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A novel mathematical model of solid-state digestion

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Abstract

The proposed model of solid-state digestion assumes the development of a distinct zone of depleted waste around each viable seed particle. Biodegradation is envisaged to occur chiefly in thin shells at the interface between depleted and raw waste, at a rate proportional to the interfacial area. These shells are estimated to expand at a constant 5 cm/year. The reaction thus accelerates following a square law until neighbouring shells meet. Deceleration is then rapid as the shells merge. The proposed model agrees with available lysimeter data; first-order decay kinetics do not.

Introduction

Biogas production due to solid-state digestion (SSD) in landfilled waste shows a characteristic pattern: (1) rapid aerobic metabolism (days); (2) rapid acidogenesis (weeks); (3) a variable lag phase (months); (4) slowly accelerating methanogenesis (years); (5) very gradual deceleration (decades). Typical time-scales are given in brackets but vary widely.

Martin (1999) suggested that poor seeding might be a major source of delay and variability, as seed particles large enough to provide 'safe havens' for methanogenesis rarely arise in landfills by chance. The ideal seed particle (ISP) is just large enough to accommodate an outer buffer layer thick enough for mass-transfer resistances to protect methanogenesis from excessive acidity, as well as an adequate methanogenic core. Such ISPs would be relatively independent, so viable in any location. However, they might not be highly mobile, so their initial distribution might be as critical as their size.

This ISP concept is the starting point for a fresh approach to landfill modeling. A fundamental weakness of most models is a failure to distinguish between localized and dispersed processes. If methanogenesis can only proceed in specific micro-environments (ISPs or their natural equivalents), local conditions are crucial. Diffusion of acids into an ISP slightly relieves the acid inhibition in a thin layer immediately surrounding it, so hydrolysis, acidogenesis and acetogenesis (abbreviated below to 'acidogenesis') can proceed in this layer. Immediately within this 'acidogenic shell', lie the buffer layer then the methanogenic layer, both initially located in the ISP.

When the readily biodegradable substrate in the acidogenic shell is depleted, the shell advances into the waste, followed by the buffer layer and, probably, also by the methanogenic layer. Thus, a reaction front expands radially, leaving a growing body of depleted waste behind it, in a relatively quick but highly localized process. The recalcitrant residue is then degraded slowly after the reaction front has moved on. This secondary process is dispersed throughout the volume enclosed by the expanding shell.

The reaction front is marked by a sharp drop in acidity. This mostly occurs in the buffer layer, as the concentration driving force for diffusion across the acidogenic shell must be small at steady state. Consequently, this shell is thin and the acidity within it is only slightly below that in the bulk of the waste. Acidogenesis is therefore under constant, severe inhibition, so the overall reaction rate might be determined by the (small) volume to which acidogenesis is confined and thus by the rate of advance of the reaction

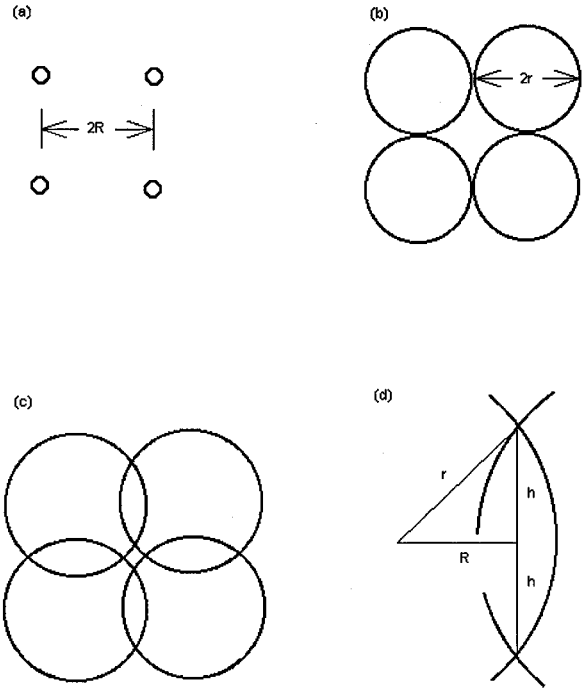

Fig. 1. Expansion of acidogenic shells. (a) Shells at an early stage (assuming small seed particles at regular spacing of 2*R*). Shells at the end of the acceleration phase ($r = R$). (c) Shells during deceleration phase. (d) Estimation of the area inactivated by merging of adjoining shells.

front. Conditions around this front are constant, so a constant rate of advance is plausible. A mathematical model of the interfacial reaction was therefore developed, on the basis of this concept, and compared with experimental data.

Model development

The model is based on the following assumptions: (1) the interfacial and dispersed processes can be separated for modeling purposes; (2) the rate-limiting step (which could be either hydrolysis or acetogenesis) occurs in thin, spherical, shells; (3) its rate is proportional to the volume of these shells; (4) their thickness is constant; (5) their initial diameter approximates to zero; (6) they expand at a constant rate; (7) the waste is evenly seeded, on a cubic grid (Figure 1a); (8) the rate of reaction is directly proportional to the production rate of biogas.

The surface area of each shell increases as it expands. The acceleration phase therefore follows a square law until neighbouring shells meet (Figure 1b), which occurs when the diameter of each shell ($2r$) equals the seed spacing ($2R$). Further expansion occurs only into the interstices between shells, so the active area rapidly decreases (Figure 1c). The deceleration phase therefore begins immediately and continues until the shells have fully merged.

Acceleration phase

Let the radius of a shell at any time be r (m), its thickness z (m) and its outer surface area S (m^2). The rate of biogas production within the enclosed volume is g (l d^{-1}) and the bulk rate is G (L kg^{-1} d^{-1}). There are N ISPs per kilogram of waste and the reaction front around each advances at F (m d^{-1}). Time in the acceleration phase, t_A, is measured in days from the end of the lag phase, (each phase being considered separately).

From assumptions (3), (4) and (8):

$$g \propto Sz$$
$$= k_0 Sz$$

Then

$$G = k_0 SzN$$

Let

$$k_0 zN = k_1$$

Then

$$G = 4\pi k_1 r^2$$

and

$$dG/dt_A = (dr/dt_A)(dG/dr)$$
$$= F(dG/dr)$$

Substitute

$$r = Ft_A$$

Integrate

$$G = 4\pi k_1 F^2 t_A^2 + k_2$$

(Assuming $r = 0$ at $t_A = 0$)

Comparison with experimental data allows the estimation of the constants. Figure 2 shows the biogas production rate from a 10-l lysimeter (an unmixed digester for solid waste) charged with a coarse mixture of food and shredded paper, then seeded with digested sewage sludge (Martin *et al.* 1997). The end of the lag phase was estimated by eye at Day 147 (so $G = 0$ at $t_A = 0$) and the peak rate was taken as 2.01 l kg^{-1} d^{-1} at $t_A = 154$, on Day 301. Visual inspection of the charge suggests that the scale

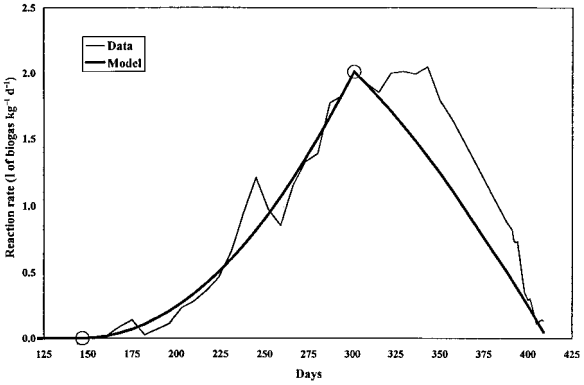

Fig. 2. Comparison of model with experimental data. Light curve: data of Martin *et al.* (1997); heavy curve: the present model. Open symbols mark the data used to calibrate the model.

of the heterogeneity providing the safe havens that acted as ISPs was approximately 4 cm. Therefore, $R = 2$ cm and the reaction front covered this distance in 154 days. This gives $F = 1.25 \times 10^{-4}$ m d^{-1} (or about 5 cm yr^{-1}). The values of G at Days 147 and 301 were then substituted to evaluate the constants. Hence

$$k_2 = 0$$
$$k_1 = 432 \text{ (l m}^{-2} \text{ d}^{-1}0)$$

So that

$$G = 8.48 \times 10^{-5} t_A^2 \text{ (l kg}^{-1} \text{ d}^{-1}). \quad (1)$$

This equation is shown in Figure 2 for Days 147–301.

Deceleration phase

The values of F and k_1 are constant, so only the geometry changes. The nomenclature is as above except that time in the deceleration phase, t_D, is rebased to Day 301 and the inactive area where one shell intersects another (Figure 1c) is denoted by A. On a cubic seeding pattern, each shell loses six such sectors. Each is approximated to a plane circle of diameter $2h$ (Figure 1d), slightly under-estimating the area lost. Now

$$A = \pi h^2$$
$$= \pi(r^2 - R^2)$$

So

$$S = 4\pi r^2 - 6\pi(r^2 - R^2)$$
$$= 6\pi R^2 - 2\pi r^2$$

Then, as above

$$G = 2.01 - 1.36 \times 10^{-2} t_D - 4.24 \times 10^{-5} t_D^2. \quad (2)$$

This equation is shown for Days 301–415 in Figure 2.

Discussion

Equations (1) and (2) are compared with experimental data in Figure 2, with the two data points used for parameter estimation marked by open circles. The proposed model matches well the general shape of the acceleration and deceleration phases, the only major deviations being consistent with the model. The breadth of the peak was expected: with a randomly distributed seed, the timing of the transition from acceleration to deceleration would be spread. The rapidity of deceleration was probably due also to uneven seeding, with the result that the interfacial process was completed earlier in some zones than in others.

The predicted square law for the acceleration phase agrees well with the experimental curve but a more convincing test is the prediction of the deceleration phase. Both the duration of this phase and the counter-intuitive convexity of the falling curve are predicted well. While further work must be done to fully validate the model, this result can leave little doubt that its broad principles are correct.

Its simplicity is attractive, as is its applicability to both Stages 4 and 5. Most other published models, based on first-order kinetics and unstructured physical models, attempt to describe only Stage 5. Even so, their agreement with operational data is imperfect (Brown *et al.* 1999). The more complex 'two-particle' physical model of Kalyuzhnyi *et al.* (1999) is probably over-simplified, yet leads to a 26-equation process model. Such complexity diminishes its utility.

The proposed three-layered reaction zone might be likened to a miniature two-stage digester, in which the buffer layer acts as the link and controls the feed rate to the second stage. There are also instructive similarities with the termite gut. Here, methanogenesis proceeds in a 1-μl 'bioreactor', within a fraction of a millimetre of the oxygenated gut wall (Brune 1998).

As each seed particle develops, it forms an independent 'micro-reactor', which does not interact with its neighbours until they merge. The kinetics displayed by a whole landfill are thus the sum of a myriad of asynchronous, discrete, small-scale, localized processes. Most landfills are, at best, unevenly seeded, so (a) the lag phase varies widely, and (b)

many areas are thinly seeded. Both effects would tend to spread the overall curve of biogas production: (a) would stagger the start-up times for individual micro-reactors, while (b) would require some to stabilize much larger volumes of waste than others. However, shorter lags and smaller micro-reactors are likely to be more common than long lags and large micro-reactors. Consequently, the distribution of completion times is skewed towards shorter times but has a tail extending for many decades. This might create a misleading illusion of first order decay.

In truth, it is likely that first-order kinetics only apply to the dispersed process, which plays a minor role on richer feedstock. In the experimental study (Martin *et al.* 1997), 94% of the final biogas yield had been reached by the time the interfacial reaction was complete. However, the dispersed process might be dominant in lean wastes.

The quantitative aspects of the model need further development but the simplifications used here may indicate orders of magnitude. The experimental method (Martin *et al.* 1997) did not lend itself to a good estimate of ISP size, since it relied on random pockets of shredded paper absorbing the sludge inoculum to form ill-defined ISPs. Nevertheless, the minimum diameter of ISP is unlikely to be more than a few millimetres and might be much less, since the model gave a good fit using a zero approximation. Seeding on a 4-cm pitch would complete the interfacial process in just 9 months, even with a reaction front advancing at only 5 cm yr^{-1}, as Figure 2 illustrates. Current landfill practice rarely approaches such rates.

The model clearly has major implications for landfill operation. It presents possibilities of much faster stabilization at modest initial cost, transforming landfill into a reliable, controllable, more sustainable waste disposal process. It might also be applicable to engineered digesters, so could have applications in those countries where legislation limits the use of landfills. Stabilization in digesters is very much faster than in landfills, so the scope for acceleration is limited. However, optimization of seed size might allow a reduction in the seeding rates, which is typically 1:1 in commercial practice.

Conclusions

The final stages of waste stabilization in landfills appear to follow first order kinetics, with a time base measured in decades. However, this is an illusion, due to the summation of thousands of relatively fast, discrete, localized processes, with quite different kinetics and wide-ranging initial lags. Two successive processes occur at any point, both localized but the first more tightly than the second. The 'interfacial' process, which has a distinctive rate curve, with a sharp peak, occurs at a well-defined zone between the raw waste and a depleted residue. Stabilization is then completed by the slower 'dispersed' process. This follows a much flatter curve and continues for some months after the interfacial process is complete, perhaps longer. Their relative importance depends on the composition of the waste. In richer wastes, the interfacial process utilizes most of the more readily available substrate, thus producing most of the biogas. It is confined to a thin reaction shell, which advances at a constant rate through the waste: an experimental study indicated a rate of the order of 5 cm yr^{-1}. A consequence of this extreme localization is that the rate of the interfacial process is determined by the surface area of the shell. This novel concept is validated by a mathematical model, which fits the data well. Thus, after a variable and, as yet, indeterminate lag phase, the acceleration phase of the interfacial process follows a square law until it peaks. Deceleration is then immediate and rapid, growing ever faster as the expanding shells merge. The deceleration phase of the interfacial process is therefore shorter than the acceleration phase. This pattern will only be manifest, however, if the seeding is uniform, synchronizing the many discrete processes. Of greater operational importance is the conclusion that the overall rate of SSD is determined by the size of the seed particles and by their initial distribution.

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