

LDAT Heat generation and transport algorithm

Summary

This article covers the theory of landfill heat generation and landfill heat transfer as it is applied in the LDAT landfill waste degradation and transfer model. There are four sections to the theory: Landfill waste heat balance; landfill heat conduction; landfill waste heat convection; landfill waste heat generation. Each section explains how the conventional analytical equations for heat generation and transfer are transformed into the algorithmic calculation procedure for the LDAT model. The article includes an example calculation of the net exothermic enthalpy of reaction for sugar for both the landfill sugar aerobic chemical pathway and the landfill sugar anaerobic chemical pathway.

Sections

- A. The heat balance equation
- B. The conduction term
- C. The convection term
- D. The heat generation term

A. The heat balance equation

The heat balance equation, equation (1), proposed in El-Fadel et al is used as a starting point. The equation is derived by balancing four terms representing,

1. Rate of change of heat due to temperature $\frac{\partial}{\partial t} \rho c_p T$

2. Heat transferred by gas convection $-\frac{\partial}{\partial x_i} \rho^G c_p^G U^G T$

3. Heat transferred by conduction $\frac{\partial}{\partial x_i} \left(\kappa \frac{\partial T}{\partial x_j} \right)$

4. Heat gain or loss from a local source or sink of heat generation or abstraction α

$$\frac{\partial}{\partial t} \rho c_p T = -\frac{\partial}{\partial x_i} \rho^G c_p^G U^G T + \frac{\partial}{\partial x_i} \left(\kappa \frac{\partial T}{\partial x_j} \right) + \alpha \quad (1)$$

The units of each of the four terms are heat/time/unit volume, for example kJ/day/m³. Note that El-Fadel et al were only concerned with the gas phase. However the equation can be extended to include all phases thus,

$$\frac{\partial}{\partial t} \rho c_p T = -\frac{\partial}{\partial x_i} \sum_P z^P \rho^P c_p^P U^P T + \frac{\partial}{\partial x_i} \left(\kappa \frac{\partial T}{\partial x_j} \right) + \alpha \quad (2)$$

Furthermore it should be noted that in the first term $\rho c_p = \sum_P z^P \rho^P c_p^P$ where z^P is the volumetric phase concentration.

To obtain the LDAT heat generation and transport algorithm it is necessary to re-cast equation (1) into the LDAT element framework and the LDAT notation (see Papers 1, 2 and 4 for details of nomenclature etc).

B. The conduction term $\frac{\partial}{\partial x_i} \left(\kappa \frac{\partial}{\partial x_j} T \right)$

In terms of an element this becomes in the single dimension of x ,

$$\frac{\left(\kappa \frac{\partial}{\partial x_j} T \right)_{x+\Delta x} - \left(\kappa \frac{\partial}{\partial x_j} T \right)_x}{\Delta x}$$

Or in LDAT notation

$$\frac{(\kappa_{e2}(T_2 - T_e))_{e2} - (\kappa_{e1}(T_e - T_1))_{e1}}{l_e} = \frac{1}{V_e} \sum_m \kappa_{em} A_{em} (T_m - T_e)$$

in which the right hand side summation over all six interfaces of the element effectively extends this expression algorithm to three dimensions.

Note that $\frac{1}{\kappa_{em}} = \frac{0.5l_e}{\kappa_e} + \frac{0.5l_m}{\kappa_m}$

C. The convection term $-\frac{\partial}{\partial x_i} \sum_P z^P \rho^P c_p^P U^P T$

In the context of an LDAT element, this becomes (in the case of just the gas phase and in one dimension),

$$-\frac{z^G \rho^G c_p^G U_{e2}^G T_{e2} - z^G \rho^G c_p^G U_{e1}^G T_{e1}}{l_e} = -\frac{z^G c_p^G \rho^G A_{e2} U_{e2}^G T_{e2} - z^G c_p^G \rho^G A_{e1} U_{e1}^G T_{e1}}{V_e}$$

If $M_{em}^G = z^G \rho^G A_{em} U_{em}^G \Delta t$ is the mass of fluid removed, and is +ve when outwards, the convective term becomes,

$$-\frac{c_p^G M_{e2}^G T_{e2} + c_p^G M_{e1}^G T_{e1}}{V_e \Delta t} = -\frac{1}{V_e \Delta t} \left(\sum_P \sum_m c_p^P M_{em}^P T_{em} \right)$$

Again the rhs term extends the application to all phases in all dimensions.

In addition we assume that the temperature associated with the mass M_{em} is that of the source element so if $M_{em} > 0$ $T_{em} = T_e$ and if $M_{em} < 0$ $T_{em} = T_m$

Substituting the conduction and convection terms into equation (2) gives,

$$\frac{\partial}{\partial t} \rho c_p T_e = -\frac{1}{V_e \Delta t} \left(\sum_P \sum_m c_p^P M_{em}^P T_{em} \right) + \frac{1}{V_e} \sum_m \kappa_{em} A_{em} (T_m - T_e) + \alpha$$

Multiply through by $V_e \Delta t$ and the heat balance for the element over the time interval is obtained,

$$\Delta t \frac{\partial}{\partial t} \rho V_e c_p T_e = - \left(\sum_P \sum_m c_p^P M_{em}^P T_{em} \right) + \Delta t \sum_m \kappa_{em} A_{em} (T_m - T_e) + \alpha V_e \Delta t$$

$$\Delta t \frac{\partial}{\partial t} \rho V_e c_p T = - \left(\sum_P \sum_m c_p^P M_{em}^P T_{em} \right) + q_e^K + q_e^E$$

Now, recalling that $\rho c_p = \sum_P z^P \rho^P c_p^P$,

$$\rho V_e c_p = \sum_P m^P c_p^P$$

where m^P is the mass of phase P in the element. Both the temperature and the mass in the phases change in the time interval so we allow for this as follows using just the gas phase here as an example.

The part of the term on the left hand side concerned with the gas phase is,

$$\Delta t \frac{\partial}{\partial t} m^G c_p^G T_e = \Delta t c_p^G m^G \frac{\partial T_e}{\partial t} + \Delta t c_p^G T_e \frac{\partial m^G}{\partial t} = c_p^G m^G \Delta T_e + c_p^G T_e \Delta m^G$$

Δm^G is the sum of the individual interface transfers associated with the gas phase. Thus, bearing in mind that in LDAT the M_{em}^P are +ve when outwards,

$$\Delta m^G = - \sum_m M_{em}^G$$

And therefore, after adding back in the other phases from the left hand side we can write the heat balance for an element as,

$$\Delta T_e \sum_P m^P c_p^P - c_p^G T_e \sum_P \sum_m M_{em}^P = -c_p^G \left(\sum_P \sum_m M_{em}^P T_{em} \right) + q_e^K + q_e^E$$

Or

$$\Delta T_e \sum_P m^P c_p^P = \sum_P \sum_m c_p^P M_{em}^P (T_e - T_{em}) + q_e^K + q_e^E = q_e^C + q_e^K + q_e^E$$

Finally,

$$\Delta T_e = \frac{q_e^C + q_e^K + q_e^E}{\sum_P m^P c_p^P}$$

The assumption that the temperature associated with the mass transfer M_{em}^P in the convective term is that of the source element. This means that if, $M_{em}^P > 0$ $T_{em} = T_e$, and if $M_{em}^P < 0$ $T_{em} = T_m$. Thus in the algorithm since,

$q_e^C = \sum_P \sum_m c_p^P M_{em}^P (T_e - T_{em})$ only transfers into the element will have any impact on the calculation of q_e^C .

D. The heat generation term α

Heat generation in LDAT is calculated from the enthalpy change of the waste degradation chemical reactions. The basic equation for the enthalpy change of a chemical reaction, $\Delta H_{\text{Reaction}}$, is calculated using the following equation,

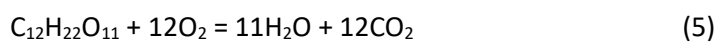
$$\Delta H_{\text{Reaction}} = \sum H_{\text{PRODUCTS}} - \sum H_{\text{REACTANTS}} \quad (3)$$

Where $\sum H_{\text{PRODUCTS}}$ is the sum of the enthalpies of formation of the products of the reaction and, $\sum H_{\text{REACTANTS}}$ is the sum of the enthalpies of formation of the reactants.

Equation (3) may be written in terms of h_n the enthalpy of formation of a compound n in kJ/mole, and ΔM_n as the change in the number of moles of compound n taking part in the reaction to which equation (3) is being applied. This gives equation (4).

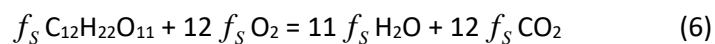
$$\Delta H_{\text{Reaction}} = \sum_{\text{Products}} \Delta M_n h_n - \sum_{\text{Reactants}} \Delta M_n h_n \quad (4)$$

The aerobic degradation of sugar provides an example of the conventional way to write an equation representing a chemical reaction.



The reactants are on the left hand side and the products are on the right. The equation 'balances'. For example there are $11 + 12 * 2 = 35$ oxygen elements on the left hand side balancing the 35 on the right hand side. This type of equation is known as a stoichiometric equation. The molar (or stoichiometric) coefficients in this equation (1, 12, 11, 12) will be designated as s_n , being the values of the multipliers of the expressions for the compounds each of which represents one mole of the compound.

It is important to remember that equation (5) states what will happen to one mole of sugar when it combines with 12 moles of oxygen and degrades to become 11 moles of water and 12 moles of carbon dioxide. The reaction will probably be taking place in an aqueous environment in which many other moles of these compounds may be present. In addition over a time interval of Δt only a fraction of a mole of sugar f_S may degrade in which case equation (5) needs to be modified to,



so that it can be interpreted specifically as representing the degradation of f_S moles of sugar which combines with $12 f_S$ moles of oxygen and produces $11 f_S$ moles of water and $12 f_S$ moles of carbon dioxide.

Each compound in equation (6) is multiplied by a coefficient. These coefficients give the moles of each compound involved in the reaction and are therefore equal to the ΔM_n in equation (4). If each compound is tagged as a product P , or reactant R , and one mole of the compound is replaced by c_n^{PorR} in equation (6) it becomes,

$$f_S c_1^R + 12 f_S c_2^R = 11 f_S c_3^P + 12 f_S c_4^P$$

or

$$f_S s_1 c_1^R + f_S s_2 c_2^R = f_S s_3 c_3^P + f_S s_4 c_4^P$$

or

$$\Delta M_3 c_3^P + \Delta M_4 c_4^P - \Delta M_1 c_1^R - \Delta M_2 c_2^R = 0$$

Finally, if a convention is adopted that the stoichiometric coefficients of the reactants, s_n , are treated as negative quantities, it is seen that equation (6) is equivalent to,

$$\sum_1^4 \Delta M_n c_n = 0$$

Furthermore, if there are a system of stoichiometric equations each involving compounds selected from the group of all the compounds present in the system then a more general representation of each of these equations is given by,

$$\sum_1^N \Delta M_n c_n = 0 \quad (7)$$

where N is the total number of compounds in the system. If c_n is not present in a particular reaction then its stoichiometric coefficient s_n is put equal to zero. Note that from the above $\Delta M_n = f_S s_n$ and is the change in the number of moles of compound n as the result of the reaction degrading the substrate compound $n = S$ over the time interval Δt .

Since the numbers of the individual elements balance in equations (5), (6) and (7) the equations also balance mass. This also means that when the representation of one mole of the compound c_n in equation (7) is replaced by the compound's molecular weight in kg/mole, the equation is also satisfied.

The left hand side of equation (7) has the same form as the right hand side of equation (4) when c_n is replaced by the compound's enthalpy of formation, h_n .

Thus an alternative and more general way of writing equation (4) is,

$$\Delta H_{\text{Reaction}} = \sum_1^N \Delta M_n h_n$$

provided the convention is observed that the stoichiometric coefficients, s_n , of the reactants are treated as negative quantities, and recalling that $\Delta M_n = s_n \Delta M_S$.

Note that the calculation of $\Delta H_{\text{Reaction}}$ is undisturbed if each of the terms is multiplied and divided by the relevant molecular weight of the compound mw_n kg/mole.

$$\text{Thus } \Delta H_{\text{Reaction}} = \sum_1^N (\Delta M_n mw_n) h_n / mw_n = \sum_1^N \Delta m_n h'_n$$

Where Δm_n is the change in mass of the compound (+ve if increasing, -ve if decreasing) and h'_n is the enthalpy of formation of the compound in kJ/kg.

Note that there is a further convention that reactions that result in the liberation of heat (exothermic reactions) result in a negative change in $\Delta H_{\text{Reaction}}$. As discussed below this implies that compounds that liberate heat on formation (and most do) have a -ve enthalpy of formation.

Thus the heat generation source term q_e^E in the LDAT algorithm is given by,

$$q_e^E = -\Delta H_{\text{Reaction}} = -\sum_1^N \Delta m_n h'_n$$

Recalling that in the case of a single compound being formed from its elements the reference enthalpy of the elements is assumed to be zero, equation (4) may be applied as follows,

The reaction is E = C (reactants = products).

The sum of the enthalpies of the reactants is zero.

There is only one compound C.

So, if enthalpy of formation of C is h_C , equation (4) reduces to,

$$\Delta H_{\text{Reaction}} = \Delta M_C h_C - 0$$

Or

$$h_C = \frac{\Delta H_{\text{Reaction}}}{\Delta M_C} \text{ kJ/mole}$$

The convention that reactions that result in the liberation of heat (exothermic reactions) result in a negative change in $\Delta H_{\text{Reaction}}$ thus implies that compounds that liberate heat on formation will have a -ve enthalpy of formation.

All of the values of enthalpies of formation listed in Droste, and quoted elsewhere for example at

<http://chemistry.about.com/od/thermodynamics/a/Heats-Of-Formation.htm>.

are given as -ve values.

The chemistry.about.com contains the statement 'most heats of formation are negative quantities, which implies that the formation of a compound from its elements usually is an exothermic process'.

Example of the calculation of the reaction enthalpy.

The following reactions represent the anaerobic and aerobic degradation of sugar $C_{12}H_{22}O_{11}$.

Anaerobic	$C_{12}H_{22}O_{11} = 2C_4H_8O_2 + H_2O + CH_4 + 3CO_2$	Stage 1 Sugar degrades to aqueous acid, water, and carbon dioxide.
	$2C_4H_8O_2 + 2H_2O = 2C_2H_4O_2 + 3CH_4 + CO_2$	Stage 2 Aqueous acid reacts with water to form acetic acid methane and carbon dioxide
	$C_2H_4O_2 = CH_4 + CO_2$	Stage 3 Acetic acid forms methane and carbon dioxide
Aerobic	$C_{12}H_{22}O_{11} + 12O_2 = 11H_2O + 12CO_2$	Sugar oxidises to water and carbon dioxide

Droste provides the following information about the enthalpy of formation of the following compounds.

Compound	Enthalpy of formation	
	kcal/mole	kJ/mole
CO ₂	-93.69	-391.62
CH ₄	-17.89	-74.78
H ₂ O	-68.32	-285.58
O ₂	0.00	0
C ₂ H ₄ O ₂	-116.74	-487.97
H ₂ CO ₃	-167.0	-698.06
NH ₃	-19.32	-80.76
SO ₄ ⁻	-216.9	-906.64
H ₂ S	-9.4	-39.3
NH ₄ ⁺	-31.74	-132.673

Assuming that the aerobic pathway has a reaction enthalpy of -5606 kJ/mole, equation (2) in this case becomes, [note that the calculations in this note are confirmed in Excel spreadsheet 'Support calcs for LDAT heat generation model', sheet 'Sugar anaerobic and aerobic'].

$$-5606 = -11 * 286 - 12 * 392 - 1 * h_{Sugar}$$

Thus, the formation enthalpy of sugar is given by,

$$h_{Sugar} = -2240 \text{ kJ/mole}$$

The reaction enthalpy of the third stage acetic acid anaerobic reaction is,

$$-75 - 391 + 488 = 22 \text{ kJ/mole}[\text{C}_2\text{H}_4\text{O}_2] \text{ (endothermic)}$$

Based on an assumed enthalpy of formation of -716 kJ/mole for aqueous acid, the reaction enthalpy of the second stage aqueous acid reaction is (for one mole of aqueous acid),

$$-488 - 112 - -196 + 716 + 286 = 206 \text{ kJ/mole} [\text{C}_4\text{H}_8\text{O}_2] \text{ (endothermic)}$$

The reaction enthalpy of the first stage of the sugar anaerobic reaction is,

$$-75 - 1175 - 1432 - 286 + 2240 = -728 \text{ kJ/mole}[\text{C}_{12}\text{H}_{22}\text{O}_{11}] \text{ (exothermic)}$$

Note that in a complete reaction the heat produced by the first stage is partially consumed by the degradation of 2 moles of C₄H₈O₂ in the second stage (2*206 = 412 kJ) and 2 moles of C₂H₄O₂ in the second stage (2*22 = 44 kJ) leaving a net exothermic enthalpy of anaerobic reaction for sugar of -272 kJ/mole. This may be compared with the enthalpy of the aerobic reaction which was assumed above to be -5606 kJ/mole.