# The Use of Thermodynamics to Model the Biodegradation Processes in Municipal Solid Waste Landfills

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**Abstract** Landfill degradation is a complex system of physical, chemical and biological processes. In recent years there has been an increasing amount of interest in the biological and biochemical processes within landfills. Traditionally, these processes have been modelled using empirical-based methods. This paper presents a new approach to modelling the biodegradation of solid waste based on thermodynamic principles. Details of the formulation of the series of complex, non-linear equations and the method of solution are included. The advantages of this approach include fewer empirical constants, inherent account of some inhibitory effects and ease of prediction of heat generation.

## INTRODUCTION

### Background

The aim of this model is to simulate the biodegradation of carbohydrates under anaerobic conditions. The computerised model can then be incorporated into one of the available pollution migration models, to produce a complete model that predicts the production and emission of pollutants (in the gas and leachate) from landfills.

The conventional approach for modelling biological processes is to use an empirical equation for cell growth, such as the Monod Equation, and assume that pollutant production is proportional to cell growth.(Andrews & Graef, 1971; Battaglia, 1990; Costello, Greenfield, & Lee, 1991; Hill, 1982; Hill, 1983; Morin & Monod, 1978; Mosey, 1983; Williams, Pohland, McGowan, & Saunders, 1987; Young, 1989)

The concept behind the model presented here is to use equilibrium thermodynamics to predict the concentration of the main pollutants in the leachate and gas at any one time. It is assumed that the rate of solid substrate solubilisation and the removal of gas from the system are the rate-determining steps in the overall series of reactions that influence the internal landfill environment. If this is the case, then, at any one time, the rest of the system is in equilibrium, waiting for the next change in solubilised substrate or gas concentration.

### The System

The system being modeled is a closed system, consisting of one litre of leachate, 0.71 L gas headspace and 1.86L of solid material. It is assumed that the solid material contains 5.0 moles worth of glucose, but in insoluble, solid form. The whole system is assumed to be at atmospheric pressure. Initially, the gas is air, containing roughly 71% nitrogen gas, 28% oxygen gas and 1% carbon dioxide gas. The liquid is assumed to contain a low concentration of acetic acid.
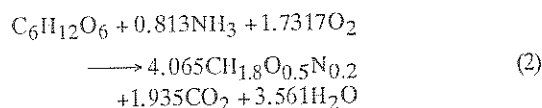
## REACTION EQUATIONS

### Solid Substrate Breakdown

The solid substrate breakdown is assumed to be be the main rate-determining step in the whole process. Therefore, it needs to be described kinetically. At this point in time, a Michelis-Menton type equation is used to describe the release of glucose into the system from the breakdown of solid substrate (assumed to be an insoluble glucose polymer). The amount of glucose released per time step is given by:

$$glualliquot = \frac{vmax * ss}{K + ss} \tag{1}$$

### Aerobic

Because the aerobic step is relatively fast and is a minor component of the model, the pathways are not considered and it is assumed that the glucose goes directly to $CO_2$ & water. The cell yield is assumed to be 100g cells per mole glucose. The unit cell formula is assumed to be $CH_{1.8}O_{0.5}N_{0.2}$.(Battley, 1987; Roels, 1983)
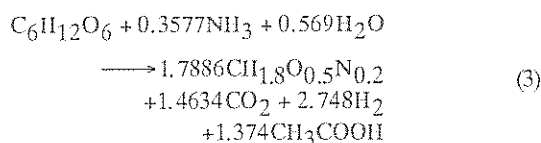
*Glucose to $CO_2$ & $H_2O$*

$$C_6H_{12}O_6 + 0.813NH_3 + 1.7317O_2$$
$$\longrightarrow 4.065CH_{1.8}O_{0.5}N_{0.2} \tag{2}$$
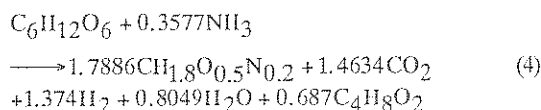$$+1.935CO_2 + 3.561H_2O$$

### Anaerobic

The following reaction equations were formulated using cell yields of 44g/mol glucose consumed for acidogens, 15g/mol substrate consumed for acetogens, 0.1g/mol $CO_2$ consumed for $CO_2$ & $H_2$ utilising methanogens and 1.5g/mol acetic acid consumed for acetic acid utilising methanogens. The unit cell formula is assumed to be $CH_{1.8}O_{0.5}N_{0.2}$.(Battley, 1987; Roels, 1983; Thauer, Jungermann, & Decker, 1977)
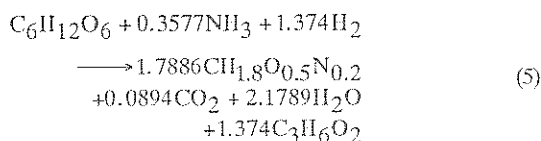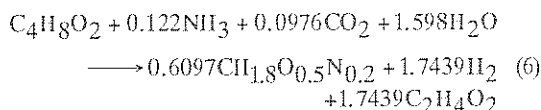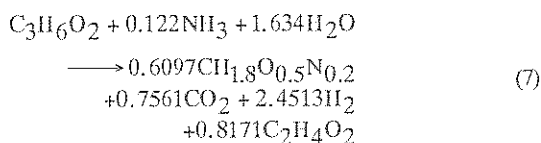
*Glucose to Acetic Acid*

$$C_6H_{12}O_6 + 0.3577NH_3 + 0.569H_2O$$

$$\longrightarrow 1.7886CH_{1.8}O_{0.5}N_{0.2}$$
$$+1.4634CO_2 + 2.748H_2 \qquad (3)$$
$$+1.374CH_3COOH$$

*Glucose to Butyric Acid*

$$C_6H_{12}O_6 + 0.3577NH_3$$

$$\longrightarrow 1.7886CH_{1.8}O_{0.5}N_{0.2} + 1.4634CO_2 \qquad (4)$$
$$+1.374H_2 + 0.8049H_2O + 0.687C_4H_8O_2$$

*Glucose to Propionic Acid*

$$C_6H_{12}O_6 + 0.3577NH_3 + 1.374H_2$$

$$\longrightarrow 1.7886CH_{1.8}O_{0.5}N_{0.2}$$
$$+0.0894CO_2 + 2.1789H_2O \qquad (5)$$
$$+1.374C_3H_6O_2$$

*Butyric Acid to Acetic Acid*

$$C_4H_8O_2 + 0.122NH_3 + 0.0976CO_2 + 1.598H_2O$$

$$\longrightarrow 0.6097CH_{1.8}O_{0.5}N_{0.2} + 1.7439H_2 \quad (6)$$
$$+1.7439C_2H_4O_2$$

*Propionic Acid to Acetic Acid*

$$C_3H_6O_2 + 0.122NH_3 + 1.634H_2O$$

$$\longrightarrow 0.6097CH_{1.8}O_{0.5}N_{0.2}$$
$$+0.7561CO_2 + 2.4513H_2 \qquad (7)$$
$$+0.8171C_2H_4O_2$$

*$CO_2$ to $CH_4$*

$$CO_2 + 3.9935H_2 + 0.000813NH_3$$

$$\longrightarrow 0.00406CH_{1.8}O_{0.5}N_{0.2} \qquad (8)$$
$$+1.00204H_2O + 0.9959CH_4$$

*Acetic Acid to $CH_4$*

$$CH_3COOH + 0.0122NH_3$$

$$\longrightarrow 0.06097CH_{1.8}O_{0.5}N_{0.2}$$
$$+0.9715CO_2 + 0.968CH_4 \qquad (9)$$
$$+0.0274H_2O$$
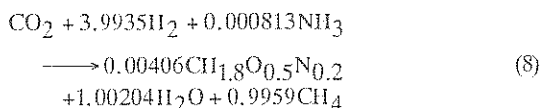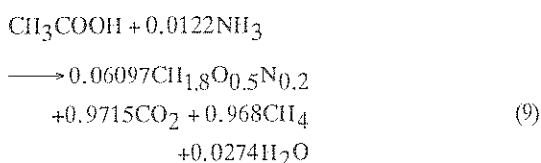
## EQUILIBRIUM EQUATIONS

The equilibrium constant for the above reactions could be found using the free energy of the reaction:

$$K_{eq} = \exp\left[\frac{-\Delta G^{o'}}{RT}\right] \qquad (10)$$

Using the above equations, the following equilibrium equations are written, assuming cells to be solid and therefore having an activity of 1.0. For example, the equilibrium equation for the reaction glucose to acetic acid is written as:

$$k_1 = \exp\left(\frac{0.687 * 199.02 * 1000}{8.314 * 300}\right)$$

$$= \frac{nco2^{1.4634} \, nh2^{2.748} \, HAc^{1.374}}{GluNH_3^{0.3577} xwater^{0.569}} \qquad (11)$$

The components participating in the system are then rewritten in terms of *reaction co-ordinates*.(Smith & Ness, 1987) Each reaction equation has a reaction co-ordinate which is a measure of how far the reaction moves in the forward direction after a certain change. The following equations are then substituted into the equilibrium equations, as mentioned above.

$$Glu = Glu_i - \varepsilon_1 - \varepsilon_2 - \varepsilon_3 - \varepsilon_8 \qquad (12)$$

$$CO_2 = (CO_2)_i + 1.4634\varepsilon_1 + 1.4634\varepsilon_2 + 0.0894\varepsilon_3$$
$$-0.0976\varepsilon_4 + 0.7561\varepsilon_5 - \varepsilon_6 + 0.9715\varepsilon_7 - 1.935\varepsilon_8$$
$$(13)$$

$$H_2 = (H_2)_i + 2.748\varepsilon_1 + 1.374\varepsilon_2 - 1.374\varepsilon_3 + 1.7439\varepsilon_4$$
$$+2.4513\varepsilon_5 - 3.9935\varepsilon_6$$
$$(14)$$

$$HAc = HAc_i + 1.374\varepsilon_1 + 1.7439\varepsilon_4 + 0.8171\varepsilon_5 - \varepsilon_7 \quad (15)$$

$$HBut = HBut_i + 0.687\varepsilon_2 - \varepsilon_4 \qquad (16)$$

$$HPr = HPr_i + 1.374\varepsilon_3 - \varepsilon_5 \qquad (17)$$

$$meth = meth_i + 0.9959\varepsilon_6 + 0.96799\varepsilon_7 \qquad (18)$$

$$O_2 = (O_2)_i - \varepsilon_8 \qquad (19)$$

Subject to:

$$Gt = CO_2 + O_2 + N_2 + H_2 + meth \qquad (20)$$

$$PCO_2 = \frac{1.013 \, CO_2}{Gt} \quad (21) \qquad PH_2 = \frac{1.013 \, H_2}{Gt} \quad (22)$$

$$Pmeth = \frac{1.013 \, meth}{Gt} \quad (23) \qquad PO_2 = \frac{1.013 \, O_2}{Gt} \quad (24)$$

$$nCO_2 = PCO_2 \frac{55.56}{86175} \quad (25) \qquad nH_2 = PH_2 \frac{55.56}{3681396} (26)$$

$$nCH_4 = Pmeth \frac{55.56}{21647.16} \quad (27) \qquad nO_2 = PO_2 \frac{55.56}{43996.39} \quad (28)$$

NB: partial pressures in bars.

Where subscript $i$ denotes the concentration or number of moles at the beginning of the time step, prior to the induced change (i.e. increase in glucose concentration).

The resulting 8 equations (Eqns 12 to 19) need to be solved simultaneously, subject to Eqns 20 to 28. This is quite difficult given the highly non-linear nature of the equations.

## COMPUTATIONS

The key to success of the model is to be able to find a reliable method of solving these equations again and again, so that the model can be computerised. The solution method needs to be reliable so that a solution can be found for any given inputs. In addition, the model "time-steps", i.e. the solution for one time step becomes the new input parameters for the next time step. So, the computerised model needs to be able to cope with changing inputs, both increasing and decreasing.

The general procedure for the model calculations is as follows:

1) Input initial concentrations/number of moles for each component (these will be the values obtained in the last time step);

2) Induce a change by setting the initial glucose concentration to what is released from the solid substrate over the time step interval;

3) Determine the gas concentrations within the system according to given boundary conditions;

4) Solve the seven non-linear equations to obtain values for the reaction co-ordinates;

5) Calculate new concentration values for components;

6) Move onto next time step.

The 8 non-linear equations of the model are solved by iteration. Firstly, the matrix is solved by LU decomposition. The individual $\varepsilon$-values are then solved by iteration, using the matrix solutions as a starting point. This method appears to work well, provided the $\varepsilon$-values are solved in the correct order, otherwise they do not converge. An essential element in model is to not allow the $\varepsilon$-values to be negative. In the program, if the iteration returns a negative number then the $\varepsilon$-value is taken as zero.

## CONTAMINANT MIGRATION

In keeping with the philosophy that forced change in the system causes the change in the intermediates' concentrations, it is felt that removal of contaminants from the system is an important factor affecting the rate of degradation and the pollutant profiles. In this developmental stage, a very simple approach has been taken to simulate the migration of pollutants out of the system.

For gas, it is assumed that the system remains at contant pressure, namely atmospheric pressure. At the end of each time step, the program calculates how many moles of gas were generated in that time step. Assuming the gas in the system to be perfectly mixed, the excess number of moles of gas are removed from the system. This means that the gas concentrations in the system and in the portion of gas removed are the same, for that time step.

For aqueous contaminants, a leachate dilution subroutine is called at regular intervals. This is supposed to simulate a rain event. It is assumed that a certain amount of pure water enters the system, diluting the aqueous solution. The same quantity of liquid then leaves the system, carrying some contaminants with it.

The gas removal and leachate dilution routines are not intended to be good simulations of contaminant migration. These two subroutines have been included in the program to enable it to be written in such a way as to allow the program to be integrated into a real contaminant transport model as easily as possible. It will be a simple procedure to modify these model componenets once more information is known.

## HEAT GENERATION

The proposed model includes prediction of the heat generated during the reactions. This inclusion was relatively straightforward, from a computational perspective. The Heat of Reaction was calculated for each of the reactions from the components' Heats of Formations. The overall heat change in the system is then the sum of the Heats of Reactions mulitplied by their respective reaction co-ordinates, as per the following equation:

$$\Delta H(\text{system}) = \Delta H_{(rxn1)} * \varepsilon_1 + \Delta H_{(rxn2)} * \varepsilon_2 \\ + \Delta H_{(rxn3)} * \varepsilon_3 + \Delta H_{(rxn4)} * \varepsilon_4 \\ + \Delta H_{(rxn5)} * \varepsilon_5 + \Delta H_{(rxn6)} * \varepsilon_6 \\ + \Delta H_{(rxn7)} * \varepsilon_7 + \Delta H_{(rxn8)} * \varepsilon_8 \quad (29)$$

The change in temperature of the system can then be estimated using the standard equation:

$$\Delta T = \left( \frac{-\Delta H}{Cpm * mass} \right) \quad (30)$$

However, a significant problem encountered is choosing an appropriate values for the heat capacity due to an acute lack of data. At this stage, the heat capacity of water is being used.

## RESULTS

The outputs from the model simulations have been encouraging. Based on the experience of the authors with a more conventional approach to modelling anaerobic digestion, this method appears to be just as good at simulating generation of key pollutants. The general trends that have been observed in landfill operation are reflected in the model outputs. (Christensen & Kjeldsen, 1989) However, the model does not seem to produce good temperature

simulations. While there is little field data available, it is generally believed that significant temperature rises can be expected.
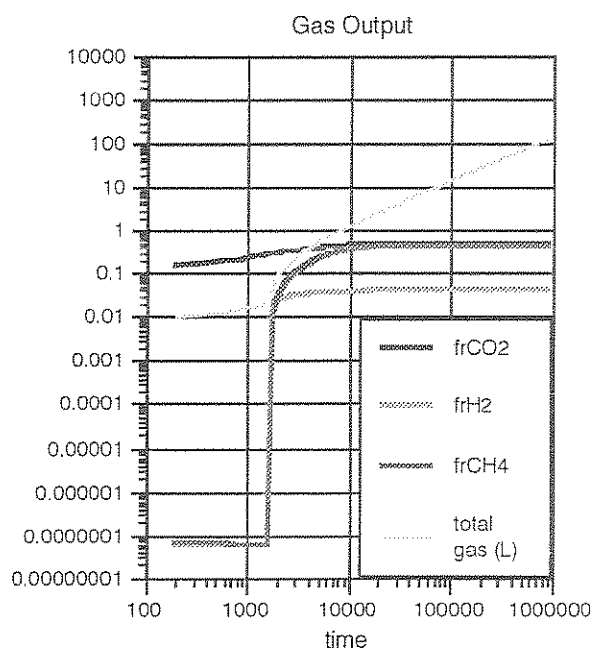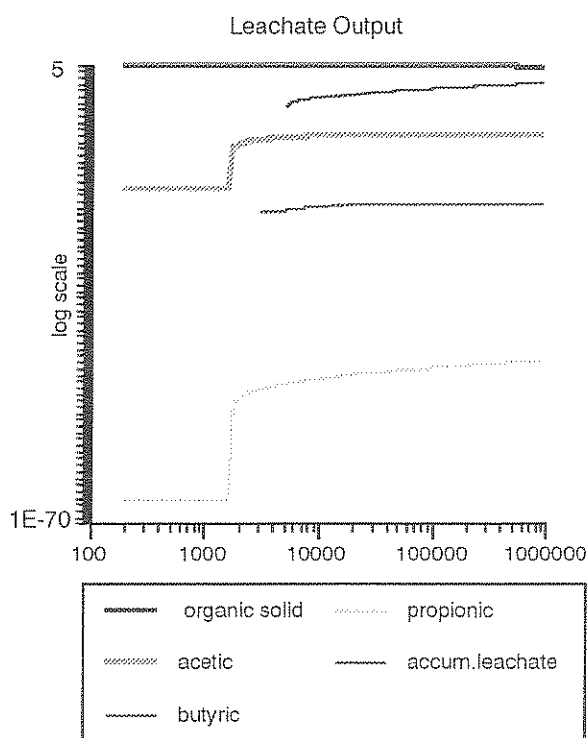
## Gas Output



Figure 1: Predicted Gas Concentrations

## Leachate Output



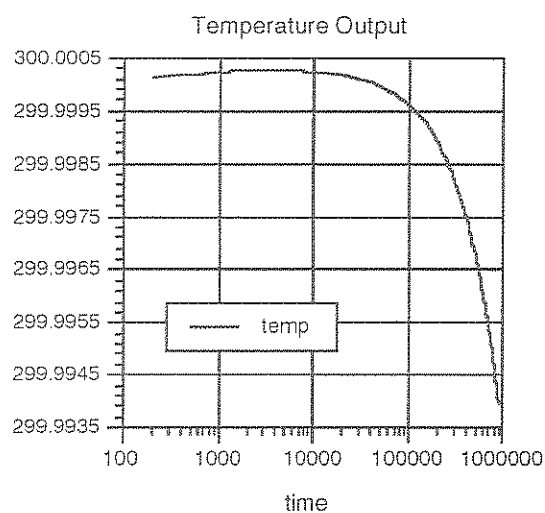Figure 2: Predicted Leachate Concentrations

## Temperature Output



Figure 3: Predicted Temperature Changes

## CONCLUSION

This paper presents an alternative method for modelling the anaerobic biodegradation of solid organic material using the principles of chemical equilibrium. At present, it appears to be as similar in accuracy as more conventional methods.

The model displays the ability to predict both gas and leachate concentrations as well as heat generation in one formulation. The manner in which this is done is based upon hollistic theoretical principles, rather than experimentally derived empirical relationships. This allows the model to be both flexible and relatively simple. It also means that the model is based on relatively few parameters, most of which are available from published chemical and/or biological data.

Further development of the model should see the emergence of a flexible tool for predicting solid waste degradation. It is believed that them model can be improved to a point where it is a reliable and useful modelling tool for use in waste management applications.

## ACKNOWLEDGMENT

## NOMENCLATURE

glualliquot = No. moles glucose released during a time step
vmax = max rate of breakdown of solid substrate
ss = No. moles solid substrate remaining
K = empirical constant
$K_{eq}$ = equilibrium constant
$\Delta G^{o}$' = change in free energy adjusted to pH 7
R = gas constant
T = temperature
$nCO_2, nH_2, nCH_4, nO_2$ = concentrations of gases in leachate
HAc, HBut, Hpr = conc'ns of acetic, butyric & propionic
xwater = mole fraction of water in leachate

Glu, NH3 = conc'ns of glucose & ammonia
$\varepsilon_i$ = reaction co-ordinate for reaction i
Pi = partial pressure of gas i
$\Delta H$ = change in enthalpy
$\Delta T$ = change in temperature
Cpm = heat capacity of material (mass based)
mass = mass of system

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