Chemical degradation stoichiometric equations

The anaerobic degradation pathways that are used in LDAT are shown in Table 1. These are derived from those proposed by (Young 1995, Reichel et al. 2005, El-Fadel et al. 1996).

First stage	Protein as $C_{46}H_{77}O_{17}N_{12}S$ forms aqueous acid $C_4H_8O_2$ and acetic acid $C_2H_4O_2$ anaerobically
	$C_{46}H_{76}O_{17}N_{12}S^- + 27.5H_2O = 7.39C_4H_8O_2 + 5.15C_2H_4O_2 + 6.14H_2CO_3 + 12NH_3 + H_2S + OH^-$
	Fat represented as $C_{55}H_{104}O_6$ forms aqueous and acetic acid anaerobically
	$C_{55}H_{103}O_6^- + 9.88H_2O + 6.56H_2CO_3 = 10.56C_4H_8O_2 + 6.72C_2H_4O_2 + 5.88CH_4 + OH^-$
	Carbohydrate high order forms aqueous acid anaerobically
	$C_{12}H_{23}O_{12}^- + 2H_2O= 2C_4H_8O_2 + CH_4 + 3H_2CO_3 + OH^-$
	Glucose - Carbohydrate forms acetic acid anaerobically
	$C_6H_{11}O_6^- + 2H_2O = 2C_2H_4O_2 + CH_4 + H_2CO_3 + OH^-$
Second stage	Aqueous acid $CH_3(CH_2)_2COOH$, $C_4H_8O_2$ forms acetic acid anaerobically
	$4C_4H_8O_2 + 6H_2O = 4C_2H_4O_2 + 6CH_4 + 2H_2CO_3$
Third stage	Acetic acid forms methane
	$C_2H_4O_2 + H_2O = CH_4 + H_2CO_3$

Table 1 Anaerobic degradation pathways

Associated with each of the primary degradation pathways is a bacteria growth and death pathway, (Barlaz et al. 1992).

Following (Reichel et al. 2005), for a general substrate $C_aH_bO_cN_dS_e$ it is assumed that the growth pathways in which bacteria $C_5H_7NO_2$ are produced from the substrate are given by,

$$5C_aH_bO_cN_dS_e + ANH_4^+ = aC_5H_7NO_2 + 4\alpha DH_2 + (1-4\alpha)DH^+ + EH_2O + 5eSO_4^- \tag{1}$$

in which the hydrogen terms have been split to provide some flexibility in the $CH_4 : CO_2$ ratio that the model produces. This is based on the assumption that this is achieved by bacteria utilising hydrogen to convert CO_2 to CH_4 through,

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

Or, in terms of H_2CO_3

$$H_2CO_3 + 4H_2 = CH_4 + 3H_2O$$

A stoichiometric balance of equation (1) gives,

$$(1+4\alpha)D = a + 5b - 10c - 20d + 40e$$

$$E = 5c - 2a - 20e$$

$$A = a - 5d$$

We can replace the term $4\alpha DH_2$ by $\alpha D(CH_4 - H_2CO_3) + 3\alpha DH_2O$ which through the parameter α controls the extent to which CH_4 is produced at the expense of CO_2 (H_2CO_3) and which impacts on the CH_4 : CO_2 ratio.

Equation (1) then becomes,

$$5C_aH_bO_cN_dS_e + ANH_4^+ =$$

$$aC_5H_7NO_2 + \alpha DCH_4 - \alpha DH_2CO_3 + (1-4\alpha)DH^+ + (E+3\alpha D)H_2O + 5eSO_4^- \qquad (2)$$

With maximum conversion to CH_4 taking place when α = 0.25.

The death pathway is, (Reichel et al. 2005),

$$6C_5H_7NO_2 + 19H_2O = 5\beta C_6H_{11}O_6^- + 6NH_4^+ + OH^- + 5(1-\beta)I_{C_6H_{12}O_6} - 5(1-\beta)H^+ \qquad (3)$$

Where $C_6H_{11}O_6^-$ is degradable glucose and $I_{C_6H_{12}O_6}$ is an inert compound with mathematically the same molecular weight characteristics as glucose.

Here β controls the tail developed as the result of the bacteria feeding back degradable glucose into the system as the populations die back. With $\beta = 0$ there is no feedback and the dead biomass forms an inert product. With $\beta = 1$ full feed back to degradable glucose is assumed to take place.

The influence on the CH_4 : CO_2 ratio of α and β in equations (3) and (4) is however quite small because the bacteria pathways are thought to be only about 10% of the degradation chemistry the other 90% passing through the reactions given in Table 9, which have an output CH_4 : CO_2 ratio of around 50:50 by volume. Indeed some additional direct delivery of CH_4 is needed to add to equation (4) to achieve 60:40. Such an addition could take the form,

$$C_5H_7NO_2 + 21H^+ = 5CH_4 + NH_4^+ + 2H_2O \qquad (4)$$

Theoretically a 60:40 ratio can be obtained by adding 20% of equation (4) into equation (3).

The aerobic pathways used in LDAT are shown in Table 2.

Aerobic degradation of Protein ion
$C_{46}H_{76}O_{17}N_{12}S^- + 49.75O_2 + 26.5H_2O = 46H_2CO_3 + 12NH_3 + SO_4^- + OH^-$
Aerobic degradation of Fat ion
$C_{55}H_{103}O_6^- + 78O_2 + 4H_2O = 55H_2CO_3 + OH^-$
Aerobic degradation of Carbohydrate ion
$C_{12}H_{23}O_{12}^- + 12O_2 + H_2O= 12H_2CO_3 + OH^-$
Aerobic degradation of Glucose ion
$C_6H_{11}O_6^- + 6O_2 + H_2O= 6H_2CO_3 + OH^-$

Formation of biomass using protein $C_{46}H_{77}O_{17}N_{12}S$
$5C_{46}H_{76}O_{17}N_{12}S^- -14NH_4^+ = 46C_5H_7NO_2 + 56H^+ - 27H_2O + 5SO_4^{2-}$
Formation of biomass using fat represented as $C_{55}H_{104}O_6$
$5C_{55}H_{103}O_6^- + 55NH_4^+ = 55C_5H_7NO_2 + 510H^+ - 80H_2O$
Formation of biomass using carbohydrate high order
$5C_{12}H_{23}O_{12}^- + 12NH_4^+ = 12C_5H_7NO_2 + 7H^+ + 36H_2O$
Formation of biomass using glucose (TUB)
$C_6H_{11}O_6^- + 1.2NH_4^+ = 1.2C_5H_7NO_2 + 0.2H^+ + 3.6H_2O$

Nitrification by nitrosomonas bacteria
$NH_4^+ + 1.5O_2 = NO_2^- + 2H^+ + H_2O$
Nitrification by nitrobactor bacteria
$NO_2^- + 0.5O_2 = NO_3^-$

Formation of biomass following denitrification by nitrosomonas bacteria
$5C_6H_{11}O_6^- + 6NH_4^+ = 6C_5H_7NO_2 + 18H_2O + H^+$
Formation of biomass following denitrification by nitrobactor bacteria
$5C_6H_{11}O_6^- + 6NO_2^+ +18H_2 + 11H^+ = 6C_5H_7NO_2 + 30H_2O$

Methane oxidation
$CH_4 + 2O_2 = H_2O + H_2CO_3$

Formation of biomass using Methane CH_4
$5CH_4 + NH_4 + 2H_2O = C_5H_7NO_2 + 21H^+$

Table 2 Aerobic pathways

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