
Paper:
Horan, NJ, Siqqiqui, Z and Anaman, K (2011) *Optimisation of C:N Ratio for Co-Digested Processed Industrial FoodWaste and Sewage Sludge Using the BMP Test.* International Journal of Chemical Reactor Engineering (in preparation).

An Article Submitted to

INTERNATIONAL JOURNAL OF
CHEMICAL REACTOR ENGINEERING

Optimisation of C:N Ratio for Co-Digested Processed Industrial Food Waste and Sewage Sludge Using the BMP Test

Zuhaib Siddiqui[*] N.J. Horan[†]
Kofi Anaman[‡]

[*]University of Leeds, zuhaib80@hotmail.com
[†]University of Leeds, n.j.horan@leeds.ac.uk
[‡]University of Leeds, judanaman@yahoo.co.uk

ISSN 1542-6580

Optimisation of C:N Ratio for Co-Digested Processed Industrial Food Waste and Sewage Sludge Using the BMP Test

Zuhaib Siddiqui, N.J. Horan, and Kofi Anaman

Abstract

Biomethane production from processed industrial food waste (IFW) in admixture with sewage sludge (primary and waste activated sludge: PS and WAS) was evaluated at a range of C:N ratios using a standard biochemical methane potential (BMP) test. IFW alone had a C:N of 30 whereas for WAS it was 5.4 and thus the C:N ratio of the blends fell in that range. Increasing the IFW content in mix improves the methane potential by increasing both the cumulative biogas production and the rate of methane production. Optimum methane yield 239 mL/g VSremoved occurred at a C:N ratio of 15 which was achieved with a blend containing 11 percent (w/w) IFW. As the fraction of IFW in the blend increased, volatile solids (VS) destruction was increased and this led to a reduction in methane yield and amount of production. The highest destruction of volatile solids of 93 percent was achieved at C:N of 20 followed by C:N 30 and 15. A shortened BMP test is adequate for evaluating optimum admixtures.

KEYWORDS: biochemical methane potential (BMP), co-blending, methane yield, volatile solids

1. INTRODUCTION

Anaerobic digestion of thickened sludge has been practiced by the UK water industry for over one hundred years (Watson, 1923). The process was initially employed to stabilise the sludge before recycling to agricultural land, thus preventing nuisance odours. More recently the main focus has been on the production of biogas often in association with combined heat and power (CHP) schemes (Coffey, 2009). There has been a surge of interest in the technology over the past decade, in particular from the waste industry for its application to the digestion of biodegradable organic wastes. The UK Government has also recognised the important contribution that anaerobic digestion can make to help it achieve a number of key national targets. These include use of renewable energy, reducing CO_2 and other greenhouse gas emissions and reducing the amount of biodegradable municipal waste sent to landfill.

A key strategy to achieve all these targets is for the Water Companies to ensure that at least 20% of all energy used by the water industry comes from renewable sources by 2020 (Defra, 2009; Defra, 2009a). The industry has an additional incentive to achieve this figure as it will be included in the EU's carbon trading scheme and so it will soon be required to pay for its carbon emissions (Craven, 2009). The Water Industry is well placed to achieve the targets and there are a number of reasons for this. It has been estimated that there is an overcapacity of at least 30% in its existing anaerobic digestion infrastructure. If this could be utilised, it would increase biogas production by at least 43%. However sewage sludge is a poor feed source for anaerobic digestion as it is high in nitrogen and low in carbon (Kim et al. 2004). Thus the methane yield is reduced as a result both of the paucity of carbon and the ammonia released during digestion, which may prove inhibitory to the process. As a consequence it would prove beneficial to supply the additional feed needed to utilise the extra capacity, as an easily degradable, high carbon substrate. Co-digestion in admixture with sewage sludge would then further enhance the methane yield.

There is a wide range of potential substrates that could be employed in admixture during digestion. For instance food and vegetable waste are high in carbon and lack nitrogen and phosphorus, so are ideal candidates. By contrast animal wastes such as cow slurry and chicken manure are unsuitable due to their high nitrogen content (Callaghan et al. 2002). When co-digestion has been evaluated either at a laboratory or pilot-scale, the results have been encouraging and blended wastes generally demonstrate enhanced methane yields. But there are barriers to the application of co-digestion in the water industry, in particular with establishing quality control of the imported feedstock. Sweenie (2009) has summarised these barriers and considers achieving a consistent digester feed in terms of moisture content and C:N ratio, to be most important. If the carbon content is too high then rapid acidification can occur and methanogenesis is inhibited by the low pH (Carucci et al. 2005). It appears that the ideal C: N ratio is waste specific over a range from 9 to 30. Sosnowski et al. (2003) observed two-fold higher biogas production, co-digesting sewage sludge and the organic fraction of municipal solids at a C: N of 9.26, when compared to sewage sludge alone. Sievers and Brune (1978) used paper pulp and sewage sludge mixtures and reported optimal operation with a C: N ratio of 16:1. Rizk et al. (2007) used FVW and sewage sludge and found this was optimal at a C:N of 20:1. Others consider that the variables with the biggest impact on the quantity and composition of methane are pH, alkalinity, volatile acid concentration, nutrient availability and the presence of toxic materials (Heo et al. 2004). Whereas sewage sludge has a relatively constant composition, its volume and solids concentration are highly variable which makes digester optimisation difficult. Thus blending sewage sludge with a waste of a higher dry solid concentration will permit better control of digester performance and enhance digestibility. However other feedstocks are likely to have a more variable composition than sewage sludge and it would be helpful to evaluate rapidly the optimal sludge mix ratio in order to provide confidence in the feedstock and act as a quality control procedure. Thus it is the aim of this study to identify those factors which are the most important for enhancing the methane yield during co-digestion and suggest a rapid batch technique to aid in optimising the admixture and minimising variability in digester performance. The specific objectives of this study were to: (i) evaluate the optimised C:N ratio enhancing the highest methane yield, rate of methane production and anaerobic biodegradability (ii) determine the rate limiting stage for common toxicants and their effect on rate of biogas production (iii) comparing the results obtained from the conventional biochemical methane potential (BMP) test with theoretical methane potential (TMP) and suggest a rapid batch technique to aid in optimising the admixture and minimising variability in digester performance.

2. MATERIAL AND METHODS

2.1 Feed stocks and seed inocula

Processed industrial food waste (IFW), comprised pig Waste (name of the holding tank: PW) and screened refuse (SR) were collected from Kerry Ingredients, Okehampton, UK. Waste arising from food processing was termed PW and during wastewater treatment as SR. The former comprised solids such as rejected finished-products, processing waste and surplus fruit. The last consisted of the residue left after the industrial wastewater was screened through a 3 mm screen. The sewage sludge (SS) comprised primary sludge (PS) and waste activated sludge (WAS) was collected from the Knostrop WwTw in Leeds, UK. Feedstocks were stored at 4^{o}C and prior to their use were maintained at room temperature. Seed inoculum was obtained from a laboratory scale mesophilic anaerobic digester. The digester was operated at a temperature of 37^{o}C±0.2 and hydraulic retention time (HRT) of 10 days by feeding co-blended IFW and SS maintaining the organic loading rate (OLR) of 3.4 g VS/L/.d. The pH, alkalinity, VFA and methane composition was 6.5±0.3, 6,000 mg/L 40,000 mg/L and 70.7%.

2.2 Analytical methods

The pH value was monitored with a hydrogen ion sensitive electrode using a Corning pH Meter. The analytical determinants of total solids (TS), volatile solids (VS), total alkalinity (TA), ammoniacal nitrogen (NH_4-N), total volatile fatty acids (TVFA) and fat (FAT) were carried out following the procedures outlined in APHA (1998). Samples for analysis of TA, NH_4-N, and TVFA were centrifuged at 60,000 rpm for 1 hour prior to analysis. TS were the fraction of the total wet weight of sample from which moisture (water) had been evaporated in an oven at 105^{o}C for twenty-four hours. VS measure the difference between TS and weight of the inert or fixed solids (FS) from a sample after ignition in muffle furnace at 550^{o}C until constant weight ensures. TA was determined potentiometrically by titrating against standard sulphuric acid (0.1M). NH_4-N was determined after distilling the sample with 50% sodium hydroxide. The distillate was recovered in indicating boric acid solution thereby titrating against standard sulphuric acid (0.01M). The elemental composition of all feedstocks was determined with vanadium pentoxide by flash combustion method using the CHNSO Analyser (Thermo Flash EA-1112 series, Italy). Theoretical methane potential was calculated following Heo et al. (2004).

2.3 Biochemical methane potential (BMP) test

The BMP was determined in anaerobic batch reactors of 500 mL capacity with hermetically sealed stoppers and controlled-opening valves for gas removal. The effective volume was 400mL and the gas phase was 100mL. Each bottle contained the organic load of 4 g VS/L (1.6 g VS/400 mL) of feed-stock and selected seed inocula adjusting the $VS_{seed\text{-}sludge}$:$VS_{feed\text{-}stock}$ ratio as 2.5. To investigate the impact of co-digestion on bio-mehtane potential four different C:Ns (10, 15, 20 and 30) were volumetrically blended using the industrial food waste (IFW) and sewage sludge (PS, WAS). Before starting the experiment, nutrient media (Kim et al. 2003) was added at 1mL/1000mL for mixed anaerobic cultures and corrected to pH 7.0 ± 0.2 using 6M NaOH and 1M HCl. A constant internal temperature of 37^{o}C was achieved by incubating the reactors in a temperature controlled mechanical shaker. Samples were mixed at 140 rpm for a 15 minute period followed by 15 minutes with no shaking. For corrections, a control employing only seed sludge was used to account for the biogas contribution of the seed. The quantity of biogas produced was measured by connecting the valve on the batch reactor to the inlet tube of an hermetically-sealed, water displacement aspirator bottle filled with 5% (w/v) NaOH (Shanmugham and Horan, 2009) to scrub off CO_2. A measuring cylinder placed at the outlet of the aspirator bottles collected the displaced solution which measures the CH_4 at atmospheric temperatures and pressure (N mL CH_4/d). The measured biogas volume was adjusted to standard temperature (0^oC) and pressure (1 atm) STP using Eq-1.

$$V_S = \frac{V_m \times T_S \times P_m}{T_m \times P_S} \qquad (1)$$

Where, V_S volume of measured gas at STP (mL), V_m volume of measured gas at ambient condition (mL), T_S ambient temperature (^oK), P_m ambient pressure (atm), T_m standard temperature (0^oC or 273^oK), P_m standard pressure (1 atm).

The initial and final characterisation of the 500 mL bottles was taken for the mass balance analysis and the serum bottle samples were used for anaerobic process evaluation analysis. The serum bottles contents were withdrawn periodically for analysis of anaerobic products. The samples from the serum bottles were used to analyse the anaerobic product such as total alkalinity (TA), volatile fatty acids (VFA), and NH_4-N. The BMP yield was then calculated from Eq-2.

$$BMP\ yield\ (mL\ CH_4 / g\ VS_{removed}) = \left[\frac{mL\ H_4\ produced}{\left(g\ VS_{inital} - g\ VS_{final}\right)}\right] \qquad (2)$$

3. RESULTS AND DISCUSSION

3.1 Waste characterization

Successful anaerobic digestion requires analysis of the feedstock to ensure that it is balanced in terms of carbon, nitrogen, TS and VS content and where waste are to be blended, to ensure the optimum blend. Four wastes were used in this study. Processed industrial food waste (IFW) known as Pig waste (PW), and screened refusal (SR) were highly organic with a VS of 99 and 92% respectively and with very similar carbon content at 57.2 and 57.5 % (Table 1). The primary sludge (PS) and the waste activated sludge (WAS) had higher ash content and so their VS content was much lower at 66.2 and 65.2% and the carbon content was also reduced at 36.7 and 37.6% (Table 1). All four wastes and seed inoculum had a high alkalinity and adequate volatile fatty acids to suggest they should prove amenable to anaerobic digestion. Food waste alone had the highest C:N of 31.8, whereas it was lowest for WAS at 5.4. Based on the results of the waste characterization, the four waste types were blended volumetrically to provide four feedstocks across the C:N range of 10 to 30.

Table 1. Characteristics of feedstock

Parameters	PW	SR	PS	WAS
pH	3.4	4.0	5.5	6.6
TS (%)	33.9	1.7	4.8	2.6
VS (%TS)	98.7	91.5	66.2	65.2
Alkalinity(mg$CaCO_3$/L)	4,500	4,000	5,000	4,000
TVFA (mgCH_3COOH/L)	73,200	29,100	34,800	47,400
NH_4-N(mg/L)	98	80	143	650
C(%TS)	57.2	57.5	36.7	37.6
N(%TS)	1.8	3.3	3.2	6.9
H(%TS)	5.8	6.9	5.5	5.7
S(%TS)	< 0.3	<0.3	0.6	0.6
O(%TS)	31.9	25.8	14.4	21.5
C:N ratio	31.8	17.4	11.6	5.4

3.2 Effect of C:N ratio on theoretical methane potential (TMP)

Generally, the organic waste is represented by $C_aH_bO_cN_d$. Assuming the complete conversion of the biodegradable organic constituents to carbon dioxide and methane. The TMP was calculated using the Bushwell equation (Bushwell and Mueller, 1952) Eq-3. Heo et al. (2004); Sosnowski et al. (2003); Tchobanoglous et al. (1993) predicted the TMP using the same.

$$C_aH_bO_cN_d + \tfrac{1}{4}(4a-b-2c+3d)\,H_2O \longrightarrow \tfrac{1}{8}(4a+b-2c-3d)\,CH_4 + \tfrac{1}{8}(4a-b+2c+3d)\,CO_2 + dNH_3 \qquad (3)$$

The TMP vary over the range 370 to 480 mL with the most gas produced at a C:N of 15 and the least at 20 (Table 2).

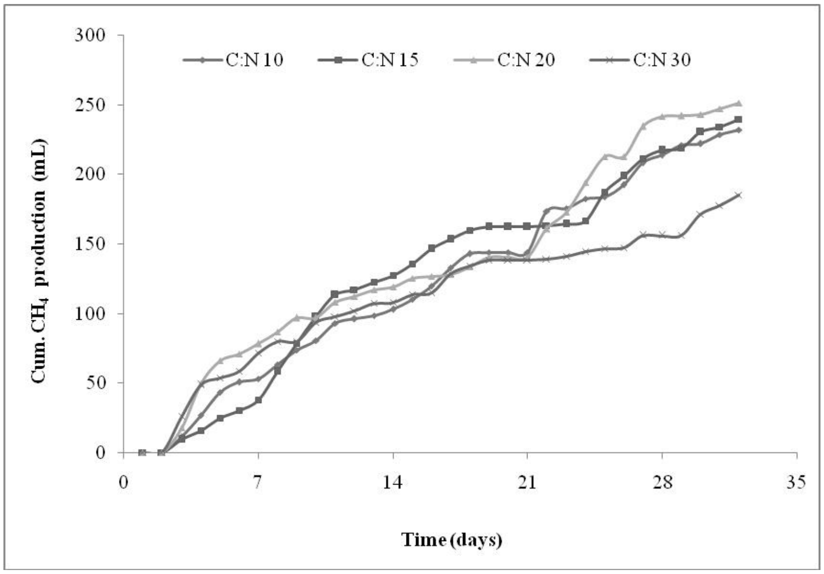

Figure. 1 Cumulative CH_4 production for all analysed C:N ratios

3.3 Effect of C: N ratio on methane production

The cumulative methane production for each of the four blends was measured over a period of 30 days and was observed to vary over the range 185 to 251.4 mL, with the most gas produced at a C:N of 20 and the least at 30 (Figure 1). The rate at which methane was produced was increased by increasing the C:N and varied 15.1 to 29.1 mL/(L.d) (Figure 2). The highest methane production rate was noted at C:N 30, observed during the first day of experiment and later decreased to 11.6 mL/(L.d). For all the wastes the majority of methane production occurred during the first 15 days of the test ranging from 50 to 70% of the total. So it was thought possible to reduce the time of the BMP test to 15 days without detracting from the value of the test as an absolute measure of the amount of methane produced not required. The digester retention time is a key process design parameter that is selected to ensure that the microorganisms in the reactor have adequate time to grow and reproduce (Heo et al. 2004; Li and Fang, 2007). At the same time it is important for economic success to ensure that the digester is operated at the maximum rate of gas production. For a batch system as employed in the BMP test this is extrapolated from the linear part of the curve, in other words before the cumulative gas production ceased to be linear and again in all cases it was determined within 15 days. This was further corroborated by Kim et al. (2003), who have performed the standard BMP for 15 days. Although the specific methane potential (SMP) for all the blends, achieved through TMP were noted higher compare to the SMP achieved through the BMP test (Shanmugam and Horan, 2009). The methane yield for the blended waste was much higher and varied over the range 125 to 239 mL/g $VS_{removed}$ (Table 2). At C:N 15, the methane yield 239 mL/g $VS_{removed}$ (454 mL/g $COD_{removed}$) was two folds higher than the methane yield noted at C:N 30 (Table 2) and higher than earlier reported values 50 – 230 mL/g VS (Hedge and Pullammanappallil 2007; Heo et al. 2004; Lahoz et al. 2006; Gunasleen, 2004; Kim et al. 2003; Callaghan et al. 2002; Rizk et al. 2007) or 57 mL CH_4/g COD (Kim et al. 2007) and 424 mL CH_4/g COD (Egruder et al. 2001).

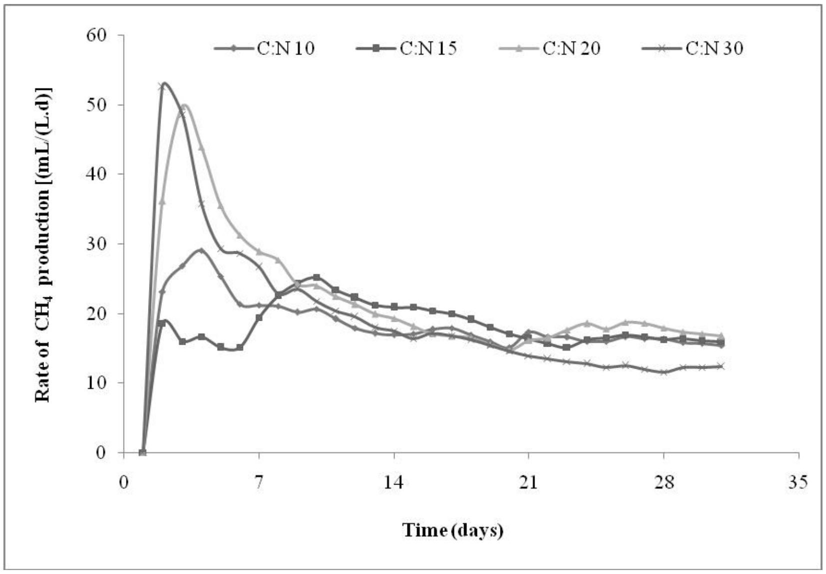

Figure. 2 Rate of CH_4 production for all analysed C:N ratios

3.5 Effect of C: N ratio on ammonia

McCarty and McKiney (1961) were amongst the first to suggest that free ammoniacal nitrogen may be toxic to methanogenic activity and they considered this occurred at concentrations greater than 150 mg/L. A range of values have since been proposed to define ammonia toxicity. For instance Val Velsen (1979) thought that ammoniacal nitrogen concentrations up to 1,500 mg/L had no significant effects on methanogenesis while Koster and Lettinga (1984) concluded that concentration of ammonia in excess of 700 mg/L would decrease methanogenic activity. In this study ammoniacal nitrogen showed a variation over the range 100 to 300 mg/L (Figure 3) but this was not related to the initial C:N ratio, and consequently to the amount of methane produced, thus inhibition was not demonstrated. In most cases there was a decrease in ammonium levels then followed by a inclination which might reflect some volatilisation at the high incubation temperatures.

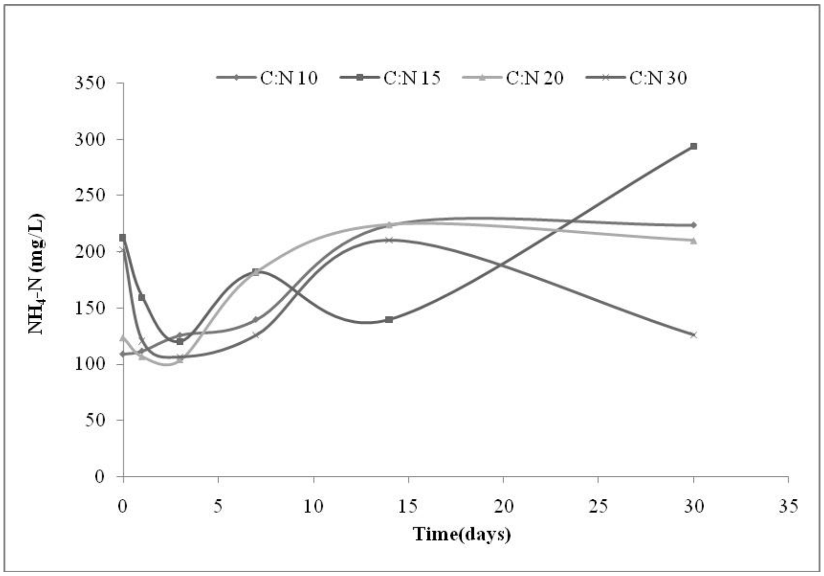

Figure. 3 Ammonium release during digestion for all analysed C:N ratios

Table 2 Performance data for experiments during 30-days BMP test, TMP and 15-days rapid BMP test

C:N	Standard BMP			TMP	Rapid BMP		
	CH_4 Yield mLCH_4/g $VS_{removed}$	$VS_{removed}$ %	SMP mL	SMP mL	SMP mL	$VS_{removed}$ %	ATP mg/L
10	205.3	75.6	232.2	470	83	26.9	5.3
15	211	76.3	239.8	480	153	40	9.6
20	180.4	93.8	251.4	370	128.3	76.4	6.3
30	134.4	92.5	185.3	380	80.5	40.3	3.5

3.6 Application of ATP analysis

Biological activity during the BMP test was monitored using adenosine triphosphate (ATP) concentration in order to determine whether this test could act as a rapid measure of optimum activity. The highest ATP concentration coincided with the highest methane yield at a C:N of 15 (Table 2) and although there was no clear mathematical relationship, an increasing methane yield was associated with a high cellular ATP and *vice versa*. ATP concentration started to decline once the rate of methane production had slowed after 15 days, again suggesting that a reduced testing period would be adequate for optimising waste admixtures. For the purpose of quality controlling admixtures, ATP analysis offers the opportunity to simplify the BMP test by omitting the time consuming gas collection and measurement stage and relying on the relative ATP concentration after 15 days.

4. CONCLUSION

Processed Industrial food waste has a very high C:N ratio of around 30:1 and is predominantly carbohydrate whereas by contrast, waste activated sludge has a low ratio of around 5.4:1 and comprises high fat and protein. Co-blending of food waste with the sewage sludge from wastewater increases both the amount and the rate of methane produced during anaerobic digestion.

The optimum blend occurs at a C: N ratio of 15 which is achieved with 11% (w/w) food waste. The highest methane yield 239 mL/gVS$_{removed}$ was also observed at C:N 15

The highest destruction of volatile solids of 93% was achieved at C:N of 20 followed by C:N 30 and 15.

ATP concentration reflects methane yield and offers a simplified test to optimise admixtures. Further work is required to refine the methodology.

At all C: N values 50 to 70% of the total methane production is achieved in the first fifteen days. Linear methane generation slows after 15 days although optimum mix does not change after a further 15 days. A shortened BMP test is adequate for evaluating optimum admixtures.

5. REFERENCES

American Public Health Asssociation. (1998). “Standard methods for the examination of water and wastewater.” 20th ed. Washington, DC, USA.

Bouallagui, H., Touhami Y., Cheikh R.B. and Hamdi M., “Bioreactor performance in anaerobic digestion of fruit and vegetable wastes”, Process Biochemistry, 2005, 163, 989–995.

Bushwell, A.M., and Mueller, H.F., “Mechanisms of methane fermentation”, Ind. Eng. Chem., 1952, 44,550.

Li, C., and Fang, H.H.P., "Fermentative hydrogen production from wastewater and solid wastes by mixed cultures", Crit. Rev. Environ. Sci. Technol., 2007, 37, 1–39.

Callaghan, F.J., Wase, D.A.J., Thayanithy, K. and Forster, C.F., "Continuous co-digestion of cattle slurry with fruit and vegetable wastes and chicken manure", 2002, Biomass and Bioenergy, 27, 71–77.

Carucci, G., Carrasco, F., Trifoni, K., Majone, M. and Beccari, M., "Anaerobic digestion of food industry wastes: effect of codigestion on methane yield", 2005, J. Environmental Engineering ASCE, 131, 1037–1045.

Coffey, M., "Energy and power generation: maximising biogas yields from sludge", 2009, Filtration and Separation, 46, 12–15.

Craven P., "Waste recycling fuels Severn Trent works", 2009, Water and Wastewater Treatment, 52, 35–36.

Defra., "Shared goals – anaerobic digestion", 2009, Defra, London, UK.

Defra., "Developing an implementation plan for anaerobic digestion, report of the anaerobic digestion task group", 2009a, Defra, London, UK.

Erguder, T.H., Tezel, U., Guven, E. and Demirer, G.N., "Anaerobic boitransformation and methane generation potential of cheese whey in batch and UASB reactors", 2001, Waste management, 21, 643–650.

Gunasleen, V.N., "Biochemical methane potential of fruits and vegetable waste feedstocks". Biomass and Bioenergy, 2004, 6, 389–399.

Hedge, G. and Pullammanappallil, P., "Comparison of thermophilic and mesophilic one-stage, batch, high solids anaerobic digestion", 2007, Environmental Technology, 28, 361–369.

Heo, N.H., Park, S.C. and Kang, H., "Effects of mixture ratio and hydraulic retention time on single-stage anaerobic co-digestion of food waste and waste activated sludge", 2004, Environmental Science Health, A39, 7, 1739–1756.

Koster, I.W. and Lettinga, G., "The influence of ammonium–nitrogen on the specific activity of palletized methanogenic sludge", 1984, Agric. Wastes, 9, 205–216.

Kim, H.W. and Shin, H.S., “Response surface optimisation of substrates for thermophilic anaerobic codigestion of sewage sludge and food waste”, 2007, J. Air and Waste Management, 57, 309–318.

Kim, S.H., Han, S.K. and Shin, H.S., “Feasibility of biohydrogen production by anaerobic co-digestion of food waste and sewage sludge”, 2004, Int. J. Hydrogen Energy, 29, 1607–1616.

Kim, W.H., Han, S.K. and Shin, H.S., “The optimisation of food waste addition as a co-substrate in anaerobic digestion of sewage sludge”, 2003, Waste Management Research, 21,515–526.

Lahoz, C.G., Fernandez-Gimenez, B.F., Garcia-Herruzo, F., Rodriguez-Maroto, J.M. and Vereda-Alonso, J.M., “Biomethanization of mixtures of fruits and vegetables solid wastes and sludge from a municipal wastewater treatment plant”, 2007, Journal of Environmental Science and Health Part A, 42,481–487.

McCarty, P. L. and McKinney, R., “Salt toxicity in anaerobic digestion”, 1961, J. Water Pollution and Control Federation, 33, 399–415.

Rizk, M.C., Bergamasco, R. and Tavares, C.R.G., “Anaerobic co-digestion of fruit and vegetable waste and sewage sludge”, 2007, Intl. J. Of Chemical Reactor Engineering, 5, A29, 173–185.

Shanmugam, P. and Horan, N.J., “Simple and rapid methods to evaluate methane potential and biomass yield for a range of mixed solid wastes”, 2009, Bioresource Technology, 100, 471-474

Sievers, D.M. and Brune, D.E., “Carbon/nitrogen ratio and anaerobic digestion of swine waste”, 1978, Transactions of the ASAE, 21, 537–549.

Sosnowski, P., Weiczorek, S. and Ledakowicz, S., “Anaerobic co-digestion of sewage sludge and organic fraction of municipal solid waste”, 2003, Advances in Environmental Resources, 7, 609–616.

Sweenie P., “The Future of AD”, 2009, CIWM, Macnhester, UK, May, 44-45.

Tchobanoglous, G. Theisen, H. and Vigil, S. “Integrated solid waste management: engineering principles and management issues”, 1993, McGraw-Hill, New York. USA.

Val Velsen, A.F.M, “Adaptation of methanogenic sludge to high ammonia-nitrogen concentrations”, 1979, Water Research, 13, 995–999.

Watson J. D. “Sludge digestion”, 1923, Assoc. Man. Sew. Disp. Works. 117 – 122.