temperatures and B.O.D. loading has been developed. Also kinetic constants have been correlated with digestion temperatures and B.O.D. loading.

Index Terms- Kinetic Parameters in Anaerobic Digestion Process, Anaerobic digestion of distillery wastes, Distillery Wastes

I. INTRODUCTION

Anaerobic digestion of distillery wastes has positive effects on depollution of high organic loading, low sludge production, high pathogen removal, high yield of methane rich biogas and low energy consumption.

The increased interest in this process has stimulated mathematical modeling, because it is usually much faster and less expensive to model a system and to simulate its operation than to perform extensive laboratory experiments. The application of sophisticated methods of process control is only possible if mathematical models are available for the system to be optimized [1].

The anaerobic degradation of organic matter is a complicated biological process. The conversion of organic matter consists of several independent, consecutive, and parallel reactions in which close-knit communities of bacteria cooperate to form a stable, self-regulating fermentation that transforms organic matter into a mixture of methane and Carbon dioxide gases. These processes go through six main stages: 1) hydrolysis of biopolymers (proteins, carbohydrates, lipids) into monomer (amino acids, sugars, and long-chain fatty acids); 2) fermentation of amino acids and sugars; 3) anaerobic oxidation of long-chain fatty acids and alcohols; 4) anaerobic oxidation of intermediary products such as volatile fatty acids; 5) conversion of acetate to methane; and 6) the conversion of hydrogen to methane [2]. Several simulation models of these processes have been proposed by Husain, [3]; Jeyaseelan, [2]; v. Munch., [4]. Angelidaki [5], Boopathy, Larsen and Senior [6], Goyal, Seth and Handa [7], Harada, Uemura, Chen and Jaydevan [8], Gorcia-Calderon, Buffiere, Moletta and Elmalch [9], Blonskaja, Menert and Vilu [10].described the hydrolysis of un-dissolved carbohydrates and the hydrolysis of un-dissolved proteins as separate paths. Their model included eight bacterial groups. 19 chemical compounds, and a detailed description of pH and temperature characteristics. The specific growth and decay rates can also be presented with differing levels of complexity by Angelidaki [5], Hill [11], MocheandJordening [12], Thomas and Nordstedt [13].

The models described require the simultaneous solution of mass-balance equations for each individual substrate and bacterial population. Such a treatment is extremely complex yielding equations with numerous unknown parameters. Therefore, simpler treatments have been developed to predict the dynamic behavior of digesters. The six main groups of bacteria were divided into two major groups: acid producing microorganisms and methane producing microorganisms. [2], [3], [11].

In this study we investigated such a simplified model, which is a modified version of Hill and Barth's model [11]. Although the model is simplified, it still has a large number of unknown parameters and only a little experimenta1 data being available, it makes the parameter identification problem difficult.

The main goal of our work was first to investigate the structural and practical identifiability of the model and, second, based on these results estimate the most important identifiable parameters for three data sets obtained from laboratory experiments.

II. MATERIAL AND METHODS

A semi batch digester was designed and fabricated to carry out the experimental work. This is cylindrical equipment made of mild steel of capacity 10 liters with the provision of feed inlet opening, gas outlet nozzle and pressure measurement nozzle. There is an opening at the bottom through which the effluent can be discarded after experiment. The digester is surrounded by water jacket to maintain constant temperature of

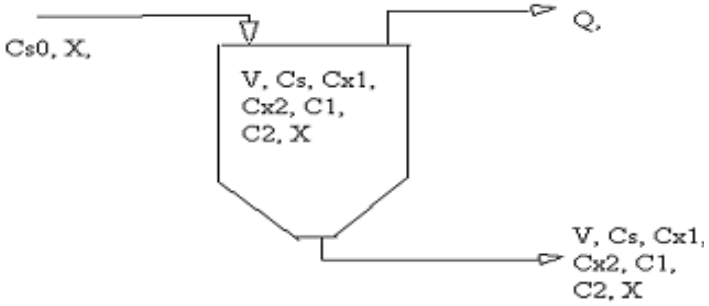
the slurry inside the digester. One limb of the U-tube manometer is connected to the pressure measurement nozzle and the other opening of the U-tube is kept open to the atmosphere. The digester contains two thermometer wells through which thermometers are introduced to measure the temperature of the feed slurry and that of the water in the jacket. The manometer measures the pressure of the produced gas. The digester also fitted with stirrer and motor with a speed-controlling regulator so as to keep the slurry at constant agitation at controlled stirrer speed. A schematic diagram of the digester set-up is given in figure-1.

In order to carry out the biomethanation process 5 liters of distillery wastes slurry of known substrate concentration in terms of B.O.D. loading was fed into the digester in which 1% mixed culture as inoculums was added, which was prepared using cow dung dissolved in distilled water maintaining pH within the range of 6.8 to 7.2 being incubated at 35^0C for 7 days under anaerobic condition and preserved in the incubator at 0^0C.

In this study three experimental data sets have been used. The first and second data and the experimental methods used to obtain these data were published previously [14] by the authors. The last data set was obtained in the same laboratory using same setup. Biogas generated at different retention days was collected and measured, and the same was analyzed in a gas analyzer [15] to ascertain contents of methane and carbon dioxide in the gas produced. It was found that there was no other component present in the biogas.

III. MODELING

In our model the anaerobic digestion is represented as a three-stage process [16], [11], [17]. During the first hydrolytic stage, the hydrolytic bacteria produce extra cellular enzymes that hydrolyze the organic compounds into simple soluble compound. The second stage is the acid producing stage, in which acid-forming bacteria convert simple organic compounds into volatile acids. During the last, methanogenic stage, methanogenic bacteria convert volatile fatty acids into methane and carbon dioxide.



The interpretation of all variables, parameters and their dimensions are described under nomenclature.

Overall mass balance:

(Rate of accumulation of substrate within the system) = (Rate of flow of substrate into the system) – (Rate of flow of substrate from the system) + (Rate of utilization of substrate within the system)

So, $V.\ dC_s/dt = L_1.\ C_{s0} - L_2.\ C_s + V.(r_{su})$……(1)

For semi batch digester, $L_1, L_2 = 0$

So, $dC_s/dt = r_{su}$

Now, $dC_s/dt = r_{su} = k.X.\ C_s/(k_s + C_s)$…….(2)

Overall microorganism balance:

(Rate of accumulation of microorganism within the system) = (Rate of flow of microorganism into the system) – (Rate of flow of microorganism from the system) + (Rate of growth of microorganism within the system).

So, $V.\ dX/dt = L_1.X_0 - L_2.X + V.(r_g)$……(3)

For semi batch digester, , $L_1, L_2 = 0$, $X_0 = 0$,

So, $dX/dt = r_g$, ……(4)

Or, $dX/dt = \mu.X$, and from the monod equation we get, $\mu = \mu_m.\ C_s/(k_s + C_s)$……(5)

Now, $dX/dt = r_g = \mu_m.X.\ C_s/(k_s + C_s)$……(6)

Rearranging equation 2 & 5 we get,

$(dC_s/dt).\ \mu_m = (dX/dt).k$……(7)

Integrating and rearranging the equation within the limit $C_s = C_{s0}$, $X=0$ and $C_s = C_s$, $X=X$

$\mu_m.(C_{s0} - C_s) = k.X$

or, $C_s = C_{s0} - (k/\mu_m).X$……(8)

If we balance acidogenic and methanogenic bacteria separately we get,

$dC_s/dt = -\beta.C_{X1}.\ C_s$……(9)

Mass balance for acidogenic bacteria:

(Rate of accumulation of acidogenic substrate within the system) = (Rate of flow of acidogenic substrate into the system) – (Rate of flow of acidogenic substrate from the system) + (Rate of utilization of acidogenic substrate within the system).

$DC_1/dt = \beta.C_{X1}.\ C_s - \mu_1.\ C_{X1}/Y_1$……(10)

Acidogenic microorganism balance:

(Rate of accumulation of acidogenic microorganism within the system) = (Rate of flow of acidogenic microorganism into the system) – (Rate of flow of acidogenic microorganism from the system) + (Rate of growth of acidogenic microorganism within the system).

$dC_{X1}/dt = (\mu_1 - k_1).\ C_{X1}$……(11)

from the monod kinetics, , $\mu_1 = \mu_{1m}.\ C_1/(k_{s1} + C_1)$……(12)

from equation 7 & 8 we get, $dC_{X1}/dt = [\mu_{1m}.\ C_1/(k_{s1} + C_1) - k_1].\ C_{X1}$……(13)

Mass balance for methanogenic bacteria:

(Rate of accumulation of methanogenic substrate within the system) = (Rate of flow of methanogenic substrate into the system) – (Rate of flow of methanogenic substrate from the system) + (Rate of utilization of methanogenic substrate within the system).

$dC_2/dt = Y_b.\ \mu_1.\ C_{X1} - \mu_2.\ C_{X2}/Y_2$……(14)

Methanogenic microorganism balance:

(Rate of accumulation of methanogenic microorganism within the system) = (Rate of flow of methanogenic microorganism into the system) – (Rate of flow of methanogenic microorganism from the system) + (Rate of growth of methanogenic microorganism within the system).

$dC_{X2}/dt = (\mu_2 - k_2).\ C_{X2}$……(15)

from the monod kinetics, , $\mu_2 = \mu_{2m}.\ C_2/(k_{s2} + C_2)$……(16)

$dC_{X2}/dt = [\mu_{2m}.\ C_2/(k_{s2} + C_2) - k_2].\ C_{X2}$……(17)

Further methane production rate can be derived by,

$Q = Y_g.\ \mu_2.\ C_{X2}$

Or, $Q = Y_g.\ \mu_{2m}.\ C_{X2}.\ C_2/(k_{s2} + C_2)$……(18)

Again, (Total cell mass concentration) = (Cell mass concentration of acidogenic bacteria) + (Cell mass concentration of methanogenic bacteria)

So, $X = C_{X1} + C_{X2}$……(19)

Differentiating with respect to t we get,

$dX/dt = dC_{X1}/dt + dC_{X2}/dt$……(20)

or, $\mu_m.X.\ C_s/(k_s + C_s) = (\mu_1 - k_1).\ C_{X1} + (\mu_2 - k_2).\ C_{X2}$……(21)

or, $\mu_m.X.\ C_s/(k_s + C_s) = [\mu_{1m}.\ C_1/(k_{s1} + C_1) - k_1].\ C_{X1} + [\mu_{2m}.\ C_2/(k_{s2} + C_2) - k_2].\ C_{X2}$……(22)

IV. PARAMETERS EVALUATION

The identification problem is difficult to solve because of the high number of parameters to be estimated, the complexity of the model, and the scarcity of experimental data. Therefore, we did not expect all 12 parameters in our model to be identifiable. Consequently, we have to take help of published data about some of the parameters from the studies as made by other researchers.

Determining C_s and dC_s/dt

As we know the X, k, μ_m, and C_{s0} from the data set, which is tabulated in table-1, 2 and 3, we can calculate C_s for each retention days at different initial substrate concentration. The values of C_s for each retention days at different initial substrate concentration are tabulated in table-1, 2 and 3.

It appears from the table-1, 2, and 3 that as the retention days increases C_s is decreases, which is corroborate with the previous workers. dC_s/dt is also evaluated from the $C_s$vs t plot, which is also tabulated in table- 1, 2 and 3 at 323K digestion temperature for BOD loading of 1.54, 2.12 and 2.74 kg/Cu.m respectively.

Determining C_{x1}

Assuming $\beta = 0.4$ from the literature [11], [16], [12] C_{x1} is calculated using equation 9. C_{x2} is evaluated from equation 19 using the value of C_{x1} and X. The value of C_{x1} and C_{x2} is tabulated in Table-1, 2 and 3 at 323K digestion temperature for BOD loading of 1.54, 2.12 and 2.74 kg/Cu.m respectively.

It is further revealed from Table-1, 2 and 3 that as retention time increases C_{x1} is decreases because more acidogenic biomass is converted into biogas and simultaneously C_{x2} is also increases with increase in retention days.

Determining dC_1/dt and μ_1

Figure 2 shows the plot of $\beta.C_s$vs inverse acidogenic substrate concentration, $(1/C_{x1})$ at 323K digestion temperature for BOD loading of 1.54, 2.12 and 2.74 kg/Cu.m. Comparing with the equation 10 intercept and slope of the straight lines in figure 2 represents the term μ_1/Y_1 and dC_1/dt respectively from which μ_1 and dC_1/dt have been determined assuming the value of Y_1 as 0.2. The values of μ_1 and dC_1/dt have been tabulated in Table-4.

Determining k_1 and μ_2

Figure 3 and 4 shows the plot of acidogenic and methanogenic cell mass concentration against retention time for different substrate concentration, from which dC_{x1}/dt and dC_{x2}/dt is calculated. Hence, k_1 is estimated from equation 11 as dC_{x1}/dt, $\mu_1$and C_{x1} is known.

μ_2 is also determined from equation 15 assuming $k_2 = 0.04$ from the literature.[3], [11], [17]. The values of k_1 and μ_2 are tabulated in Table-4.

Determining μ_m from the model equation

Knowing all the parameters and assuming $k_s = 0.82$ from the literature. [3], [11], [18], we estimated the value of μ_m from equation 21 and is tabulated in Table- 4.

Figure 5 shows the variation of maximum specific growth rate from the model equation and maximum specific growth rate from the experimentation against substrate concentration in terms of BOD loading. It is observed from the graph that the deviation is within 5%. So the model equation is simulated and suitable within these data range.

V. CONCLUSION

We investigated a modified nonlinear semi batch digester model, conducting practical identifiability analyses. The results show that the model is practically identifiable and the parameter estimated is reliable.

In addition, we have provided a review of literature concerning the possible parameter values. These values show the possible parameter boundaries, which can assist the work of other researchers in this area, too.

Finally, few main important parameters were estimated. One important feature of the estimation procedure is the simultaneous estimation of the parameters, which make the parameter estimates more reliable.

The results from the parameter estimation show that the model can describe different experimental phenomena.

VI. NOMENCLATURE

C_s = substrate concentration in time 't' in terms of BOD loading, kg/Cu.m DW

C_{s0} = initial substrate concentration in terms of BOD loading, kg/Cu.m DW

C_1 = substrate concentration for acidogenic bacteria in terms of BOD loading, kg/Cu.m DW

C_2 = substrate concentration for methanogenic bacteria in terms of BOD loading, kg/Cu.m DW

C_{x1} = cell mass concentration of acidogenic bacteria, kg/Cu.m DW
C_{x2} = cell mass concentration of methanogenic bacteria, kg/Cu.m DW
L_1 = loading rate in kg/Cu.m
L_2 = discharge rate in kg/Cu.m
Q = methane production rate, Cu.m/Cu.m DW
r_g= Rate of growth of microorganism within the system per unit volume, kg/Cu.m DW
r_{su}= Rate of utilization of substrate within the system per unit volume, kg/Cu.m DW
T = Hydraulic retention time in day.
V = digester volume, Cu.m
X = total cell mass concentration, kg/Cu.m DW
X_0 = initial cell mass concentration, kg/Cu.m DW
μ = specific growth rate of bacteria, day^{-1}
μ_1 = specific growth rate of acidogenic bacteria, day^{-1}
μ_2 = specific growth rate of methanogenic bacteria, day^{-1}
μ_m = maximum specific growth rate of bacteria, day^{-1}
μ_{1m} = maximum specific growth rate of acidogenic bacteria, day^{-1}
μ_{2m} = maximum specific growth rate of methanogenic bacteria, day^{-1}
k = kinetic parameter
k_1 = decay coefficient for acidogenic bacteria, day^{-1}
k_2 = decay coefficient for methanogenic bacteria, day^{-1}
k_s = saturation constant, kg/Cu.m DW
k_{s1} = saturation constant of acidogenic bacteria, kg/Cu.m DW
k_{s2} = saturation constant of methanogenic bacteria, kg/Cu.m DW
Y_1 = yield coefficient for acidogenic bacteria, kg organism/kg soluble organics.
Y_2 = yield coefficient for methanogenic bacteria, kg organism/kg soluble organics.
Y_g = gas yield coefficient, Cu.m/ Cu.m DW
β = solubilization rate per unit of acidogenic biomass, Cu.m/kg.day.

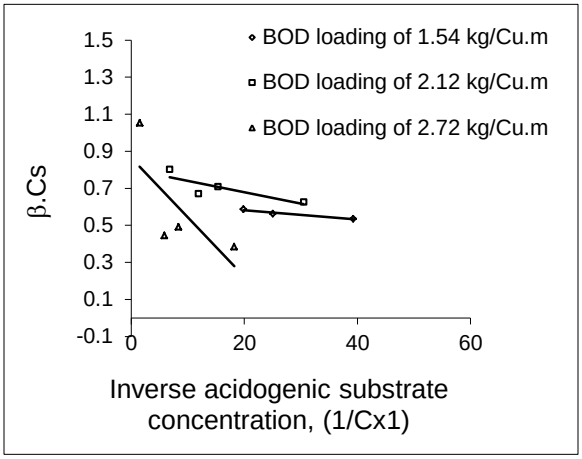


Fig. 2.Variation of $\beta.C_s$ against inverse acidogenic substrate concentration for different BOD loading at 323K digestion temperature

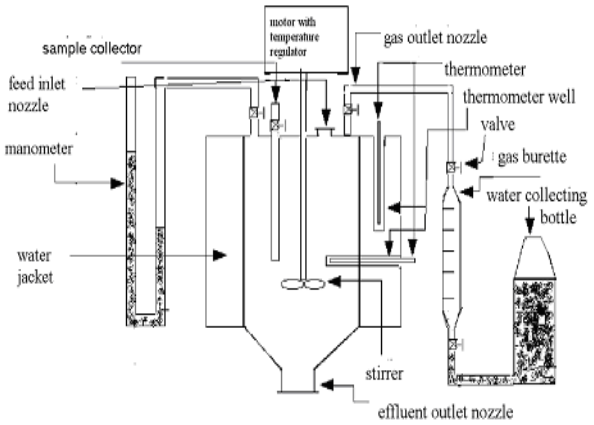


Fig. 1. A schematic diagram of a digester set-up

VII. APPENDIX

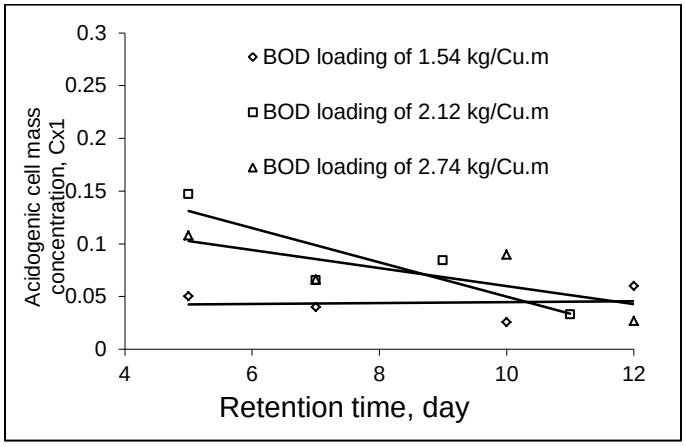


Fig. 3.Variation of acidogenic cell mass concentration against retention time in day for different BOD loading at 323K digestion temperature

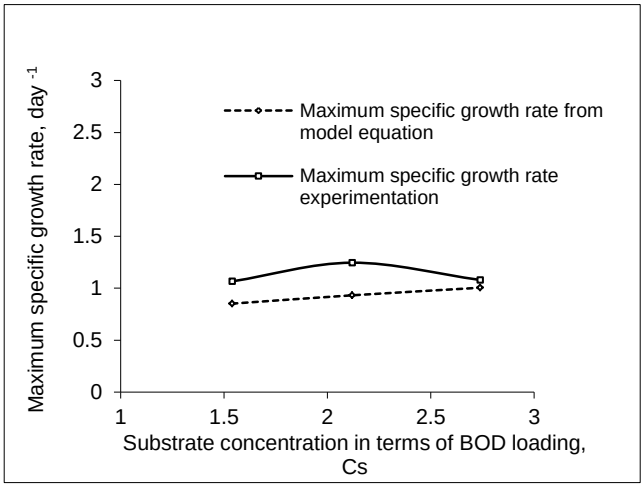


Fig. 5.Variation of maximum specific growth rate from model equation and from experimentation against substrate concentration in terms of BOD loading at 323K digestion temperature

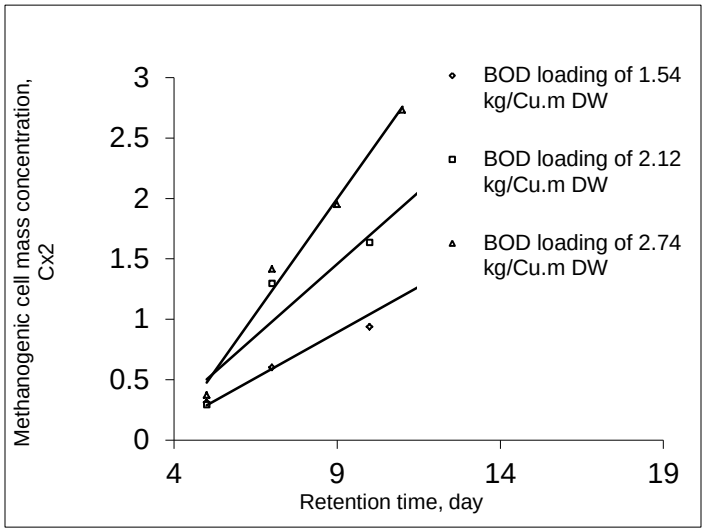


Fig. 4.Variation of methanogenic cell mass concentration against retention time in day for different BOD loading at 323K digestion temperature

Table-1 Results of model parameters for 323K digestion temperatures at B.O.D. loading of 1.54 kg/Cu.m

Retention time, (t)	**Cell mass conc. (x)kg/Cu.m DW**	**Substrate conc. C_s**	**dC_s/dt**	**C_{X1}**	**C_{X2}**
5	0.36	1.464	-0.029	0.050	0.309
7	0.64	1.405	-0.022	0.039	0.6
10	0.96	1.337	-0.054	0.025	0.934
12	1.48	1.228	-0.029	0.059	1.42
14	1.76	1.169	0.083	-0.17	1.93

Table-2 Results of model parameters for 323K digestion temperatures at B.O.D. loading of 2.12 kg/Cu.m

Retention time, (t)	**Cell mass conc. (x)kg/Cu.m DW**	**Substrate conc. C_s**	**dC_s/dt**	**C_{X1}**	**C_{X2}**
5	0.44	2.006	-0.11	0.14721	0.292
7	1.36	1.77	-0.04	0.065	1.294
9	1.72	1.67	-0.05	0.084	1.635
11	2.16	1.56	-0.02	0.032	2.127
13	2.32	1.52	0.117	-0.19	2.512

Table-3Results of model parameters for 323K digestion temperatures at B.O.D. loading of 2.74 kg/Cu.m

Retention time, (t)	Cell mass conc. (x)kg/Cu.m DW	Substrate conc. C_s	dC_s/dt	C_{X1}	C_{X2}
5	0.48	2.6310	-0.11347	0.107821	0.372
7	1.48	2.404	-0.06355	0.06608	1.413
9	2.04	2.277	-0.0817	0.089702	1.95
11	2.76	2.113	-0.02269	0.026843	2.73
13	2.96	2.068	0.159095	-0.19231	3.152

Table-4 Values of process parameters for different substrate concentration

Substrate concentration (C_s), Kg/Cu.m DW	μ_1	dC_1/dt	k_1	μ_2	μ_m
1.54	0.125	-0.002	0.12	0.125	0.8521
2.12	0.160	-0.006	0.35	0.33	0.9321
2.74	0.173	-0.032	0.49	0.219	1.005

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