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D21: Comparative data on mixed and static bed reactors for inducing high rates of solids hydrolysis

1 Introduction

From a microbiological prospective the process of anaerobic digestion is often described as having 3 main phases: hydrolysis, acidification/acetogenesis and methane production (methanogenesis) (see Figure 1). These processes are entirely mediated by bacteria, which gain energy from the reactions and allow their growth and establishment in system.

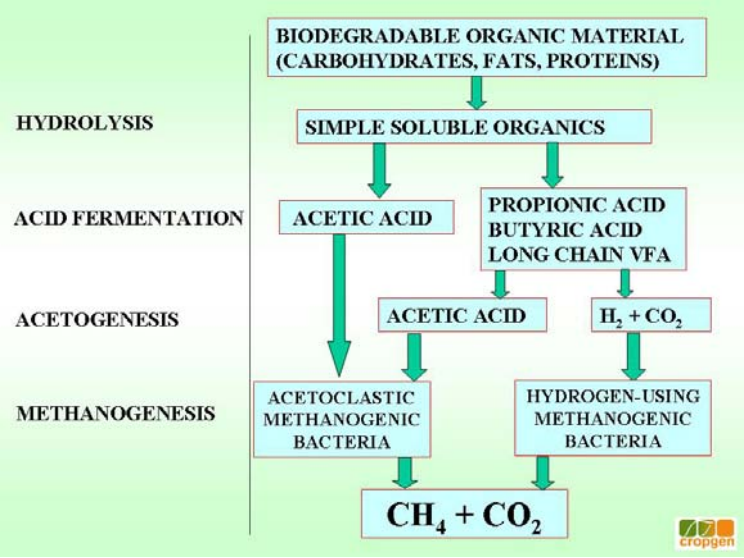


Figure 1. Main stages in anaerobic digestion

Hydrolysis is an essential stage as complex molecules that are too large to pass through the bacterial cell walls are broken down into smaller and simpler molecules that can be transported into the cell and then used for cell growth and maintenance. Breakdown products are thus simple molecules. The breakdown process is extra-cellular and is mediated by extra-cellular enzymes that are secreted by these hydrolysing/acidifying bacteria. The rate at which hydrolysis proceeds will depend on the nature of the substrate, but often in situations where the hydrolysable material is present as fibres it is a relatively slow process, as this makes penetration by extra-cellular enzymes difficult. A large number of bacteria are capable of hydrolysing solid substrates and these same organisms are also the ones that carry out the second stage of digestion, namely acidification.

A relatively high proportion of plant biomass is present as the structural component cellulose, which has to be broken down to glucose before it can be taken up by the bacteria to use as an energy source. Starch is also a common plant storage material and is a polymer of glucose which again has to be hydrolysed before it can be used by bacteria. The rates of hydrolysis of these two materials are very different despite the end product being the same.

Typically the breakdown products of complex biomass components are:

polysaccharides	→	simple sugars
proteins	→	amino acids
fats	→	fatty acids and glycerol

In the process of acidification the small molecules that are formed during the hydrolysis step are taken out of solution by the fermentative and acid-producing bacteria. In the absence of oxygen these small molecules are converted predominantly to acid products by a metabolic process known as fermentation. Fermentation allows the bacteria to gain energy from these food molecules without the need for oxygen; however the energy yield is far lower than if the same molecules were used aerobically (ie. with oxygen) in the process known as respiration. Fermentations are therefore energetically inefficient reactions leaving organic molecules (acids and alcohols) that still have potential for further breakdown.

The balance of acids (and other products) formed during the fermentation depends upon the nature of the substrate and reactor conditions. Generally the product is a mixture of:

Acetic acid	CH_3COOH
Proprionic acid	C_2H_5COOH
Valeric acid	C_3H_7COOH
Butyric acid	C_4H_9COOH
Caproic acid	$C_5H_{11}COOH$

The fermentation mix may also contain traces of lactic acid, ethanol, acetone, indols and skateols (highly odoriferous)

Of all the acids and other potential fermentation products formed, only acetic acid (acetate) can be used as a substrate by the bacteria that produce methane gas (methanogenic bacteria). There is therefore another very important group of bacteria active in the anaerobic digestion process that convert longer chain volatile fatty acids (VFA) to acetate. These are known as the hydrogen-producing acetogenic bacteria because in the conversion of VFA to acetate hydrogen gas is released.

Again this specialist group of bacteria derives energy from the breakdown of the larger acid molecules and uses hydrogen ions as electron acceptors in the reduction process. The general equation for the reaction is:

$$\mathbf{4C_2H_5COOH + 8H_2O \rightarrow 4CH_3COOH + 4CO_2 + 12H_2}$$

The process of acetate production is important as without it the longer chain volatile fatty acids would constitute a metabolic 'dead end' under anerobic conditions and would accumulate in the reaction mixture. If this happened there would be an increase in acidity and a lowering of pH to a point where other reactions such as methane production would stop. The process is also important in that the hydrogen produced as a result of the reaction can also be used by the methane-producing bacteria

Methane production is carried out by a very special group of bacteria collectively known as methanogenic bacteria or sometimes just 'methanogens'. Two groups of methanogens are recognised:

those which produce methane from H_2 and CO_2 (autotrophic)

$$\mathbf{4\ H_2 + CO_2 \rightarrow CH_4 + 2H_2O}$$

those which produce methane from acetate (acetoclastic)

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Methane can also be formed from formic acid (HCOOH), but this is thought to be due primarily to its instability and tendency to break down to hydrogen and carbon dioxide, which can then be used by the autotrophic methanogens.

$$HCOOH \rightarrow CO_2 + H_2$$

Methanol and other alcohols can also form methane, but this is less common. Conversion from methanol can be direct or via acetate or CO_2 and H_2, while other alcohols must be converted to acetate or formate with other co-products.

From the above description it is clear that the microbial populations within a methane-producing anaerobic environment have a high degree of interdependence. For the process to work, which is essential if it is to be harnessed for energy production, a balance must be maintained between these microbial groups to promote the energy and carbon flow through to methane. If we consider each of the groups individually then:

- Fermentative bacteria are relatively fast growing and under ideal laboratory conditions could double their mass every few hours providing they have the right food supply and environmental conditions
- Hydrogen-producing acetogenic bacteria are also relatively rapid growers under ideal conditions but are highly sensitive to environmental conditions
- Methanogenic bacteria are extremely slow growing and are only capable of doubling their mass every few days

In a conventional digester the slow growth rate of the methanogens is often rate limiting as the digester has to be operated at retention times shorter than the doubling time of the methanogens. It has therefore been suggested that if the phases within the process could be split microbiologically into separate reactors, and the conditions within each reactor optimised for the growth and function of different microbial groups, then benefits might include overall reduction in reactor size and better process control. The first attempts at this date back to the late 1970s with the introduction of two stage systems with a short hydraulic retention time in the first stage, to allow hydrolysis and acidification to occur, and a second reactor where methanogenic reactions predominated. In these early types of 2 phase reactor there was no attempt at phase separation and the process usually required pH buffering between phases. The 1980s saw the advent of high rate methanogenic reactors in which the problems of wash-out were overcome by artificially retaining the methanogens within the reactor, either by using biomass support material (anaerobic filters), or by developing a dense granular biomass that formed an expanded bed in the so called 'upflow anaerobic sludge blanket reactor' (UASB). This development opened up the opportunity for two phase processes in which the phases could also be separated hydraulically, and created the potential for highly loaded short retention time methanogenic reactors which could be used to convert the acid fermentation products through to methane.

Further developments showed the potential advantages of uncoupling the solids and liquids retention time in the first phase hydrolysis acidification reactor to produce a constant flow of high strength acid products in a highly loaded reactor whilst maintaining the solids fraction for extended hydrolysis. It is this concept hat has been explored within the current research using 2 types of first phase reactor, both of which allow the uncoupling of solids and liquids retention time. The first is a static bed reactor (leach bed, permeating bed) where the solid substrate biomass is maintained as a static bed of material over which liquid is permeated to induce mass transfer and to washout the fermentation products ina 'hydraulic flush'. The second type of reactor used is continuously mixed (CSTR) and the liquid separated from the solids by external means (membrane separation, gravity settlement or centrifugation. Some of the concepts explored within the research have been successfully tried with municipal solid waste as a substrate and the processes scaled up for commercial application. There are no current examples of such processes being used with energy crop substrates.

The key findings of the research carried out in the CROPGEn project are summarised here, and the full results will be published in peer-reviewed academic journal papers.

2 Static bed reactors

2.1 Materials and methods

Equipment design: Eight leach bed reactors (LBR) were used in this work, with the design shown in Figure 2. The reactors were constructed from 150 mm diameter uPVC pipe, with a stainless steel mesh in the bottom to hold the solid substrate in place and prevent clogging of tubes. The reactors were operated in downflow mode on a batch fed basis. In the early runs, leachate was continuously recirculated through the reactor by a peristaltic pump at a rate of 4 litres hour^{-1}. The reactor was partially drained once per day, allowing the desired volume of leachate to be removed. After that, the same volume of water or recycled effluent was pumped through the influent tube into the reactor. In subsequent runs the replacement liquid was pumped into the reactor to displace the leachate over a 24-hour period.

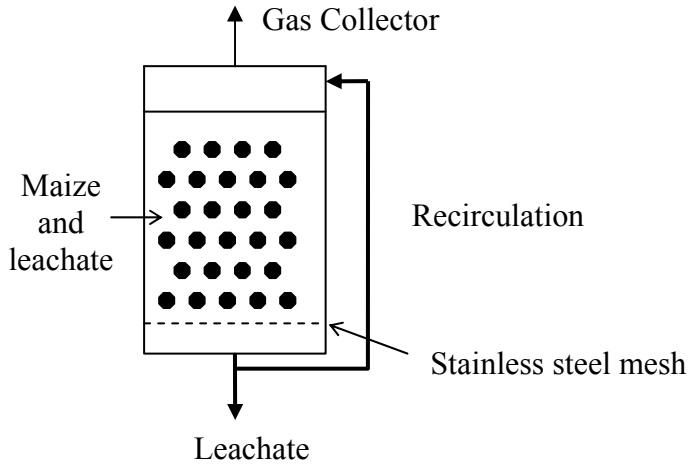


Figure 2. Design of leach bed reactors

Start up and sampling: At the beginning of the experimental period the working volume of the reactors was filled with ensiled maize (1.4 kg wet weight, 378 g of VS) and sieved sludge (2.6 litres) taken from the municipal sewage sludge digester at Millbrook WWTP, Southampton UK. This was circulated for 14 days and then drained and replaced with water. In subsequent runs the each reactor was filled with the appropriate combination of inoculum, in the form of material remaining from a previous run, and fresh feed in the form of ensiled maize. Leachate samples for analysis were taken from the liquid displaced from the reactor on a daily basis, while solid samples were obtained at the end of the run.
Analytical Techniques: pH was measured on alternate days using a Jenway pH probe. Total solids (TS) and volatile solids (VS) were analysed according to Standard Method 2540 G (APHA 2005). Total and soluble chemical oxygen demand (COD) was measured using the closed tube method (APHA 2005). Volatile fatty acids (VFA) and ethanol were quantified in a Shimazdu 2010 gas chromatograph, using a flame ionization detector and a capillary column type SGE BP 21 with helium as the carrier gas. Three standard solutions containing 50, 250 and 500 mg l^{-1} of acetic, proprionic, iso-butyric, n-butyric, iso-valeric, valeric, hexanoic and heptanoic acids were used for VFA calibration; and concentrations of 50, 250 and 500 mg l^{-1} for ethanol calibration.

Biogas was collected in tedlar bags (SKC Ltd, UK) and the volume measured in a water displacement column containing acidified tap water (pH 2). Gas composition was measured using a Varian CP 3800 gas chromatograph with a gas sampling loop using argon as the carrier gas at a flow of 50 ml min^{-1}. The GC was fitted with a Haysep C column and a molecular sieve 13 x (80-100 mesh) operated at a temperature of 50 ^{o}C. The GC was calibrated using a standard gas containing 35% CO_2 and 65% CH_4. Where leachate was not fed to a secondary methanogenic reactor, methane potential is calculated stoichiometrically from COD as 0.35 l CH_4 $gCOD^{-1}$ based on measured COD or the total VFA expressed as COD.

2.2 Experimental work

2.2.1 Initial trial for inoculum: substrate ratio

An initial trial was carried out to establish the best inoculum:substrate (I:S)

Five reactors were set up with I:S ratios of 1:0.5, 1:1, 1:2, 1:3 and 1:4 on a wet weight basis. Each reactor was filled with a total of 1.4 kg (wet weight) of acclimated inoculum and ensiled maize in the desired ratio, and 3 litres of tap water. Leachate was continuously recirculated through the leach bed in the reactor with a peristaltic pump at a rate of 4.0 l/h. The reactors were flushed once per day by allowing 500 ml of leachate to drain. After that, the same volume of tap water was pumped through the influent tube into the reactor to replace effluent drained. Leachate was analysed every alternate day for pH, VFA and COD. Gas was collected in tedlar bags and volumes measured daily, but production was very low and results are not presented here.

The results are summarised in Table 1 and Figure 3. While the ratio 1:0.5 has a marginally higher VFA production in terms of gCOD $gVSfresh^{-1}$ day^{-1}, the second highest and the highest overall methane potential is given by the ratio 1:4. On the basis of these results the I:S ratio of 1:4 was adopted for the following runs.

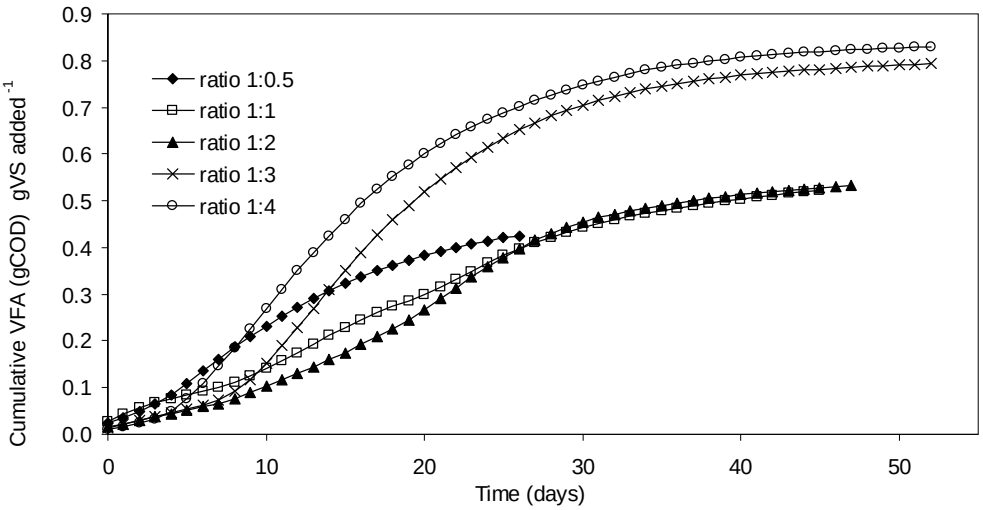


Figure 3. Cumulative VFA production for initial I:S ratio trials

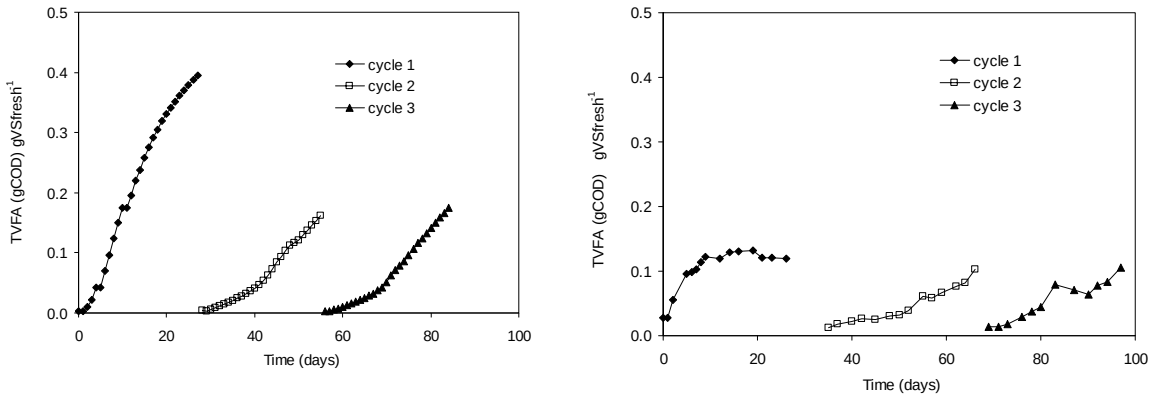
Table 1. Results of initial I:S trial

Feed		I:S ratio	VFA	Run	VFA		methane potential
g wet weight	g VS fresh		g	days	gCOD $gVSfresh^{-1}$	gCOD $gVSfresh^{-1}$ day^{-1}	l CH4 $gVSfresh^{-1}$
467	122	1/0.5	52	26	0.43	0.0164	0.15
700	184	1/1	96	47	0.52	0.0111	0.18
933	245	1/2	131	47	0.53	0.0114	0.19
1050	275	1/3	219	52	0.79	0.0153	0.28
1120	294	1/4	244	52	0.83	0.0160	0.29

2.2.2 Sequencing

Five reactors were operated at an I:S ratio of 1:4 on a 4-week feeding cycle sequenced in such a way that one reactor was refilled weekly and each reactor was refilled every 28 days. The purpose of this was to produce a continuous flow of leachate giving a constant loading rate onto secondary methanogenic reactors. Four of the reactors were operated in hydraulic flush mode, with 500 ml of leachate removed each day and replaced by the same volume of liquid effluent from methanogenic reactors. Tap water was used to make up the flush volume as there was insufficient methanogenic effluent. One reactor was used as a control without flushing. At the end of each run, reactors contents were weighed and digestate and inoculum were sampled and analysed for TS and VS.

Results for the first 3 cycles in reactor 4 and in the control are shown in Figure 4. While the chosen I:S ratio of 1:4 resulted in high VFA production in the first 28-day cycle, production dropped considerably in subsequent cycles. One possible explanation considered was that the initial inoculum still had a high level of activity from the sewage sludge added at start up, which was being lost when large amounts of biomass were wasted at the end of the cycle before the reactors were re-inoculated for the next run.



a) Flushed reactor b) Control (no flush)

Figure 4. VFA production in successive cycles

2.2.3 Second inoculum:substrate ratio trials

Trials were carried out at I:S ratios of 1:2.5, 2.5:1 and 4:1 with results as summarised in Table 2. As a result of these, the I:S ratio of 2.5:1 (wet weight basis) was adopted for subsequent experiments.

Table 2. Results of I:S trials at 1:2.5, 2.5:1 and 4:1

HRT 1.5 d	I:S ratio	1:2.5		2.5:1		4:1	
Solids destruction		total VS	fresh VS	total VS	fresh VS	total VS	fresh VS
Experiment	Cycle 1	39%	51%	28%	67%	17%	56%
	Cycle 2	42%	57%	34%	74%	21%	67%
Control	Cycle 1	27%	36%	26%	62%	14%	45%
	Cycle 2	28%	38%	29%	64%	16%	51%

2.2.4 Flush ratio

The effect of varying the hydraulic retention time by increasing the amount flushed from the reactor was trialled. Leach-bed reactors were operated as above in a 4-week feeding cycle sequenced so that one reactor was refilled weekly and each reactor was refilled every 28 days. Reactors were operated with flush volumes of 500, 1000 and 2000 ml per day corresponding to hydraulic retention times (HRT) of 6, 3 and 1.5 days based on a liquid volume of 3 litres. One reactor was used as a control, without flushing.

	HRT days	6	3	1.5	6	3	1.5
Methane Potential	(m^3CH_4 kg^{-1} VS)	total VS			fresh VS		
Experiment	Cycle 1	0.12	0.16	0.19	0.15	0.22	0.25
	Cycle 2	0.12	0.17	0.19	0.15	0.23	0.26
Control	Cycle 1	0.06	0.10	0.08	0.08	0.13	0.10
	Cycle 2	0.06	0.08	0.09	0.08	0.11	0.12
Solids destruction	(% VS total)	total VS			fresh VS		
Experiment	Cycle 1	34%	34%	41%	41%	48%	52%
	Cycle 2	31%	34%	40%	38%	47%	55%
Control	Cycle 1	22%	29%	27%	27%	41%	34%
	Cycle 2	25%	22%	28%	31%	31%	39%

The theoretical methane potential in m^3CH_4 kg^{-1} fresh VS added was highest at a HRT of 1.5 days. This was only 10% above the corresponding value for a 3-day HRT, however, and represents a doubling in the volume of liquid to be treated in a secondary methanogenic reactor: the specific volumetric values were respectively around 0.23 and 0.13 m^3CH_4 (kg fresh VS added)$^{-1}$ (litre)$^{-1}$. An HRT of 1.5 was therefore selected for the subsequent experiments. The theoretical methane potential in terms of inoculum ratio was around 0.0060 and 0.0067 m^3CH_4 (kg fresh VS added)$^{-1}$ (kg inoculum VS)$^{-1}$ for the 3 and 1.5-day HRTs respectively, and this value was found to indicate a reasonable level of performance in the other trials carried out.

2.2.5 Buffering

While the choice of inoculum ratio and flush rate were able to improve the performance of the LBR, the results in terms of solids destruction and theoretical specific methane yield were still relatively poor in relation to those achieved in conventional single pass reactors (see WP4 and deliverable D29). An experiment was therefore carried out to investigate the effect of buffering on the first stage of the system. Four reactors were operated in the combinations buffer and flush, buffer no flush, flush no buffer, and no flush no buffer. At the start of the run the reactors were filled with 1.4 kg of mixed inoculum and maize at an I:S ratio of 2.5:1, and 3 l of either tap water or buffer solution (7 g l^{-1} of $NaHCO_3$) was added. Liquid was recirculated through the reactors at 2 litres day^{-1} and the HRT was maintained at 1.5 days with fresh buffer or water added to replace the leachate removed. In the buffered control reactor $NaHCO_3$ was added to a small volume of leachate which was bled from the system and then returned. In all cases the amount of buffer added was calculated to bring the pH to between 6 and 6.5. COD was measured rather than calculated from total VFA to allow for the presence of some ethanol in the leachate.

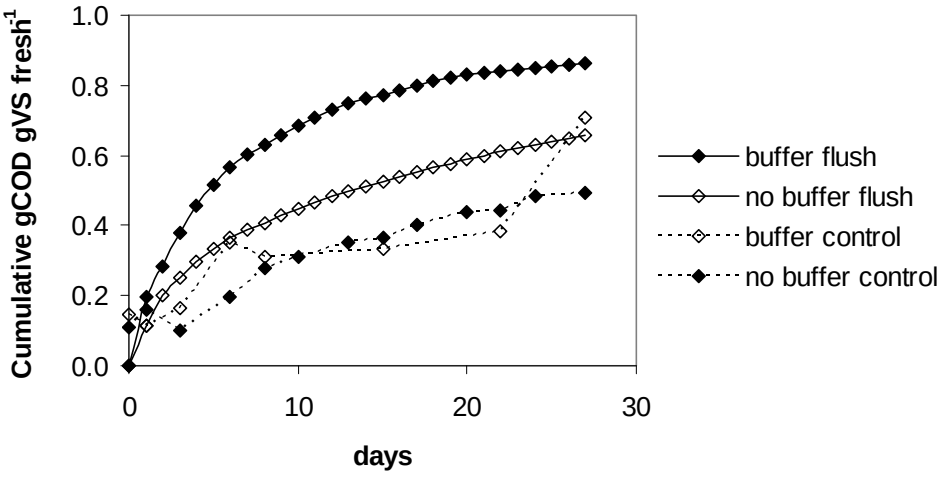


Figure 5. Cumulative COD production with/without buffering and hydraulic flush

The results of the experiment are summarised in Table 3 and Figure 5. Table 4 presents average values for some key parameters. There is a clear improvement in performance between the unflushed unbuffered reactor, the reactor with flush but no buffer and the reactor with both flush and buffering. The very high and increasing level of solids destruction in the buffered reactors is likely to be due to the breakdown of VS in the

inoculum which were not degraded during previous runs in conditions of uncontrolled pH. In this trial and previous ones the pH in unbuffered reactors remained mainly in the range 4-5, and sometimes even lower at the start of a run. The irregular pattern of cumulative COD production in the unflushed buffered reactor reflects the effects of addition of buffering; the increase at the end is mirrored by an increase in VFA production and could indicate the establishment of conditions suitable for microbially mediated acidification and hydrolysis. Work carried out on the microbiology of the reactors is not reported here but will be presented in journal papers currently in preparation.

Table 3. Effects of buffering and hydraulic flush

Conditions	**Methane Potential ($m^3CH_4\ kg^{-1}$ VS $_{total\ or\ freshly\ added}$) (MP)**							
	Solids destruction (% VS $_{total\ or\ freshly\ added}$) (SD)							
I:S 2.5:1	**Buffer**				**No buffer**			
HRT 1.5 days	**MP**		**SD**		**MP**		**SD**	
	total	fresh	total	fresh	total	fresh	total	fresh
Experiment	**flush**				**flush**			
Cycle 1	0.14	0.30	37%	81%	0.10	0.23	29%	65%
Cycle 2	0.17	0.41	42%	100%	-	-	27%	65%
Control	**no flush**				**no flush**			
Cycle 1	0.11	0.25	31%	70%	0.08	0.17	25%	55%
Cycle 2	0.12	0.28	34%	81%	0.07	0.17	24%	56%

Table 4. Results of buffer and flush trials

	Yield per g inoculum	specific volumetric yield	VS destruction	specific yield (VS destroyed)	specific yield (VS added)	volumetric yield
	gCOD gVS_{fresh}^{-1} $gVS_{inoculum}^{-1}$	$thCH_4$ m3 gVS_{fresh}^{-1} $litre^{-1}$ day^{-1}	%	$thCH_4\ m^3\ gVS_{destroyed}^{-1}$	$thCH_4\ m^3\ gVS_{fresh}^{-1}$	$thCH_4\ m^3\ m^{-3}$ reactor day^{-1}
buffer and flush	0.0065	0.0032	91%	0.37	0.36	0.34
buffer no flush	0.0054	0.0023	76%	0.36	0.26	0.25
no buffer flush	0.0050	0.0021	65%	0.35	0.23	0.22
no buffer no flush	0.0038	0.0015	55%	0.31	0.17	0.17

2.3 Continuous operation and conclusions

The experimental work described above established some of the key parameters for the leach bed reactors. The performance of the flushed and buffered reactors showed considerable improvement over the earliest runs and in terms of solids destruction and theoretical specific methane yield is similar to that found in single pass reactors for the ensiled maize substrate. This improvement was maintained with the introduction of full recycling from the second-stage methanogenic reactors. The volumetric methane yield is low, however, due to the relatively long feeding cycle.

From cumulative COD values, for example such as those shown in Figure 5, it is clear that with a 28-day operating cycle the majority of COD production occurs in the first few days of the run. In the next stage of the work, reactors are being operated sequentially at different run times. In this mode of operation the reactor is filled with a mixture of inoculum and substrate and allowed to run for periods of 7, 14 or 28 days. At the end of

this period the contents are sampled to determine VS destruction and an amount equivalent to the VS destroyed is replaced with fresh feedstock. This work will be completed as part of a PhD thesis extending beyond the duration of the CROPGEN project. Final results cannot be given here due to the long overall retention times to reach steady state conditions, but from the initial results it appears likely that increasing the loading rates may have the potential to improve volumetric methane yields to a level that may be acceptable for a simple low-cost system of this type.

3 Hydraulic flush reactors

3.1 Materials and methods

Equipment design and mode of operation: Four typical continuously stirred tank reactors with a working volume of 4 litres were used as the first hydrolysis/acidification stage. After settling, liquid from each reactor was passed to a separate 4-litre anaerobic filter (AF) operating in upflow mode.

The first stage reactors were operated in hydraulic flush (HF) mode with uncoupled liquid and solids retention times (SRT). The HF reactors were designed so that the top could be removed and replaced with a coarse membrane: the reactors were allowed to drain freely, and any material not passing stainless steel mesh of approx 0.64 mm^2 mesh size was regarded as solid and a proportion of it removed to give the required solids retention time. A proportion of the liquid fraction was then introduced into a cone settler and allowed to settle for 24 hours. The settleable fraction was returned to the HF reactor, and 1.4 litres of settled supernatant was fed to the second stage anaerobic filter. Effluent displaced from the anaerobic filter was returned to HF reactor. Figure 6 provides a schematic of the mode of operation.

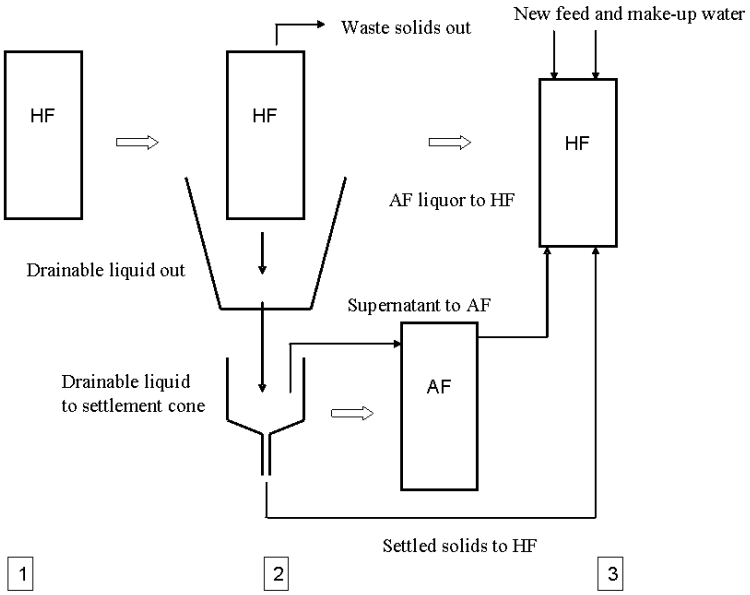


Figure 6. Schematic showing mode of operation of HF-AF reactor system

The HF reactors were operated at loading rates and solids retention times ranging from 2-20 gVS litre^{-1} day^{-1} and 5-40days, under a variety of operating modes as described below and summarised in Table 5.

- The HF reactors were initially flushed by removing 1.4 litres of supernatant without recycle from the AF reactors. The volume was made up with tap water.
- The amount of HF supernatant fed to the AF reactors was increased in stages of 0.5, 0.75, 1 up to 1.4 litres day^{-1}, with equal volume of effluent recycled to the HF.
- The AF reactors were initially fed over a period of 45 minutes with the incoming liquid allowed to displace an equivalent volume of effluent. This worked well at first but as the volume of biomass inside the AF increased it led to shortcircuiting between the effluent and influent and consequent loss of VFA from the AF reactor. The feeding system was therefore changed to allow the total load to be added in the same time period but then to be cycled around the reactor throughout the next 24 hours.
- Gas was originally collected from the AF headspace. As the loading increased, the rate of gas evolution in higher-loaded AF reactors was so rapid that gas became entrained in the liquid and escaped as this was pumped into the effluent reservoir. The feeding method was therefore changed to a completely sealed system so that this gas could be captured and measured.
- Gas production in the HF reactors was initially negligible but as the pH rose, especially at longer SRT, it became more significant and the gas was captured and measured.

Table 5. Operating parameters for HF reactors

day	HF1	day	HF3
1	2 gVS/l-d, SRT 20 days	1	2 gVS/l-d, SRT 40 days
51	Full recycling of flush liquid from 2nd stage anaerobic filter	51	Full recycling of flush liquid from 2nd stage anaerobic filter
102	Loading rate from 2 to 4 gVS/l-d	102	Loading rate from 2 to 4 gVS/l-d
256	SRT reduced to 10 days	256	SRT reduced to 20 days
392	Loading rate from 4 to 5 gVS/l-d	288	SRT reduced to 10 days
421	Loading rate from 5 to 7.5 gVS/l-d	326	SRT reduced to 5 days
455	Loading rate from 7.5 to 10 gVS/l-d	392	Loading rate from 4 to 5 gVS/l-d
492	Loading reduced to 5 gVS/l-d and SRT increased to 40 days	421	Loading rate from 5 to 7.5 gVS/l-d
		455	Loading rate from 7.5 to 10 gVS/l-d
		492	Loading rate from 10 to 15 gVS/l-d
		516	Loading rate from 15 to 20 gVS/l-d
	HF2		**HF4**
1	2 gVS/l-d, SRT 20 days	1	2 gVS/l-d, SRT 40 days
51	Full recycling of flush liquid from 2nd stage anaerobic filter	51	Full recycling of flush liquid from 2nd stage anaerobic filter
102	Loading rate from 2 to 4 gVS/l-d	102	Loading rate from 2 to 4 gVS/l-d
420	Loading rate from 4 to 5 gVS/l-d	359	pH 7 methanogenic
492	SRT changed to 30 days	420	Loading rate from 4 to 5 gVS/l-d

Sampling and analytical methods: Samples were taken twice weekly for analysis of HF reactor solid fraction solids, supernatant solids and SF effluent solids, for VFAs in HF supernatant and AF effluent. pH of the HF supernatant and AF effluent was measured daily and AF effluent alkalinity weekly. Analysis was carried out as described in section 2 above.

3.2 Results

Results from operation of the HF-AF reactors are summarised in Tables 6 to 9. The values are averages taken over a period of 1-2 weeks of steady operation after acclimation to the selected loading rate and conditions. Volumetric methane yield is based on the capacity of the HF reactor.

Table 6. Summary results for HF-AF reactors at 40-day SRT

40-day SRT		HF3	HF4	HF3	HF4	HF4	HF4
load	ww g	29.4	29.4	58.0	58.0	58.0	72.5
	VS g/l	2.0	2.0	4.0	4.0	4.0	5.0
AF feed		batch	batch	batch	batch	cycle	cycle
HF solid	TS g/l	- [1]	- [1]	- [1]	- [1]	36.4	39.7
HF Solid destruction	TS %	62	62	55	59	71	78
	VS %	63	61	58	61	72	80
VFA	g/gVSadded-day	1.0	0.9	1.1	1.0	0.3	0.1
thCOD	g/gVSadded-day	1.8	1.6	2.2	2.0	0.6	0.1
HF biogas	litres	-	-	-	0	7.48	10.22
HF CH_4	litres	-	-	-	0	3.78	5.05
AF biogas	litres	1.48	1.53	3.33	3.40	1.53	0.55
AF CH_4	litres	1.17	1.21	2.63	2.69	1.32	0.31
AF biogas	%	100	100	100	100	17	5
AF CH_4	%	100	100	100	100	26	6
AF thCH_4	litres	1.28	1.14	3.04	2.81	0.79	0.24
actual:thCH_4	%	91	106	87	96	167	131
specific CH_4	l/gVSadded	0.143	0.148	0.163	0.167	0.317	0.266
volumetric CH_4	m^3/ m^3 reactor -day	0.29	0.30	0.66	0.67	1.28	1.34

[1] Value potentially low or omitted due to loss of biogas from HF reactor

Table 7. Summary results for HF-AF reactors at 20-day SRT

20-day SRT		HF1	HF2	HF1	HF2	HF1	HF2	HF2
load	ww g	29.4	29.4	58.0	58.0	58.0	58.0	72.5
	VS g/l	2.0	2.0	4.0	4.0	4.0	4.0	5.0
AF feed		batch	batch	batch	batch	cycle	cycle	cycle
HF solid	TS g/l	-	-	-	-	-	35.9	41.5
HF Solid destruction	TS %	58	58	53	57	59	60	57
	VS %	58	60	55	57	60	61	59
VFA	g/gVSadded-day	1.0	1.1	1.3	1.4	1.1	1.2	1.1
thCOD	g/gVSadded-day	1.9	2.0	2.5	2.5	2.0	2.2	1.8
HF biogas	litres	- [1]	- [1]	- [1]	- [1]	1.57	2.05	1.68
HF CH_4	litres	- [1]	- [1]	- [1]	- [1]	0.41	0.53	0.37
AF biogas	litres	1.71	1.72	4.29	4.26	4.06	3.82	3.82
AF CH_4	litres	1.35	1.36	3.27	3.26	3.40	3.22	3.12
AF biogas	%	100	100	100	100	72	65	69
AF CH_4	%	100	100	100	100	89	86	89
AF thCH_4	litres	1.39	1.41	3.46	3.49	2.85	3.07	3.22
actual:thCH_4	%	103	103	106	107	84	95	103
specific CH_4	l/gVSadded	0.166	0.167	0.203	0.202	0.237	0.233	0.174
volumetric CH_4	m^3/ m^3 reactor -day	0.34	0.34	0.82	0.81	0.95	0.94	0.87

Table 8. Summary results for HF-AF reactors at 10-day SRT

10-day SRT		*HF3*	*HF1*	*HF1*	*HF1*
load	ww g	58.0	72.5	108.8	145.0
	VS g/l	4.0	5.0	7.5	10.1
AF feed		cycle	cycle	cycle	cycle
HF solid	TS g/l	19.0	22.5	41.8	57.9
HF solid destruction	TS %	60	56	46	45
	VS %	61	57	48	46
VFA	g/gVSadded-day	1.2	1.1	1.0	0.8
thCOD	g/gVSadded-day	2.0	2.0	1.9	1.5
HF biogas	litres	0.66	2.06	2.60	3.03
HF CH_4	litres	0.18	0.49	0.42	0.38
AF biogas	litres	4.07	5.33	7.36	7.18
AF CH_4	litres	3.37	4.17	5.62	5.45
AF biogas	%	86	72	74	70
AF CH_4	%	95	90	93	93
AF $thCH_4$	litres	2.86	3.59	5.13	5.21
actual:$thCH_4$	%	118	86	91	96
specific CH_4	l/gVSadded	0.220	0.232	0.200	0.145
volumetric CH_4	m^3/ m^3 reactor -day	0.89	1.16	1.51	1.46

Table 9. Summary results for HF-AF reactors at 5-day SRT

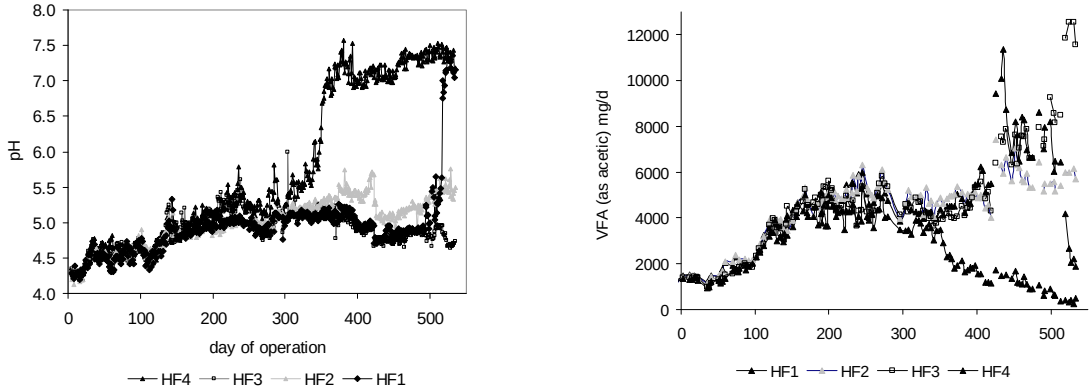
5-day SRT		*HF3*	*HF3*	*HF3*	*HF3*	*HF3*	*HF3*
load	ww g	58.0	72.5	108.8	145.0	217.0	290.0
	VS g/l	4.0	5.0	7.5	10.1	15.1	20.1
AF feed		cycle	cycle	cycle	cycle	cycle	cycle
HF solid	TS g/l	10.7	12.5	17.2	26.7	41.3	56.9
HF solid destruction	TS %	56	48	58	46	48	45
	VS %	57	49	59	47	50	46
VFA	g/gVSadded-day	1.1	0.9	1.0	0.8	0.6	0.6
thCOD	g/gVSadded-day	2.0	1.8	1.9	1.5	1.3	1.5
HF biogas	litres	1.43	1.69	2.05	2.75	3.57	7.06
HF CH_4	litres	0.38	0.38	0.37	0.29	0.39	0.04
AF biogas	litres	3.35	3.89	4.73	0.56	12.73	17.11
AF CH_4	litres	2.79	3.15	3.54	0.43	9.12	12.39
AF biogas	%	70	70	70	17	78	71
AF CH_4	%	88	89	91	60	96	100
AF $thCH_4$	litres	2.78	3.24	4.97	5.11	6.92	10.42
actual:$thCH_4$	%	101	97	71	8	132	119
specific CH_4	l/gVSadded	0.197	0.175	0.129[2]	- [2]	0.158	0.154
volumetric CH_4	m^3/ m^3 reactor -day	0.79	0.88	0.98[2]	- [2]	2.38	3.11

[21] Value potentially low or omitted due to biogas loss through AF pump feed

In general the performance of the HF-AF reactors in terms of solids destruction and specific methane yield was poor in comparison with that of conventional single pass reactors. Some operational advantages were associated with the HF-AF reactors: in contrast to single pass reactors, it was possible to raise the organic loading rate (OLR) by as much as 50% in one step without causing instability. Several of the CROPGEN

partners and a number of other researchers have reported problems of reactor frothing in single pass reactors at high loading rates, but these did not occur with the HF reactors.

At shorter SRTs the OLR on the HF reactor was limited by the difficulty of stirring at the low solids destruction rates achieved and consequent high solid concentrations found in the reactor: this suggests that unstirred digesters of the leach bed or high solids type may have an advantage at such loading rates.



a) pH b) VFA production, mg day^{-1}

Figure 7. pH and total VFA (as acetic) for HF supernatant

Figure 7 shows the pH and VFA concentrations in the HF supernatant. Around day 360 of operation the HF reactor with a 40-day SRT became methanogenic. This was associated with a number of effects: an increase in pH from around 5.4 to 7.3; an increase in solids destruction from around 50 to 70%; and the majority of methane production occurring in the HF reactor. There was very little residual VFA in the supernatant of the methanogenic HF and consequently little gas production in the associated AF. The HF supernatant solids content was high throughout the run (see also deliverable D20) but increased sharply on becoming methanogenic. HF reactors with a 20-day SRT reached a pH of 5.4 but did not jump to being methanogenic. At the end of the experimental period described above HF1 was seeded with waste solids from HF4 and operated for a total of 44 days at a SRT of 30 days to see if it would become methanogenic but although the pH rose (Figure 7) the reactor did not make a stable transition.

Increases in loading on the HF reactors produced a shift in VFA profile, with increasing amounts of butyric acid. This was already evident at a 10-day SRT and an OLR of 7.5 gVS l^{-1} day^{-1} where the concentration of butryic was similar to that of propionic at 1.5-2 g l^{-1}, with valeric acid also increasing to just under 1 g l^{-1}. At a 5-day SRT butyric acid concentrations in the HF reached 2, 4 and 6 g l^{-1} respectively at OLRs of 10, 15 and 20 gVS l^{-1} d^{-1}.

The above work demonstrated that a lab-scale HF reactor could run at an OLR of 20 gVS l^{-1} d^{-1} without any obvious sign of overloading. From the viewpoint of renewable energy production, however, this is not good in terms of yield per kg of VS added or ultimately in net joules per hectare: this is indicated by the low solids breakdown as well as specific methane production, in both of which the single pass reactor currently outperforms the hydraulic flush regime. Future work will look at a number of possible applications: for short SRT reactors, residual solids could be digested in a conventional single pass or high-solids reactor, where, once the readily degradable fraction has been removed, it may

be possible to increase the OLR rate above the maximum possible for undigested maize silage. For longer SRT reactors which become methanogenic, future research will investigate the potential of increasing the loading rate to a level where the HF is under stress, with significant concentrations of residual VFA. This should increase the gas production in the AF and again may allow a higher loading to be sustained than in a conventional single pass reactor. It is possible these options may lead to a greater overall methane yield; but the increased operational complexity of a 2 or even 3-stage system means that even if this further development is successful it may be more suited to an industrial-scale approach to energy farming rather than to application in a mixed farming environment.

4 Comparison and conclusions

The leach bed reactors achieved rates of solids destruction and specific methane production that were broadly comparable with those found in conventional single pass reactors, and acceptable for a simple low-cost system. The sequencing approach offered a practical way of providing a continuous supply of VFA to feed to secondary methanogenic reactors from a batch system. The volumetric methane yield was low, however, and further work is in progress to see how far this can be improved by adopting shorter cycle times. The HF-AF reactor system was not able to achieve such high levels of solids destruction, and therefore of specific methane yield, as that obtained in the leach bed reactors or in conventional single pass reactors operated elsewhere in the project using the test substrate of ensiled maize. The advantage of the HF-AF system was that it allowed a much higher VS loading to be applied. This was possible due to the semicontinuous feeding mode based on separation of the liquid fraction by gravity through a coarse membrane and daily removal of a proportion of the retained solids. The HF-AF system was successfully operated at loading rates of up to 20 kgVS m^{-3} day^{-1} with SRT of 5 days and a flush rate equivalent to 2.85 days, giving VS destruction in the region of 45-50% and a volumetric solids destruction rate of 10 kgVS m^{-3} day^{-1}. The system is therefore high rate but not very efficient in recovering potential energy from the crop as much of this remains in the undigested fibre. Preliminary trials are in progress to examine the potential for a three phase system in which the third stage could be a thermophilic high solids reactor designed to maximise the energy recovery from the residual fibre fraction.

References

APHA (2005). Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association, Water Environment Federation.