Towards new indicators for the prediction of solid waste anaerobic digestion properties

P. Buffiere, D. Loisel, N. Bernet and J-P. Delgenes

INRA, Laboratoire de Biotechnologie de l'Environnement, Avenue des Etangs, 11100 Narbonne, France

Abstract The biochemical composition can be seen as a good indicator of both the biodegradability and the methane potential of a given waste. The work presented here is an attempt to elaborate a typology of wastes and to compare it to the anaerobic degradation characteristics. The first data indicate that there is a link between the ligno-cellulosic content of the waste and the biodegradability. When dealing with application to anaerobic digestion processes, having a tool to predict the ability of the waste to be degraded could be of the greatest interest for preventing failures, estimating biogas production, methane content, or for the management of co-digestion processes.

Keywords Anaerobic digestion; biochemical methane potential; fibres; fractionation; kinetics; organic matter

Introduction

The biological treatment of solid residues is a highly complex problem. In addition to the complexity of the biological ecosystems involved, solids are by nature heterogeneous in size, composition and structure. Nonetheless, both design and operation of anaerobic digesters for solid waste treatment require data on biogas (methane) potential of the waste, and on the removal kinetics. For instance, various biogas productions can be observed from one plant to another, or, in a given plant, during the year due to seasonal fluctuations (Saint-Joly et al., 2000). The most common indicator of digester performance is the amount of methane produced per mass unit of solid or volatile solid (Rintala and Järvinen, 1996). As a consequence, the methane potential of various types of wastes is generally expressed with this simple criterion (Chynoweth et al., 1993; Owens and Chynoweth, 1993; Nallathambi Gunaseelan, 2004; Jokela et al., 2005). This description is often sufficient to compare the digestibility of waste having the same nature, such as papers, or to compare different reactor designs with a given waste (Marique et al., 1989). Concerning reactor operation, most classical indicators are the organic loading rate (usually expressed as $kg_{VS}/m^3/d$) and the solid retention time (Cecchi et al., 1988), together with classical monitoring parameters such as pH, VFA, or gas production (Bjornsson et al., 2000).

Nevertheless, the description of organic matter degradation by the volatile solids (VS) as parameter alone is limited. As pointed out by Mata-Alvarez et al. (2000), there is a need for a better understanding of the degradation kinetics in relation to the biochemical composition. In addition, methane productivity not only depends on the amount of degraded volatile solids, but also on the nature of the solid: carbohydrates, proteins or fats have different methane potential, as shown by Angelidaki and Sanders (2004). Consequently, the biochemical composition has become an important descriptor for anaerobic digestion, both for methane production prediction and for kinetics assessment (Christ et al., 2000; Sanders, 2001). Moreover, even the chemical nature of the organic matter is of the highest importance. Considering the degradation of carbohydrates, it is well known that cellulose is much more difficult to degrade than sugar monomers

(Noike *et al.*, 1985). The fibre content of the solid has often been a relevant approach for solid waste degradation. The reference work by Chandler *et al.* (1980) showed that the overall anaerobic biodegradability was directly proportional to the fibre content in the cell wall of biological organic matter. Komilis and Ham (2003) proved that the degradation of organic matter during aerobic composting exhibits a positive relation to the hot water soluble content, and a negative relation to the lignin amount. The same trend was found by Pareek *et al.* (1998) for the degradation of paper under methanogenic conditions. Eleazer *et al.* (1997) also found a relation between the degree of lignification of municipal waste and the methane potential. Nevertheless, Tong *et al.* (1990) could not derive any relationship between the sole lignin content and the methane productivity of herbaceous and woody biomass. Sherer *et al.* (1990) first showed on spent grains that the most degradable part of the organic matter was the soluble and hemicellulose fraction, while cellulose and lignin were slightly attacked; later, they used the cellulose/lignin ratio as an indicator of anaerobic digestion achievement (Sherer *et al.*, 2000). Hartmann *et al.* (2000) consider that the ligno-cellulosic part of the waste is the more recalcitrant to hydrolysis, and that its accessibility could be improved by mechanical maceration. As can be seen from these few examples, the biochemical composition, both in terms of protein, carbohydrate and fat content and in terms of soluble/fibre content, could be revealed as a new indicator of anaerobic digestion properties (Peres *et al.*, 1992). There have been very few attempts at establishing a unified typology of solids with regards to their properties. Hansen *et al.* (2003) tried to characterise different types of municipal wastes (including pre-treated ones) in terms of biochemical composition and fibre content, together with BMP tests, but the final results are still expected.

The objective of our research program is to find a correlation, if any, between the biochemical composition of the waste (including the fibre content) and its anaerobic biodegradation properties (such as methane potential, biodegradability and kinetics). We are presently working on the establishment of a typological database including all the required data. In this paper, we focus on the biochemical composition of various organic wastes (mostly kitchen wastes) in relation to their anaerobic degradation kinetics. At this stage, only the maximal (intrinsic) degradation kinetics are investigated on blended wastes: this means that the effect of size or accessible surface area has not yet been examined. Though still very limited as regards to the number of wastes that have been processed within the scope of this paper, we strongly believe that such work is a necessary starting point for powerful applications in the field of anaerobic digestion: as a predictive tool for waste digestion; as a managing tool for co-digestion processes; and as a design tool for reactor modelling and for the selection of appropriate pre-treatments.

Møller *et al.* (2004) have developed a similar approach for different types of manure and straw, and their work will be an excellent complementary source of information and comparison.

Materials and methods

Sample waste collection and preparation

Sample wastes have been collected from individual separated sources: our co-workers were asked to separate and store their kitchen waste at $-20\,^\circ$C. The waste collected was green salad residues (lettuce), harvested grass (from one single source), potato peelings, carrot peelings, fresh apple wastes, banana peelings and citrus peelings (mostly orange). The fruits and vegetables used here are the most consumed in France in wintertime. For each waste of the same type, the fractions coming from different sources are mixed together and stored at $-20\,^\circ$C before use, to obtain one single sample per waste during the tests. Each waste (apart from grass) is then mixed with water in a blender to obtain

a homogeneous slurry for the BMP tests. This was not possible with grass, which was the only waste treated as such (no blending). In parallel, some of the waste is freeze-dried and milled for further analysis (see next section).

P. Buffiere *et al.*

Organic matter analysis

The wastes were characterised according to the following parameters: total and VS, fibre content, total COD and TKN, proteins, lipids and total carbohydrates. Total and volatile solids measurements are performed on fresh products. The other parameters are measured on lyophilised (freeze-dried) samples milled and sieved with a 1 mm grid. The fibre content is determined according to Van Soest (1963). It is based on sequential extraction under neutral and acid detergent, followed by strong acid extraction for the cellulose content. The crude fibres are also determined according to the Weende method. These measurements are performed with the FIBERBAG system (Gerhardt). The result is a fractionation of the organic matter between soluble components, hemicellulose, cellulose and lignin.

Total COD and TKN are measured according to the standard methods adapted to solid wastes: this means that a suspension in water is prepared from the dried sample powders and treated like classical wastewater samples. Theoretical COD could also have been estimated through a calculation based on the Buswel equation from elemental analysis (CHONS content); the difference between the measured COD values and the theoretical values was inferior to 5% (results not shown). Proteins are measured according to the Lowry method, and total sugars are measured with the Anthrone reduction method. Lipids are estimated through conventional Soxhlet extraction with petroleum ether (40–60 °C) as solvent.

Biochemical methane potential

The method used for biochemical methane potential is adapted from Owens and Chynoweth (1993) and from Angelidaki and Sanders (2004). We use seven reactors in parallel with an active volume of 3.5 litres each (Figure 1). They are filled with synthetic growth medium containing nutrients and trace elements, and inoculated with anaerobic thermophilic sludge coming from a batch stock reactor fed with various waste mixtures. The final sludge concentration in the reactor is between 3 and 4 gVS/L. The temperature is kept at 55° by water circulation in a water jacket. At the beginning of each BMP test, the reactors are purged with a N_2/CO_2 (75/25) gas mixture. The biogas is collected continuously and the volume produced is measured with an electronic volumetric gas counter (based on the principle of water displacement). Gas samples of 1 mL are taken periodically for gas composition analysis by gas chromatography. Methane production is expressed under standard conditions (0 °C, 1.013 10^5Pa) and accounts for the variation of gas content in the headspace of the reactors. Among the seven reactors, one is not provided with any feed so as to recover the endogenous gas and methane production, and a second one is fed with synthetic cellulose (positive standard). The only difference with commonly used BMP tests is that in our case, waste addition is repeated three times in the same reactor in order to account for the adaptation of the sludge to the organic waste. Indeed, sludge adaptation has a slight influence on the total methane produced, but has a strong influence on the response curve and on the dynamics of the methane produced, which is important for kinetic data assessment. Since the volume of the reactors used is important, we haven't done replicates in parallel, as recommended in the cited articles. Apparently, this procedure does not affect the repeatability and accuracy of the test: in one of our experiments, two out of the seven reactors were fed with cellulose, and the

Figure 1 Picture of the reactor used for BMP assays

results obtained are of the same order from one reactor to another and from one waste addition to another (see Table 1).

Calculations

In the results section, the biochemical methane potential is expressed as $mlCH_4(STP)/gVS$. Nevertheless, it is much more convenient to express the methane produced relatively to the amount of COD instead of VS. This helps to estimate the overall biodegradability of the waste, since the theoretical maximal methane yield is constant ($350\,mlCH_4(STP)/gCOD$). What we name biodegradability is thus defined as the ratio between the methane produced and the maximal amount that would have been obtained if all the COD were converted to methane:

$$BD = \frac{BMP(mlCH_{4,STP}/gVS)}{350 \times COD_{waste}(gCOD/gVS)}$$

Table 1 Biochemical methane potential, expressed as $mLCH_4STP/gVS$, for sequential addition of cellulose on two test reactors running in parallel

	Reactor 1	Reactor 2
1st addition	340.6	336.6
2nd addition	352.2	340.0
3rd addition	346.9	356.1
Average	346.6	344.3
sd (%)	1.7%	3.0%

This definition is of course not absolutely correct, since, as mentioned by Angelidaki and Sanders (2004), a fraction of the substrate is used for bacterial mass synthesis; nevertheless, it is a good comparison criterion within the tests.

Results and discussion

Characterisation of waste properties

The characteristics of the different organic wastes tested are reported in Table 2, together with the biochemical methane potential and the absolute biodegradability. The Van Soest fibre results are expressed as four fractions: SOLU is the amount of organic matter extracted with the neutral detergent (soluble fraction), HEMI is the difference between the neutral detergent and the acid detergent residue (hemicellulose fraction), CELL is the fraction extracted by 72% sulphuric acid (cellulose fraction), and LIGN is the VS residue after 72% sulphuric acid treatment (lignin fraction). In addition to these four fractions, CF is the crude fibre obtained after boiling successively in sulphuric acid and sodium hydroxide. Most of the wastes tested show a high biodegradability. The value for cellulose standards is not shown, but can be calculated from Table 1 as 0.84 (considering $1.185\, g_{COD}.g_{VS}^{-1}$ for cellulose).

Surprisingly, the biochemical fractions of proteins, lipids and carbohydrates as measured are far from being representative of the total volatile solids. Several explanations can be put forward: first, some sugars might not be measured by the anthrone reagent method. Second, both protein and sugar measurements are colorimetric methods calibrated on a single type of component (bovine serum albumin for proteins, and glucose for sugars). Those measurements need to be taken as indicators, not as real fractionation data. In addition, we can notice that the ratio protein/TKN varies a lot from one product to another. This indicates that using TKN for estimating the protein amount can be hazardous.

Potato peelings are the most degradable and have the lowest lignin amount. Banana peelings are the less degradable and have the highest lignin amount. Nevertheless, a strict correlation between these two parameters cannot be strictly established with the different wastes used. Most representative is the sum of lignin and cellulose (LIGN + CELL), which correlates relatively correctly with the absolute biodegradability (Figure 2). The data from this study are plotted with results obtained on municipal solid waste (MSW)

Table 2 Biochemical composition, methane potential, and biodegradability of organic wastes

	Salad	Carrots	Grass	Potato	Banana	Apple	Orange
DM (g/gfresh)	0.109	0.135	0.311	0.190	0.128	0.171	0.226
VS (gVS/gDM)	0.800	0.899	0.860	0.937	0.852	0.979	0.964
TKN (gN/gVS)	0.022	ND	0.026	0.023	0.033	0.035	0.040
COD (gO$_2$/gVS)	1.46	1.40	1.43	1.28	1.52	1.36	1.35
Proteins[a] (g/gVS)	0.199	0.208	0.150	0.090	0.102	0.123	0.169
Lipids (g/gVS)	0.081	0.050	0.066	0.032	0.118	0.022	0.039
Sugars[b] (g/gVS)	0.263	0.472	0.263	0.609	0.450	0.514	0.468
SOLU (g/gVS)	0.623	0.777	0.403	0.647	0.617	0.848	0.836
HEMI (g/gVS)	0.155	0.085	0.361	0.295	0.133	0.029	0.045
CELL (g/gVS)	0.126	0.077	0.153	0.039	0.077	0.047	0.078
LIGN (g/gVS)	0.096	0.061	0.083	0.019	0.174	0.075	0.040
CF (g/gVS)	0.119	0.080	0.156	0.059	0.133	0.072	0.095
BMP (ml$_{CH_4}$/gVS)	294	388	388	390	289	317	297
SD (3 rep.)	30	35	35	25	16	14	26
BD	0.58	0.79	0.77	0.87	0.54	0.67	0.63

[a]In equivalent BSA (bovine serum albumin)
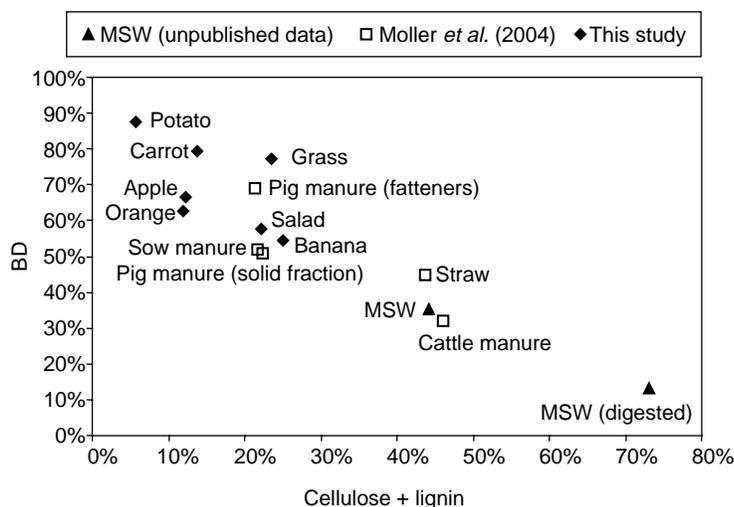[b]In equivalent glucose

237

Figure 2 Relation between biodegradability and ligno-cellulosic content of several organic wastes

before and after thermophilic dry digestion (unpublished data). We also added the results given by Møller *et al.* (2004) on different types of manure (cattle, pigs, sows) and straw. In their work, the value of cellulose fraction was not given, so the sum (cellulose + lignin) was estimated as the sum of lignin and non-degradable carbohydrates. This plot demonstrates the importance of the fibre content on the ultimate biodegradability of various wastes, since the different data are roughly arranged on a decreasing curve. Nevertheless, we are not able to draw a definitive conclusion (for instance a mathematical relation between the fibre content and the degradability) because many parameters have not been investigated yet. For instance, we have tested neither fibre-rich (such as paper wastes or woody biomass) nor protein-rich (like slaughterhouse wastes), nor fat-rich components. Many previously published data could enrich this approach (see for instance Owens and Chynoweth, 1993, for MSW, yard waste, paper and packaging wastes, or in Eleazer *et al.*, 1997, for paper and woody biomass), but there is generally missing information that is crucial for interpretation, such as the COD values or the fibre content. The value of absolute biodegradability could also be very useful for the characterisation of real solid waste digestion reactors, because it can be seen as the maximal (ultimate) reachable removal yield. As a consequence, it could be used as an abatement indicator for any type of waste, which is more representative than the amount of volatile solid reduction.

Methane production kinetics

When looking closer into the mechanisms involved in the degradation, the kinetics of methane production can bring fruitful information. First of all, if we consider successive waste addition in the BMP reactors, we observe that the second and the third additions lead to similar response curves concerning methane production (Figure 3). This means that bacterial adaptation and specialisation only occur during the first batch test. This can be explained by two reasons: first, the inoculum sludge was previously adapted to waste mixtures containing all the wastes tested. Second, the waste/inoculum ratio used is rather low ($0.5-0.8\,gVS_{waste}/gVS_{sludge}$). The difference observed between the successive ultimate methane produced is attributed to the difficulty of getting a homogeneous sample when the blended preparations were weighed, due to phase separation after thawing. The standard deviation of the BMP values for the three successive repetitions is thus
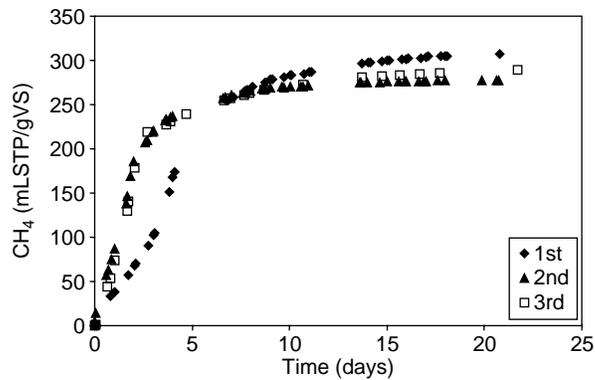
238

Figure 3 Methane production for three sequential BMP tests for banana waste

quite elevated (10% max, Table 2), while it was much lower for cellulose standards (3% max, Table 1).

A second interesting item of information that can be drawn from these results is that the methane production kinetics does not follow a regular (first-order) evolution, as could have been expected. Apparently, there are two steps in the methane production, the first step being observed during 1–2 days after waste addition, with a high methane production rate. Then, there is an inflexion of the curve prior to another high rate methane production. This is best seen in Figure 4, where the methane production rate is plotted for three successive waste (apple) additions and for one citrus (orange) addition: there are two peaks in the methane production rate. These two peaks are more pronounced and appear more early when the sludge becomes more adapted. This peculiar behaviour occurs for all the wastes tested (even synthetic cellulose), and is particularly marked with citrus wastes, as can be seen in Figure 4. This was also observed by Eleazer *et al.* (1997) for food wastes, though the experimental conditions were different in that case (landfill conditions). A possible interpretation of this result is that the first peak could be attributed to the degradation of readily accessible organic matter (soluble sugars), and the second peak to the degradation of particulate solids, limited by hydrolysis; nevertheless, no correlation could be found between the methane production during the first peak and the waste composition. Another explanation would be that the first peak corresponds to methane produced via hydrogenotrophic bacteria, and the second peak via VFA degraders. Due to this complex behaviour, it was difficult to find one (or more) simple kinetic parameter to describe the methane production rate (such as a first-order hydrolysis
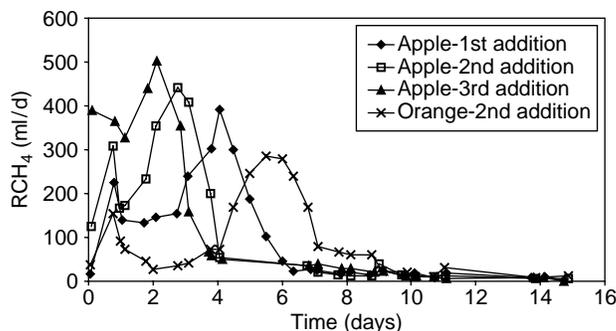

Figure 4 Methane production rate for three sequential BMP tests for apple waste, and for the second addition of orange waste

239

constant). There is thus a need for a better understanding of the basic mechanisms occurring during the degradation. This could be done by analysing the degradation products during the tests and by testing models for hydrolysis.

Conclusions

Today, many researchers focus on assessing data on various types of waste, such as the biochemical composition, the methane potential and the biodegradability. Our objective is to propose and establish a typology based on selected parameters (COD, fibre content, protein content, fat content,…) in relation to the degradation characteristics. The first results presented have been obtained on kitchen wastes and grass. Though a limited amount of products have been tested, we clearly observe a relation: the biodegradability decreases with the increase of the ligno-cellulosic content of the waste. This result is confirmed by other workers, but needs substantiation on a wider range of organic products. This parameter, if confirmed, could be used as a "new indicator" of anaerobic digestion processes.

Concerning the kinetics of degradation, the methane production rate is relatively different from first-order: it is thus difficult to find a unified parameter to represent the kinetics (such as the first-order constant); more work is required on basic hydrolysis mechanisms to assess a general model (intermediate product concentrations for instance). When achieved, a relation between the kinetic parameter(s) and the solid waste composition could reasonably be expected.

A first application of this indicator could be the analysis of digestion end-products to estimate their degradation stage, by comparison to the incoming waste. Many other applications could be imagined, for instance in the management and operation of anaerobic digesters facing waste quality variations, or in the selection and evaluation of appropriate pre-treatments.

Acknowledgements

References

Angeladiki, I. and Sanders, W. (2004). Assessment of the anaerobic biodegradability of macropollutants. *Reviews in Environmental Science and Biotechnology*, **3**, 117–129.

Bjornsson, L., Murto, M. and Mattiasson, B. (2000). Evaluation of parameters for monitoring an anaerobic co-digestion process. *Applied Microbiology and Biotechnology*, **54**, 844–849.

Cecchi, F., Traverso, P.G., Mata-Alvarez, J., Clancy, J. and Zaror, C. (1988). State of the art of R&D in the anaerobic digestion process of municipal solid waste in Europe. *Biomass*, **16**, 257–284.

Chandler, J.A., Jewell, W.J., Gossett, J.M., Van Soest, P.J. and Robertson, J.B. (1980). Predicting methane fermentation biodegradability. *Biotechnology and Bioengineering Symposium Series*, **10**, 93–107.

Christ, O., Wilderer, P.A., Angerhöfer, R. and Faulstich, M. (2000). Mathematical modelling of the hydrolysis of anaerobic processes. *Water Science and Technology*, **41**(3), 61–65.

Chynoweth, D.P., Turick, C.E., Owens, J.M., Jerger, D.E. and Peck, M.W. (1993). Biochemical methane potential of biomass and waste feedstocks. *Biomass and Bioenergy*, **5**(1), 95–111.

Eleazer, W.E., Odle, W.S., Wang, Y.S. and Barlaz, M.A. (1997). Biodegradability of municipal solid waste components in laboratory scale landfills. *Environmental Science and Technology*, **31**, 911–917.

Hansen, T.L., Svärd, A., Angeladiki, I., Schmidt, J.E., Jansen, J. and Christensen, T.H. (2003). Chemical characteristics and methane potentials of source separated and pre treated organic municipal solid waste. *Water Science and Technology*, **48**(4), 205–208.

240

Hartmann, H., Angeladiki, I. and Ahring, B.K. (2000). Increase of anaerobic degradation of particulate organic matter in full-scale biogas plant by mechanical maceration. *Water Science and Technology*, **41**(3), 145–153.

Jokela, J., Vavilin, V.A. and Rintala, J. (2005). Hydrolysis rates, methane production and nitrogen solubilisation of grey waste components during anaerobic biodegradation. *Bioresource Technology*, **96**, 501–508.

Komilis, D.P. and Ham, R.K. (2003). The effect of lignin and sugars to the aerobic decomposition of solid wastes. *Wastes Management*, **23**, 419–423.

Marique, P., Gilles, A., Edeline, F. and Joassin, L. (1989). Thermophilic semisolid anaerobic digestion of municipal refuses. *Biotechnology and Bioengineering*, **33**, 536–541.

Mata-Alvarez, J., Mace, S. and Llabres, P. (2000). Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresource Technology*, **74**(1), 3–16.

Møller, H.B., Sommer, S.G. and Ahring, B.K. (2004). Methane productivity of manure, straw and solid fractions of manure. *Biomass and Bioenergy*, **26**, 485–495.

Nallathambi Gunaseelan, V. (2004). Biochemical methane potential of fruits and vegetable solid waste feedstocks. *Biomass and Bioenergy*, **26**(4), 389–399.

Noike, T., Endo, G., Chang, J.E., Yaguchi, J.I. and Matsumoto, J.I. (1985). Characteristics of carbohydrate degradation and the rate limiting step in anaerobic digestion. *Biotechnology and Bioengineering*, **27**, 1482–1485.

Owens, J.M. and Chynoweth, D. (1993). Biochemical methane potential of MSW components. *Water Science and Technology*, **27**(2), 1–14.

Pareek, S., Kim, S.K., Matsui, S. and Shimizu, Y. (1998). Hydrolysis of (ligno)cellulosic materials under sulfidogenic and methanogenic conditions. *Water Science and Technology*, **38**(2), 193–200.

Peres, C.S., Sanchez, C.R., Matumoto, C. and Schmidell, W. (1992). Anaerobic biodegradability of the organic components of municipal solid wastes (OFMSW). *Water Science and Technology*, **25**(7), 285–293.

Rintala, J. and Järvinen, K. (1996). Full scale mesophilic co-digestion of municipal solid waste and sewage sludge: methane production characteristics. *Wastes Management and Research*, **14**(2), 163–170.

Saint-Joly, C., Desbois, S. and Lotti, J.-P. (2000). Determinant impact of waste collection and composition on anaerobic digestion perfomance: industrial results. *Water Science and Technology*, **41**(3), 291–297.

Sanders, W. (2001). Anaerobic hydrolysis during digestion of complex substrates. PhD thesis, Wageningen University, The Netherlands.

Scherer, P.A., Schultz, K.U. and Meyer-Pittrof, R. (1990). Comparison of methods to characterize the degradation rate of organic matter during solid state fermentation. *DECHEMA Biotechnology Conferences*, Behrens, D. (ed.), Wiley, VCH, Weinheim, Germany, pp. 661–665.

Scherer, P.A., Vollmer, G.R., Fakhouri, T. and Martensen, S. (2000). Development of a methanogenic process to degrade exhaustively the organic fraction of municipal grey waste under thermophilic and hyperthermophilic conditions. *Water Science and Technology*, **41**(3), 83–91.

Tong, X., Smith, L.H. and McCarthy, P.L. (1990). Methane fermentation of selected lignocellulosic materials. *Biomass*, **21**, 239–255.

Van Soest, P.J. (1963). Use of detergent in the analysis of fibrous feeds. A rapid method for the determination of fibre and lignin. *Journal of the Association of Analytical Chemists*, **46**(5), 829–835.