Project no. **SES6-CT-2004-502824**

Project acronym: **CROPGEN**

Project title: **Renewable energy from crops and agrowastes**

Instrument: Specific Targeted Research Project

Thematic Priority: SUSTDEV: Sustainable Energy Systems

D17: Database on the methane production potential from mixed digestion

Due date of deliverable: Month 36
Actual submission date: Month 36

Start date of project: 01/03/2004 Duration: 39 months

Organisation name of lead contractor for this deliverable

University of Jyväskylä (JyU)

Revision [0]

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	PU
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

D17: Database on the methane production potential from mixed digestion

Abstract

In this deliverable co-digestion of grass silage, sugar beet tops and oat straw with cow manure was evaluated in semi-continuously fed laboratory continuously stirred tank reactors (CSTRs) at the University of Jyväskylä (JyU). Co-digestion of manure and crops was shown to be feasible with feedstock volatile solids (VS) containing up to 40 % of crops. The highest specific methane yields of 270, 230 and 210 l CH_4 kg^{-1} VS_{added} in co-digestion of cow manure with grass, sugar beet tops and straw, respectively, were obtained with 30 % of crop in the feedstock, corresponding to 85-105 % of the methane potential in the substrates as determined by batch assays. Including 30 % of crop in the feedstock increased methane production per digester volume by 16-65 % above that obtained from digestion of manure alone. Increasing the proportion of crops further to 40 % decreased the specific methane yields by 4-12 %, while doubling the loading rate from 2 to 4 kg VS m^{-3} d^{-1} decreased the specific methane yields by 16-26 %. The post-methanation potential of the digestates corresponded to 0.9-2.5 m^3 CH_4 t^{-1} wet weight of digestate and up to 12-31 % of total methane production in northern climatic conditions, being highest after co-digestion of manure with straw. Also the effect of alkaline treatment of digestate from grass silage fed reactor was studied. A database of co-digestion of energy crops and manures was collected from literature (Table 6).

1 Introduction

Energy crops and crop residues can be digested either alone or in co-digestion with other materials and by employing either wet or dry processes. In the agricultural sector one possible solution to processing crop biomass is co-digestion together with animal manures, the largest agricultural waste stream. In addition to the production of renewable energy, controlled anaerobic digestion of animal manures reduces emissions of greenhouse gases, nitrogen and odour from manure management, and intensifies the recycling of nutrients within agriculture (Amon et al. 2006, Clemens et al. 2006). Animal manures typically have low solids content (<10% TS), and thus, the anaerobic digestion technology applied in manure processing is mostly based on wet processes, mainly on the use of continuously stirred tank reactors (CSTRs).

In co-digestion of plant material and manures, manures provide buffering capacity and a wide range of nutrients, while the addition of plant material with high carbon content balances the carbon to nitrogen (C/N) ratio of the feedstock, thereby decreasing the risk of ammonia inhibition (Hills & Roberts 1981, Hashimoto 1983). The positive synergy effects often observed in co-digestion, due to the balancing of several parameters in the co-substrate mixture, have offered potential for higher methane yields (Mata-Alvarez et al. 2000). However, in digestion of crop materials in wet processes floating of the crop materials along with crust or scum formation has been reported (Nordberg & Edström 1997).

In environmentally sound biogas concepts, the digestate is stored in covered structures in order to recover the residual methane potential and prevent methane emissions into the atmosphere. These post-storage tanks can act as part of the required storage capacity on a farm; for example, in Finland storage capacity corresponding to the manure production of one year is required, as the spreading of manure on farmland is allowed only during the frost-free months (Finnish Government 1998). Depending on the feed materials and process conditions, typically 5-15% of the total biogas produced can be obtained from post-methanation of residues (Weiland 2003), and for example, the addition of potato starch as a co-digestate in cattle slurry digesters was reported to result in up to 30% higher post-methanation potential in the digestate (Clemens et al. 2006).

2 Objectives

The main objective of this study was to assess the viability of the co-digestion of plant materials, energy crops (grass silage) and crop residues (sugar beet tops and oat straw) with cow manure. Additionally, the results of treating increasing proportions of crop materials in co-digestion with manure, the post-methanation potentials of the digestates and re-circulating the solid fraction of the digestate with and without alkali treatment on methane production and process performance were determined.

3 Materials and Methods

3.1 Substrates

In laboratory reactor experiments, grass silage obtained from a local farm in Central Finland (Kalmari farm, Laukaa) was used. It was prepared at the farm from grass (75% timothy *Phleum pratense*, 25% meadow fescue *Festuca pratensis*) harvested at early flowering stage, which was chopped with an agricultural precision chopper after 24 h of pre-wilting and ensiled in a bunker silo with the addition of a commercial silage additive (LAB inoculant AIV Bioprofit, Kemira Growhow Ltd.). Straw of oat *Avena sativa* from a farm in central Finland (Kalmari farm, Laukaa) and tops of sugar beet *Beta vulgaris* from a farm in southern Finland (Koskela farm, Kaasmarkku) were also used as substrates. Grass silage was used as substrate in alkali-treatment study.

Grass was chopped at harvest with an agricultural precision chopper, whereas sugar beet tops and straw were chopped with a garden chopper (Wolf Garten SD 180E) to a particle size of approximately 3 cm. The crop samples were frozen and stored at -20 °C. Before analysis and feeding to the reactors, the samples were allowed to thaw overnight at 4 °C.

Cow manure and inoculum was obtained from a dairy farm and from a mesophilic farm digester (Kalmari farm, Laukaa, Finland) treating cow manure and industrial confectionary by-products as substrate. In alkali-treatment study also inoculum from mesophilic laboratory CSTRs treating straw, grass silage and cow manure was used.

3.2 Continuously stirred tank reactors (CSTRs)

Reactor experiments were carried out in four (three in alkali-treatment study, referred to as C1-C3) parallel CSTRs (referred to as R1-R4 and) constructed of glass, each with a total capacity of 5 l and a liquid volume of 4 l, stirred continuously with magnetic stirrers at 300 rpm and incubated at 35±1 °C. Digesters were inoculated on day 0 with 4 l of inoculum and in alkali-treatment study 3 l of inoculum from farm digester and 1 l from laboratory CSTRs. Thereafter the digesters were fed with a syringe semi-continuously (once a day, 5 days a week). Prior to feeding, an equivalent volume of digester content was removed. The applied feedstock mixtures were prepared daily.

In alkali-treatment study, solids separated from the reactor digestate were re-circulated from day 75 onwards to C2 and C3 while C1 was run as control. During the re-circulation period, the removed C2 and C3 digestates were collected every week. Subsequently, the digestate was centrifuged (3000 rpm for 15 minutes) and solids were separated. The solids from C2 with 20 g NaOH kg^{-1} VS (40% NaOH solution) and the solids from C3 as such were incubated in 250 ml bottles at 35±1°C for about 65 hours and supplied back to the reactors along with the original feed (grass silage and cow manure) while, C1 was fed as previously (control).

3.3 Methane potential assays

The methane potentials of all substrates were determined in batch experiments in duplicate or triplicate in either 1 or 2 l glass bottles (liquid volume 750 ml and 1.5 l) incubated statically at 35±1 °C. Inoculum (250 and 500 ml) and substrate in a $VS_{substrate}/VS_{inoculum}$ ratio of 1 were added into the bottles, distilled water was added to produce a liquid volume of 750 ml or 1.5 l, and sodium bicarbonate ($NaHCO_3$, 3 g l^{-1}) was added as buffer. The contents of the bottles were flushed with N_2/CO_2-gas for 5 minutes and the bottles were then sealed with butyl rubber stoppers. Tubing made of PVC or PVC-based material with plasticizer (Masterflex Tygon® fuel & lubricant) was used in gas collection lines, and produced biogas was collected in aluminium gas bags. The bottles were mixed manually before each gas measurement. Assays with inoculum only were carried out to subtract the methane potential of the inoculum from that of the substrates. The assays were continued until methane production became negligible (<5 ml CH_4 d^{-1}) after 60-200 d.

The post-methanation potentials of the digestates (from R1-R3 CSTRs) were measured in batch experiments in triplicate 118 ml serum vials incubated in 5, 20 and 35 °C. Digestates (40 g) were added into the vials, after which the vials were sealed with butyl rubber stoppers and aluminium crimps, flushed with N_2/CO_2-gas for 5 minutes and incubated statically for 100 d at their respective incubation temperatures.

3.4 Analysis and Calculations

Biogas samples were taken with a pressure lock syringe and their methane content was measured with gas chromatographs (GC) equipped with a flame-ionisation detector (Perkin Elmer Arnel Clarus 500, Supelco Carboxen™ 1010 PLOT fused silica capillary column 30 m × 0.53 mm, carrier gas argon 14 ml/min, oven 100 °C, injection port 250 °C, detector 225 °C). The volume of produced biogas was measured by water displacement.

Volatile fatty acids (VFAs) were measured with a GC equipped with flame-ionisation detector (Perkin Elmer Autosystem XL, PE FFAP column 30 m × 0.32 mm × 25 µm, carrier gas helium, injection port and detector 225 °C, oven 100 to 160 °C (20 °C/min). TS and VS were determined according to the Standard Methods (APHA, 1998). Metrohm 774 pH-meter was used in pH measurements. pH of solid materials was measured from a mixture of solid substrate and distilled water (L/S ratio of 2) after homogenising with a kitchen blender. COD and NH_4-N from crop samples were analysed after extraction according to SFS-EN 12457-4 (Finnish Standards Association, 2002). The samples for NH_4-N and SCOD determination were filtered with GF50-glass fibre filter papers (Schleicher & Schuell). COD was measured according to the SFS 5504 (Finnish Standards Association, 1988) and NH_4-N and N_{tot} were determined according to the Tecator application note (Perstorp Analytical/Tecator AB 1995) with a Kjeltec system 1002 distilling unit (Tecator AB).

Methane potentials of substrates were calculated as m^3 CH_4 kg^{-1} VS_{added}, m^3 CH_4 kg^{-1} TS_{added} and m^3 CH_4 t^{-1} ww, minus the methane potential of the inoculum. OLRs and HRTs were calculated on the basis of the daily feedstock additions. Volumetric methane production was calculated as methane production per unit volume of reactor (m^3 CH_4 $m^{-3}_{reactor}$ d^{-1}).

4 Results

The chemical characteristics and the methane potentials of the substrates used in co-digestion experiments were determined. Straw had the highest TS content (64 %) and sugar beet tops and manure the lowest (10 and 7 %, respectively). Of the three crops, sugar beet tops had the highest N_{tot} and SCOD concentrations, as well as the highest methane potential per VS (0.353 m^3 CH_4 kg^{-1} VS_{added}), whereas those of straw were the lowest. The manure, obtained on three occasions during the experiment and stored at 4 °C, showed small variations in methane potential throughout the experiment (0.233 ± 0.020 m^3 CH_4 kg^{-1} VS_{added}) (Table 1). The highest methane potential per ww was for straw (117 m^3 CH_4 t^{-1} ww) and the lowest for manure (12 m^3 CH_4 t^{-1} ww), whereas the short-term (20 d) methane potentials per VS were highest for grass and manure (0.206 and 0.204 m^3 CH_4 kg^{-1} VS_{added}, respectively) but lowest for straw (0.138 m^3 CH_4 kg^{-1} VS_{added}). The highest proportion of total methane potential obtained by day 20 was with manure (88 %), whereas with the three crops the proportion varied between 51-68 % (Table 1).

TABLE 1 Methane potentials of substrates used in co-digestion experiments (average values of replicates ± standard deviations, where applicable).

Substrate	Total methane potential			Methane potential by day 20	
	(m^3 CH_4 kg^{-1} VS_{added})	(m^3 CH_4 kg^{-1} TS_{added})	(m^3 CH_4 t^{-1} ww)	(m^3 CH_4 kg^{-1} VS_{added})	(% of total)
Cow manure	0.233 ±0.020	0.190 ±0.016	12 ±1	0.204 ±.0.016	88
Sugar beet tops	0.353 ±.0.018	0.283 ±0.014	29 ±1	0.181 ±0.009	51
Grass silage	0.306 ±0.003	0.284 ±0.003	74 ±1	0.206 ±0.002	67
Oat straw	0.203 ±0.025	0.185 ±0.023	117 ±14	0.138 ±0.017	68

Four parallel laboratory CSTRs were operated to evaluate co-digestion of the plant materials with manure. Initially, all reactors were fed for 27 days with manure at OLR of 2 kg VS m^{-3} d^{-1} and HRT of 20 d. Subsequently, one reactor (R1) was run for an additional 28 days with manure alone whereas in the other reactors the feeding of crops along with manure was initiated by replacing 10 % of the feedstock VS with crops (sugar beet tops in R2, grass in R3 and straw in R4), while maintaining constant OLR and HRT. The proportion of crops in the feedstock was then gradually increased up to

40 % of the feedstock VS (Fig. 1 and 2, Tables 2-4) and, finally, the OLRs of the reactors co-digesting manure with grass and straw (R3 and R4) were increased first to 3 and then 4 kg VS m^{-3} d^{-1}, decreasing the HRTs to 18 and 16 d, respectively (Fig. 1 and 2, Tables 3 & 4).

During the first 27 days when all the reactors were fed simultaneously with manure, reactors R1, R3 and R4 showed nearly identical specific methane yields (0.151 to 0.155 m^3 CH_4 kg^{-1} VS_{added}, Tables 2-4, Fig. 1) and reactor R2 a slightly lower yield (0.133 m^3 CH_4 kg^{-1} VS_{added}, Table 2, Fig. 1). The VS removals ranged from 20 to 26 % (Tables 2-4). The initiation of the feeding of crops along with manure (day 28 in reactors R2-R4) led to a temporary decrease in specific methane yield, but as the proportion of crop in the feedstock was increased, the specific methane yields and VS removals also increased (Fig. 1, Tables 2-4). In the reactor fed with manure and grass (R3), a rapid increase in VS removal from 26 to 41 % was observed when feeding with grass was initiated, compared to feeding with manure alone (Table 3). The highest specific methane yield was obtained when the proportion of crop in the feedstock was 30 % (feeding regime 4) (0.229 m^3 CH_4 kg^{-1} VS_{added} in co-digestion with sugar beet tops (R2), 0.268 m^3 CH_4 kg^{-1} VS_{added} in co-digestion with grass (R3) and 0.213 m^3 CH_4 kg^{-1} VS_{added} in co-digestion with straw (R4)) (Fig. 1, Tables 2-4). During this feeding regime, the volumetric methane productions were 65, 58 and 16 % higher in the reactors co-digesting manure with sugar beet tops (R2), grass (R3) and straw (R4), respectively, compared with digestion of manure alone (Fig. 1). Increasing the proportion of crop further to 40 % decreased the specific methane yields by 4-12 %. The VS removals ranged from 28 to 49 % in co-digestion with sugar beet tops (R2), from 41 to 53 in co-digestion with grass (R3), and from 27 to 43 % in co-digestion with straw (R4). In reactors co-digesting manure with sugar beet tops (R2) and grass (R3), the VS removals increased as the proportion of crop in the feedstock increased, whereas in the reactor co-digesting manure with straw (R4), the removal was highest during feeding with 20 % of straw in the feedstock (Tables 2-4).

Operation of the reactors co-digesting manure with grass (R3) and straw (R4) was continued from day 204 onwards by increasing the OLRs from 2 to 3 and eventually to 4 kg VS m^{-3} d^{-1}, while maintaining the 40 % VS proportion of crop in the feedstock. Increasing the OLR from 2 to 3 kg VS m^{-3} d^{-1} decreased the specific methane yield in co-digestion of manure with grass (R3) from 0.250 to 0.233 m^3 CH_4 kg^{-1} VS_{added}, but in co-digestion with straw (R4) there was little change (Fig. 1, Tables 3-4). Further increase in OLR to 4 kg VS m^{-3} d^{-1} decreased the specific methane yield to 0.186 and 0.157 m^3 CH_4 kg^{-1} VS_{added} in co-digestion with grass (R3) and straw (R4), respectively. At OLRs 3 and 4 kg VS m^{-3} d^{-1}, the VS removals in co-digestion with grass (R3) and straw (R4) amounted to 52-53 and 40 %, respectively (Tables 3-4).

TS removals in the digestion of manure alone ranged from 12 to 19 %, but increased when crops were included in the feedstock, ranging then from 20 to 48 %, being lowest in co-digestion with straw (Tables 2-4). In all the reactors, formation of a crust layer in the upper part of the liquid space was observed from feeding regime 2 (20 % of crop in the feedstock) onwards, the layer increasing in depth as the experiment proceeded and thickest in co-digestion of straw (R4), followed by co-digestion with grass (R3), and least apparent in co-digestion with sugar beet tops (R2).

During all runs, NH_4-N accounted for 33-48 % (0.5-1.0 g/l) of N_{tot} in the digested material, whereas in the feedstock, the proportion of NH_4-N of N_{tot} varied between 30-38 %. On average, the proportion of NH_4-N of N_{tot} increased by 26, 25 and 14 % during co-digestion of manure with sugar beet tops, grass and straw, respectively. The pH of the digestates remained between 7.2 and 7.8 and the VFA concentrations were low (< 0.3 g l^{-1}) in all digestates throughout the run (VFAs measured approximately once per week, data not shown), while values for SCOD ranged from 5 to 12 g l^{-1} (Fig. 2, Tables 2-4). As the proportion of crop in the feedstock was increased, the values for TS, VS and SCOD of the digestates decreased (Fig. 2, Tables 2-4). However, as the OLR in the reactors digesting manure with grass (R3) and straw (R4) was increased, the values for these parameters increased. Also, a slight increase in digestate ammonia concentrations was observed at the higher OLRs (Fig.2, Tables 3-4).

TABLE 2 Operational conditions, feedstock and digestate characteristics, and methane production in the CSTRs fed with cow manure (R1) and cow manure with sugar beet tops (R2). Feedstock and digestate characteristics and methane production were calculated as averages (± standard deviations, where applicable) of the measurements during the last two weeks of each feeding regime.

Substrate (Reactor)		*Cow manure (R1)*	*Cow manure and sugar beet tops (R2)*				
Feeding regime		1	1	2	3	4	5
Share of crop	% VS	0	0	10	20	30	40
	% ww	0	0	5	10	15	19
OLR	kg VS m^{-3} d^{-1}	2	2	2	2	2	2
HRT	d	20	20	20	20	20	20
Duration	d	0-55	0-27	28-56	57-83	84-143	144-190
	HRT	2.8	1.4	1.4	1.4	3.0	2.3
Feedstock							
TS	%	4.9 ±0.1	4.9 ±0.1	4.9 ±0.1	5.0 ±0.1	5.0 ±0.1	5.0 ±0.1
VS	%	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1
SCOD	g l^{-1}	11.5 ±1.5	11.5 ±1.5	11.7 ±1.4	11.8 ±1.7	12.0 ±2.2	12.2 ±2.9
NH_4-N	g l^{-1}	0.8 ±0.1	0.8 ±0.1	0.7 ±0.1	0.6 ±0.1	0.6 ±0.1	0.5 ±0.1
N_{tot}	g l^{-1}	2.1 ±0.2	2.1 ±0.2	1.9 ±0.1	1.8 ±0.2	1.7 ±0.0	1.6 ±0.3
Digestate							
TS	%	4.0 ±0.2	4.0 ±0.1	3.9 ±0.2	3.4 ±0.3	3.1 ±0.2	2.9 ±0.1
VS	%	3.0 ±0.2	3.0 ±0.1	2.9 ±0.2	2.5 ±0.2	2.2 ±0.2	2.1 ±0.1
SCOD	g l^{-1}	11.6 ±0.7	11.1 ±2.5	9.5 ±1.2	9.4 ±0.5	6.1 ±0.6	5.9 ±0.6
NH_4-N	g l^{-1}	1.0 ±0.1	1.0 ±0.1	0.8 ±0.0	0.8 ±0.0	0.7 ±0.1	0.7 ±0.0
N_{tot}	g l^{-1}	2.0 ±0.1	2.4 ±0.0	1.9 ±0.0	1.9 ±0.1	1.7 ±0.0	1.7 ±0.1
pH		7.5 ±0.1	7.6 ±0.1	7.5 ±0.1	7.4 ±0.1	7.4 ±0.1	7.3± 0.1
TS removal [1]	%	19	18	22	31	38	41
VS removal [1]	%	25	26	28	38	45	49
CH_4 conc.	%	50 ±7	49 ±2	47 ±2	53 ±2	56 ±1	55 ±2
Specific CH_4	m^3 kg^{-1} VS_{added}	0.155 ±0.026	0.133 ±0.017	0.149 ±0.012	0.200 ±0.016	0.229 ±.0.054	0.220 ±0.030
yield	m^3 t^{-1} ww	6.2 ±1.0	5.3 ±0.7	6.0 ±0.5	8.0 ±0.6	9.2 ±2.2	8.8 ±1.2
% of total CH_4 potential in substrates [1]		67	57	61	78	85	78
% of short-term CH_4 potential in substrates [1]		76	65	74	100	116	112

[1] Calculated on basis of average values

TABLE 3 Operational conditions, feedstock and digestate characteristics, and methane production in the CSTR fed with cow manure and grass silage (R3). Feedstock and digestate characteristics and methane production were calculated as averages (± standard deviations, where applicable) of the measurements during the last two weeks of each feeding regime.

Feeding regime		1	2	3	4	5	6	7
Share of crop	% VS	0	10	20	30	40	40	40
	% ww	0	2	3	5	7	9	11
OLR	kg VS m^{-3} d^{-1}	2	2	2	2	2	3	4
HRT	d	20	20	20	20	20	18	16
Duration	d	0-27	28-55	56-84	85-141	142-203	204-266	267-318
	HRT	1.4	1.4	1.4	2.8	3.1	3.4	3.2
Feedstock								
TS	%	4.9 ±0.1	4.9 ±0.1	4.8 ±0.1	4.7 ±0.1	4.7 ±0.1	6.3 ±0.1	7.5 ±0.1
VS	%	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1	5.4 ±0.1	6.4 ±0.1
SCOD	g l^{-1}	11.5 ±1.5	11.3 ±1.4	11.2 ±1.6	11.0 ±2.0	10.8 ±2.6	14.6 ±2.1	17.3 ±1.1
NH_4-N	g l^{-1}	0.8 ±0.1	0.7 ±0.1	0.6 ±0.1	0.6 ±0.1	0.5 ±0.1	0.7 ±0.1	0.8 ±0.1
N_{tot}	g l^{-1}	2.1 ±0.2	1.9 ±0.1	1.8 ±0.2	1.7 ±0.0	1.5 ±0.3	2.1 ±0.1	2.4 ±0.1
Digestate								
TS	%	4.1 ±0.1	3.2 ±0.3	3.2 ±0.4	3.1 ±0.2	2.8 ±0.1	3.3 ±0.1	4.0 ±0.1
VS	%	3.0 ±0.1	2.3 ±0.3	2.3 ±0.3	2.3 ±0.2	2.2 ±0.1	2.6 ±0.1	3.1 ±0.1
SCOD	g l^{-1}	11.6 ±1.2	10.3 ±0.4	9.1 ±0.5	8.2 ±1.0	7.0 ±0.5	8.4 ±0.7	9.3 ±0.8
NH_4-N	g l^{-1}	1.0 ±0.1	0.9 ±0.1	0.8 ±0.0	0.7 ±0.1	0.7 ±0.1	0.7 ±0.0	0.9 ±0.1
N_{tot}	g l^{-1}	2.4 ±0.2	1.9 ±0.3	1.7 ±0.1	1.7 ±0.0	1.8 ±0.3	1.8 ±0.1	2.3 ±0.1
pH		7.6 ±0.1	7.5 ±0.1	7.5 ±0.1	7.4 ±0.1	7.3 ±0.1	7.4 ±0.1	7.6 ±0.1
TS removal [1]	%	17	34	34	35	41	48	47
VS removal [1]	%	26	41	42	43	46	53	52
CH_4 conc.	%	50 ±4	50 ±2	50 ±2	53 ±2	52 ±2	54 ±2	53 ±3
Specific CH_4	m^3 kg^{-1} VS_{added}	0.151 ±0.048	0.143 ±0.016	0.178 ±0.009	0.268 ±0.029	0.250 ±0.016	0.233 ±0.014	0.186 ±0.023
yield	m^3 t^{-1} ww	6.0 ±1.9	5.7 ±0.6	7.1 ±0.4	10.7 ±1.2	10.0 ±0.6	12.6 ±0.8	11.9 ±1.5
% of total CH_4 potential in substrates [1]		65	62	72	105	95	89	71
% of short-term CH_4 potential in substrates [1]		74	73	87	131	122	114	91

[1] Calculated on basis of average values

TABLE 4 Operational conditions, feedstock and digestate characteristics, and methane production in the CSTR fed with cow manure and straw (R4). Feedstock and digestate characteristics and methane production were calculated as averages (± standard deviations, where applicable) of the measurements during the last two weeks of each feeding regime.

Feeding regime		1	2	3	4	5	6	7
Share of crop	% VS	0	10	20	30	40	40	40
	% ww	0	1	1	2	3	4	4
OLR	kg VS m^{-3} d^{-1}	2	2	2	2	2	3	4
HRT	d	20	20	20	20	20	18	16
Duration	d	0-27	28-55	56-84	85-141	142-203	204-266	267-318
	HRT	1.4	1.4	1.4	2.8	3.1	3.4	3.2
Feedstock								
TS	%	4.9 ±0.1	4.9 ±0.1	4.8 ±0.1	4.8 ±0.1	4.7 ±0.1	6.4 ±0.1	7.6 ±0.1
VS	%	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1	4.0 ±0.1	5.4 ±0.1	6.4 ±0.1
SCOD	g l^{-1}	11.5 ±1.5	10.8 ±1.3	10.1 ±1.5	9.4 ±1.7	8.7 ±2.1	11.8 ±1.7	14.0 ±0.9
NH_4-N	g l^{-1}	0.8 ±0.1	0.7 ±0.1	0.6 ±0.1	0.6 ±0.1	0.5 ±0.1	0.7 ±0.1	0.8 ±0.1
N_{tot}	g l^{-1}	2.1 ±0.2	1.9 ±0.1	1.7 ±0.1	1.6 ±0.0	1.4 ±0.3	1.9 ±0.1	2.3 ±0.1
Digestate								
TS	%	4.4 ±0.1	3.9 ±0.2	3.1 ±0.4	3.5 ±0.2	3.3 ±0.3	4.0 ±0.1	4.8 ±0.2
VS	%	3.2 ±0.1	2.9 ±0.2	2.3 ±0.3	2.7 ±0.2	2.5 ±0.3	3.2 ±0.1	3.9 ±0.2
SCOD	g l^{-1}	10.7 ±3.4	7.7 ±0.5	7.0 ±1.3	6.4 ±0.7	5.0 ±0.6	6.5 ±0.6	7.7 ±1.0
NH_4-N	g l^{-1}	1.0 ±0.1	0.9 ±0.1	0.7 ±0.0	0.5 ±0.0	0.5 ±0.0	0.6 ±0.0	0.8 ±0.0
N_{tot}	g l^{-1}	2.3 ±0.2	2.1 ±0.1	1.5 ±0.1	1.7 ±0.1	1.6 ±0.1	1.7 ±0.2	2.0 ±0.0
pH		7.6 ±0.1	7.5 ±0.1	7.5 ±0.1	7.5 ±0.1	7.3 ±0.1	7.4 ±0.1	7.6 ±0.1
TS removal [1]	%	12	20	36	27	31	37	37
VS removal [1]	%	20	27	43	33	38	40	40
CH_4 conc.	%	49 ±3	49 ±2	51 ±2	51 ±1	51 ±1	53 ±2	52 ±3
Specific CH_4	m^3 kg^{-1} VS_{added}	0.151 ±0.044	0.145 ±0.009	0.159 ±0.019	0.213 ±0.017	0.188 ±0.019	0.184 ±0.023	0.157 ±0.028
yield	m^3 t^{-1} ww	6.0 ±1.7	5.8 ±0.4	6.4 ±0.8	8.5 ±0.7	7.5 ±0.8	9.9 ±1.2	10.1 ±1.8
% of total CH_4 potential in substrates [1]		65	63	70	95	85	83	71
% of short-term CH_4 potential in substrates [1]		74	73	83	116	106	104	88

[1] Calculated on basis of average values

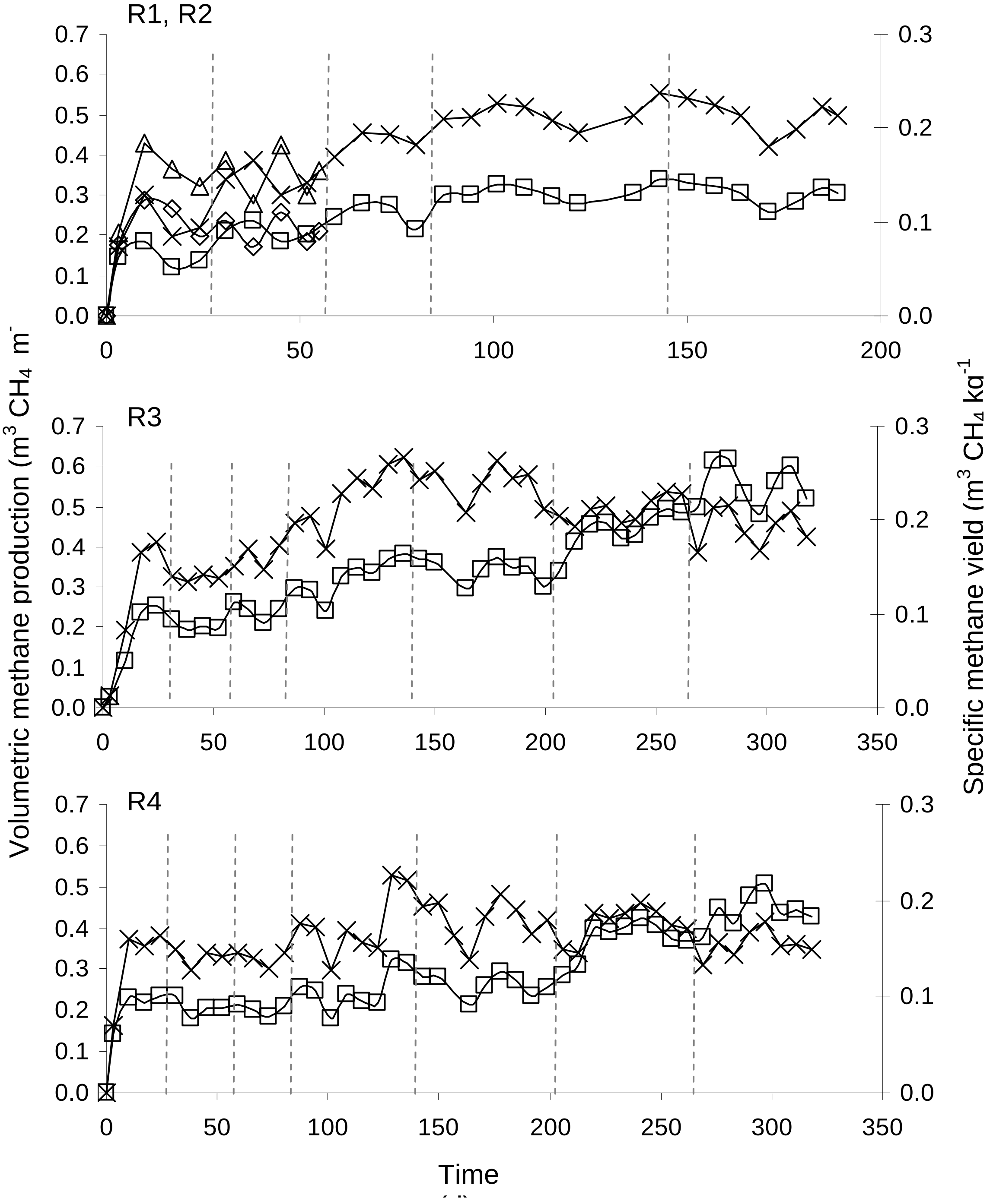

FIGURE 1 Volumetric methane production and specific methane yields as weekly averages in digestion of manure alone (R1) and in co-digestion of cow manure with sugar beet tops (R2), grass (R3) and straw (R4). Dashed lines represent the changes in feeding mode in R2, R3 and R4. Note the different time scale in R1, R2 compared with R3 and R4. ◊ Volumetric CH_4 production in R1; Δ Specific CH_4 yield in R1; □ Volumetric CH_4 production in R2, R3 and R4; x Specific CH_4 yield in R2, R3 and R4.

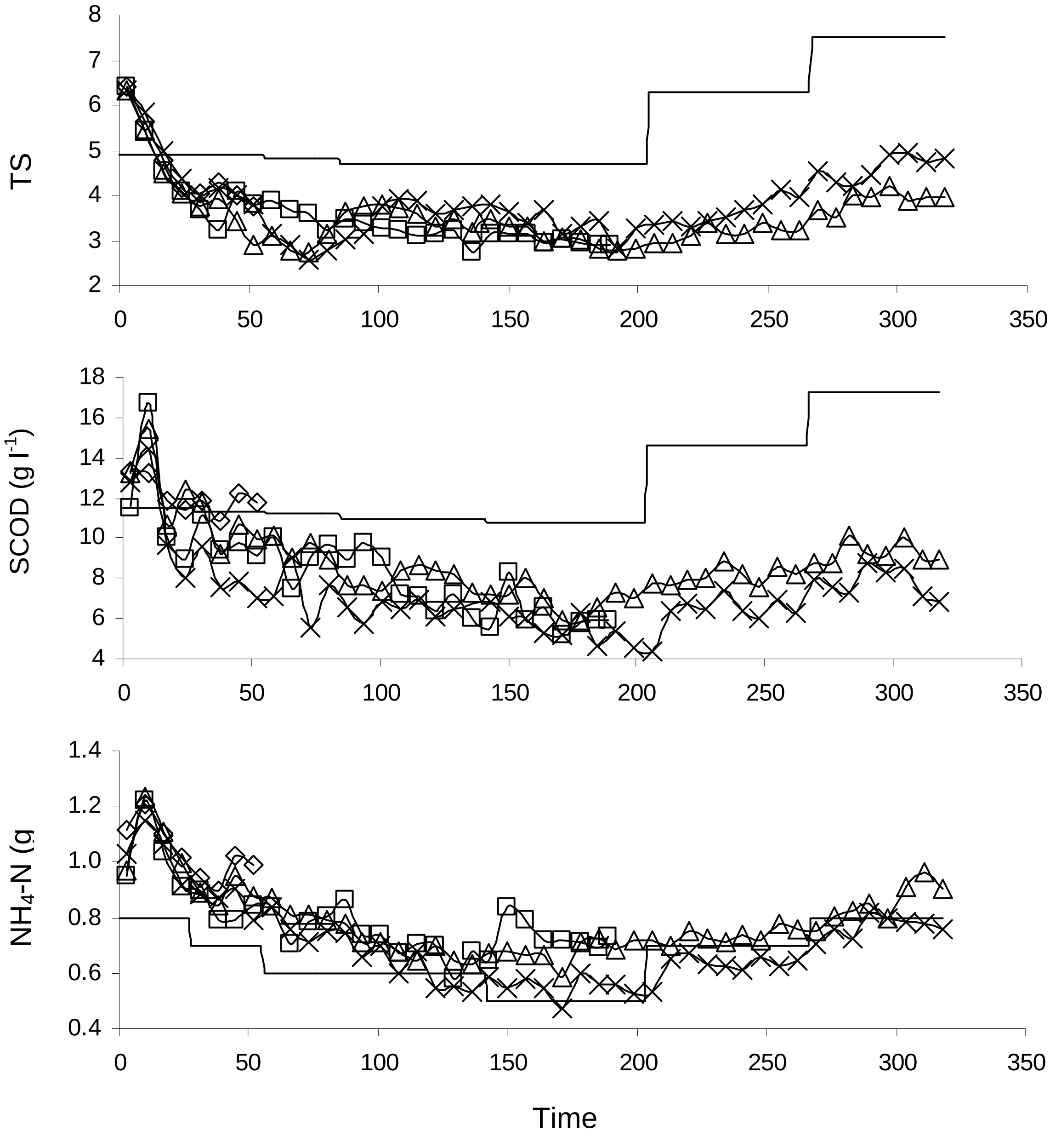

FIGURE 2 Characteristics of digestates from CSTRs as weekly averages. The solid lines represent the concentrations in the feedstock to reactor R3 as an example. ◊ R1; □ R2; Δ R3; x R4.

The post-methanation potentials of the digestates were measured on several occasions during the experiment (Table 5). Post-methanation of the digestates in batch assays incubated for 100 d at 5, 20 and 35 °C yielded 0.001-0.009, 0.073-0.120 and 0.133-0.197 m^3 CH_4 kg^{-1} digestate VS_{added}, respectively. Differences in the post-methanation potentials measured during feeding regimes with 30 and 40 % of crop in the feedstock were small, but increasing the OLR from 2 to 4 kg VS m^{-3} d^{-1} led to an increase of 30-

37 % in the post-methanation potentials of the digestates as measured at 35 °C. The digestate from co-digestion of manure and straw (R4) had the highest post-methanation potential, which reached 0.197 m^3 CH_4 kg^{-1} VS_{added} and 7.7 m^3 CH_4 t^{-1} ww at 35 °C (Table 5).

TABLE 5 Post-methanation potentials of digestates from co-digestion of cow manure with sugar beet tops (R2), grass (R3) and straw (R4) at different temperatures (average values of replicates ± standard deviations).

Sampling day	T (° C)	Post-methanation potential R2 (m^3 CH_4 kg^{-1} VS_{added})	R2 (m^3 CH_4 t^{-1} ww)	R3 (m^3 CH_4 kg^{-1} VS_{added})	R3 (m^3 CH_4 t^{-1} ww)	R4 (m^3 CH_4 kg^{-1} VS_{added})	R4 (m^3 CH_4 t^{-1} ww)
140	5	0.002 ±0	0.1 ±0	0.002 ±0	0 ±0	0.006 ±0.001	0.2 ±0
	20	0.076 ±0.001	1.7 ±0	0.073 ±0.007	1.8 ±0.2	0.073 ±0.008	2.0 ±0.2
	35	0.142 ±0.001	3.1 ±0	0.148 ±0.004	3.5 ±0.1	0.168 ±0.005	4.5 ±0.1
190	5	0.002 ±0	0 ±0	0.001 ±0	0 ±0	0.002 ±0	0.1 ±0
	20	0.081 ±0.003	1.7 ±0.1	0.080 ±0.001	1.8 ±0	0.082 ±0.003	2.1 ±0.1
	35	0.140 ±.0.005	2.9 ±0.1	0.133 ±.0009	2.9 ±0.2	0.151 ±0.009	3.8 ±0.2
265	5	-	-	0.003 ±0.001	0.1 ±0	0.006 ±0.001	0.2 ±0
	20	-	-	0.078 ±0.001	2.0 ±0	0.091 ±0.005	2.9 ±0.2
	35	-	-	0.142 ±0.003	3.7 ±0.1	0.162 ±0.003	5.2 ±0.1
318	5	-	-	0.003 ±0	0.1 ±0	0.009 ±0	0.4 ±0
	20	-	-	0.103 ±0.004	3.2 ±0.1	0.120 ±0.005	4.7 ±0.2
	35	-	-	0.182 ±0.007	5.6 ±0.2	0.197 ±0.007	7.7 ±0.3

In alkali-treatment study, all the three reactors (C1-C3) were operated in parallel co-digesting with substrate VS constituting 30 % and 70 % of grass silage and cow manure respectively, with an OLR of 2 kg VSm^3d^{-1} and HRT of 20d. Methane yields in the three reactors increased from ca 165 to 180 l $CH_4kg^{-1}VS$ during the first eight weeks of operation. On day 57, the reactors were opened and the contents of all the three reactors were mixed and then redistributed into the three reactors to ensure presence of identical materials in parallel reactors. Feeding was started the next day. After about two weeks the methane production in the reactors reached to same level as before.

From day 75 onwards, solids separated from the reactor digestate were re-circulated as such (C3) and after alkaline treatment (C2) while one reactor without solids re-circulation (C1) was continued as control. During the study, the control reactor had the highest methane yield (182 ± 0.02 l $CH_4kg^{-1}VS$) while reactor treating alkaline treated solids gave slightly more methane (161 ± 0.03 l $CH_4kg^{-1}VS$) than reactor with untreated solids (143 ± 0.03 l $CH_4kg^{-1}VS$). In the reactor supplied with alkaline treated solids SCOD was higher (9.0 gl^{-1}) than in the reactor supplied with untreated solids (7.3) or control reactor (7.5) while NH_4-N concentrations were about the same in all reactors (0.75-0.80 gl^{-1}).

5 Discussion

The present results show that anaerobic digestion of manure and crops (sugar beet tops, grass silage and oat straw) in CSTRs is feasible with at least up to 30-40% VS of crops in the feedstock (corresponding to 15-19, 5-11 and 2-4% wet weight of sugar beet tops, grass and straw, respectively). To our knowledge, the present study is the first long-term co-digestion study demonstrating that co-digestion of manure with sugar beet tops and grass is a feasible manner of increasing volumetric methane production (by up to 65%) without the need to shorten the hydraulic residence time (20 days in the present study). Co-digestion of straws and animal manures has been demonstrated also earlier, but in the present study the increase obtained in specific methane yield after the addition of straw in the feedstock was higher than previously reported (Hashimoto 1983, Fischer et al. 1983, Somayaji & Khanna 1994).

The higher specific methane yields obtained in this and previous studies (Callaghan et al. 2002, Kaparaju & Rintala 2005, Somayaji & Khanna 1994, Weiland & Hassan 2001) in co-digestion of animal manures with plant materials in given feedstock ratios (*e.g.* crop accounting for 30% of feedstock VS in the present study) than in the digestion of manure alone is apparently due to the fact that the VS in crops is in most cases more easily degradable than the VS in manure, as is indicated by the higher methane potentials obtained in batch assays for grass and sugar beet tops in the present study. In manure, which has already passed through the digestive track of the animal, most of the energy-rich substances (*i.e.* carbohydrates and proteins) contained in the crops, have already been digested. Grass, sugar beet tops and straw are primarily composed of cellulose, hemicelluloses and lignin. Lignin is poorly degraded in anaerobic conditions, and the shielding effect of lignin due to the intense cross-linking with cellulose and hemicellulose limits the degradation of these fibre fractions (Fan et al. 1981). Lignin contents of timothy-based grass and sugar beet tops were 16-19 and 10% TS, whereas that of straw was higher, 21% TS (Lehtomäki et al, submitted), which might explain the lower methane yields obtained in co-digestion of manure with straw, as well as in methane potential assays with straw, compared with the other crops. Furthermore, sugar beet tops and grass contain high amounts of readily available soluble compounds, as indicated by high SCOD values after 24 h extraction, and the potentially biodegradable fraction in grass and sugar beet tops is reported to be 74-77 compared with 70% in straw (as calculated by Viinikainen et al. 2006). The higher specific methane yields in co-digestion compared with digestion of manure alone may also be due to synergy effects owing to a more balanced nutrient composition and C/N ratio in the feedstock. This is also supported by the fact that in CSTRs with 20 d HRT, high proportions of up to 131 and 105% of the methane potentials measured in the methane potential assays after 20 and 80-100 days, respectively, were obtained. Timothy-based grass, oat straw and sugar beet tops have carbon contents of 46, 44 and 40% TS, corresponding to C/N ratios of 26, 95 and 18, respectively (Lehtomäki et al, submitted). Cow manure has a C/N ratio of 11-14 (Hills & Roberts 1981, Hashimoto 1983), and addition of 30-40% of crops increased the ratio in the feedstock to approximately 15-25, while the optimum range for anaerobic digestion is 25-32, according to Hills and Roberts (1981). The fact that in co-digestion of manure with grass higher methane yields were obtained than in co-digestion with sugar beet tops, even though on the basis of the batch assays the sugar beet tops demonstrated a higher methane potential, is explained by the higher carbon content of grass compared to that of sugar beet tops, which results in a higher C/N ratio in co-digestion with manure. Microbial adaptation could also have been partly responsible for the high specific methane yields obtained in reactor experiments, where, due to the semi-continuous feeding, the microbial community is likely to become better adapted to the crop substrate than the community used to inoculate the batch reactors in the beginning of methane potential assays.

The benefits of optimising the proportion of crops and loading rate in co-digestion were shown by the fact that during feeding with 30% VS of crop in the feedstock, up to 87% higher specific methane yield was obtained than with the lower proportions of crop, while increasing the proportion of crop further (to 40%) led to a decrease of up to 12% in specific methane yields. Furthermore, the highest specific methane yields were obtained at the OLR of 2 kg VS m^{-3} d^{-1} with 20 HRT, while increasing the OLR and decreasing the HRT (from 20 to 16 days) led to a 16-26% decrease in specific methane yield. At the higher OLRs, volumetric methane production increased, but the retention times apparently became too short for efficient degradation, as the amounts of undegraded matter in the digestates increased, leading to an increase in the post-methanation potentials. The fact that the amount of total organic matter and soluble organic matter as indicated by VS and SCOD, but not by VFA, in the digestates increased after the increase in the OLRs, indicates that VFA was rapidly consumed by the methanogens and that the rate-limiting stages of degradation were thus hydrolysis and/or acidogenesis. An increase in ammonia concentrations in the digestates was also observed at the higher OLRs, but the levels never reached the concentrations of 1.5-2.5 g-N l^{-1} considered inhibitory for unadapted methanogenic communities under mesophilic conditions (Angelidaki & Ahring 1993). Also in co-digestion of pig manure and potato waste in laboratory CSTRs with 0, 15 and 20% VS of potato waste in the feedstock, increasing the OLR from 2 to 3 kg VS m^3 d^{-1} resulted in a 7-15% decrease in specific methane yield, while the highest specific methane yields were obtained with the 20% proportion of potato waste (Kaparaju & Rintala 2005), and in laboratory digesters fed daily with manure and wheat straw, with 0-100% TS of wheat straw in the feedstock, the highest specific methane yields were observed with 40% wheat straw, whereas highest VS removal was obtained with 20% wheat straw (Somayaji & Khanna 1994). However, neither of these experiments included feedstock with 30% of crop material, which was found optimal in the present study.

In all the reactors, the accumulation of undegraded material was observed as the formation of a crust on the upper part of the liquid space, and was most apparent in co-digestion of straw and manure. The formation of crust did not cause problems in laboratory operation, but in full scale operation it might have more serious outcomes, such as fouling in gas collection pipes, scum overflow, and thermal stratification (Hobson & Wheatley 1993). It has been reported previously that crust formation in co-digestion of crops and manure at a TS concentration of about 10% could be prevented by a sufficient reduction in the particle size of crop materials along with continuous stirring (Nordberg & Edström 1997).

The re-circulation of solid fraction of digestate to the biogas process, both in treated and in untreated form was not effective and did not improve methane yields. Solids re-circulation in both the reactors basically resulted in accumulation and scum formation which further lead to operational problems.

Post-methanation of digestates sampled from CSTRs during co-digestion of manure and crops indicated that the digestates still contained degradable material with significant methane potential, which, if completely recovered, would in northern climatic conditions correspond to 0.9-2.5 m^3 CH_4 t^{-1} ww of digestate (calculated assuming post-methanation potential at 20 and 5 °C each for 6 months of a year) and up to 12-31 % of total methane production, being highest following co-digestion of manure with straw. If not recovered, part of this post-methanation potential may be lost as emissions to the atmosphere. In contrast, if the post-storage tanks were maintained at 20 or 35 °C throughout the year, a post-methanation potential of 1.7-4.7 or 2.9-7.7 m^3 CH_4 t^{-1} ww of digestate, respectively, could be obtainable, corresponding to 21-43 and 35-56% of total methane production. According to Kaparaju & Rintala (2003), digested cow manure had a post-methanation potential of 0.206-0.240 m^3 CH_4 kg^{-1} VS_{added} after 250 days at 35 °C, whereas at 20 and 5 °C it amounted to 0.087-0.088 and 0.003-0.005 m^3 CH_4 kg^{-1} VS_{added}, respectively. These values are within the same order of magnitude as those obtained in the present study, and thus, co-digestion of crop materials with manure would not seem to significantly enhance the post-methanation potential of the digestates.

Co-digestion of animal manures with various agro-industrial residues has been reported previously (Callaghan et al. 2002, Kaparaju & Rintala 2005), with particular interest being shown in the co-digestion of animal manures with straws (Hills 1980, Fischer et al. 1983, Hashimoto 1983, Somayaji & Khanna 1994) (Table 6). However, there is little published data on the co-digestion of animal manures with energy crops (Weiland & Hassan 2001, Kaparaju et al. 2002) (Table 6), although in Germany, for example, 80 % of the approximately 3 500 farm biogas plants in operation by the end of 2006 were using energy crops, mostly maize, in co-digestion with manures and other materials (Weiland 2006). Hashimoto (1983) and Fischer et al. (1983) reported lower specific methane yields in co-digestion of manure with straw compared with digestion of manure alone, but in another co-digestion study with digesters fed with cow manure and varying proportions of wheat straw, the highest specific methane yields were observed with 40% of wheat straw of TS in the feedstock (Somayaji & Khanna 1994, Table 6).

TABLE 6 Examples of co-digestion of animal manures and plant biomass in CSTRs operated within the mesophilic temperature range as reported in the literature.

Feedstock (ratio on VS basis, unless otherwise stated)	Reactor volume (l)	T (°C)	Feed TS (%)	OLR (kg VS m^{-3} d^{-1})	HRT (time of operation) (d)	VS removal (%)	Spec. CH_4 yield (m^3 CH_4 kg^{-1} VS_{added})	CH_4 (%)	Ref.
Pig manure, corn stover (75:25)	30	39	8	3.8	16	46	0.210 [a]	67	1
Cow manure	0.3	35	7.3	n.r.	15 (65)	n.r.	0.350	57	2
Cow manure, wheat straw (50:50)			7.8		15 (65)		0.100	31	
Cow manure, wheat straw (25:75)			7.6		15 (65)		0.070	16	
Cow manure, wheat straw (10:90)			7.9		15 (65)		0.030	16	
Cow manure	20	35	3	4	n.r.	n.r.	0.100 [a]	n.r.	3
Forage beet silage			11	4		93	0.500 [a]	53	
Cow manure, forage beet silage (83:17 [a])			7[a]	4		n.r.	0.400 [a]	55	
Cow manure	18	35	7.6	3.6	21 (120)	51	0.240	n.r.	4
Cow manure, fruit and vegetable waste (FVW) (80:20, ww)			n.r.	4.2	21 (28)	51	0.380	n.r.	
Cow manure, FVW (70:30, ww)			n.r.	4.5	21 (28)	30	0.340	n.r.	
Cow manure, FVW (60:40, ww)			n.r.	5.2	21 (28)	50	0.450	n.r.	
Cow manure, FVW (50:50, ww)			n.r.	5.0	21 (28)	46	0.380	n.r.	
Cow manure	120	35-37	n.r.	n.r.	22 (~140)	40-50	0.220	55-58	5
Cow manure, energy crops (n.r.)					22 (~20)	40-50	0.210	55-58	
Pig manure	3.5	35	n.r.	2	44 (10)	n.r.	0.130-0.150	61-63	6
Pig manure, potato waste (85:15)				2	39 (58)		0.210-0.240	60-63	
Pig manure, potato waste (80:20)				2	26 (41)		0.300-0.330	60-62	
Pig manure, potato waste (80:20)				3	39 (28)		0.280-0.300	58-63	
Cow manure, barley straw (80:20, volume basis)	100	35	17	5.2	25 (126)	29	0.160 [a]	65	7
			17	6.5	20 (105)	28	0.170 [a]	64	
			17	8.7	15 (77)	26	0.150 [a]	61	
			17	12.5	10 (70)	24	0.110 [a]	58	
Pig manure	20 [b]	35	n.r.	3.5	15 (74)	n.r.	0.320 [a]	62	8
Pig manure, wheat straw (75:25)				3.8	15 (74)		0.240 [a]	60	
Pig manure, wheat straw (50:50)				3.8	15 (74)		0.220 [a]	58	
Cow manure	2 [c]	n.r.	10	n.r.	40 (40)	27	0.107 [d]	60	9
Cow manure, wheat straw (80:20, TS basis)			10		40 (40)	37	0.109 [d]	58	
Cow manure, wheat straw (60:40, TS basis)			10		40 (40)	32	0.113 [d]	59	
Cow manure, wheat straw (40:60, TS basis)			10		40 (40)	34	0.103 [d]	59	
Cow manure, wheat straw (20:80, TS basis)			10		40 (40)	32	0.097 [d]	58	
Wheat straw			10		40 (40)	33	0.087 [d]	59	

[a] values calculated from the data reported, [b] daily fed, periodically mixed digester, [c] no mention of mixing, [d] l CH_4 kg^{-1} TS_{added}, OLR = organic loading rate, HRT = hydraulic retention time, n.r. = not reported. 1: Fujita et al. 1980, 2: Hashimoto 1983, 3: Weiland & Hassan 2001, 4: Callaghan et al. 2002, 5: Kaparaju et al. 2002, 6: Kaparaju & Rintala 2005, 7: Hills 1980, 8: Fischer et al. 1983, 9: Somayaji & Khanna 1994.

6 Conclusions

Anaerobic digestion of cow manure and crops (sugar beet tops, grass silage and oat straw) in CSTRs was shown feasible with up to 40% VS of crops in the feedstock. The highest specific methane yields of 0.270, 0.230 and 0.210 m^3 CH_4 kg^{-1} VS_{added} in co-digestion of cow manure with grass, sugar beet tops and straw, respectively, were obtained during feeding with 30% of crop in the feedstock, corresponding to 85-105% of the total methane potential in the substrates as determined by batch assays. Volumetric methane production increased by up to 65% in reactors fed with 30% VS of crop along with manure, compared with that in reactors fed with manure alone at a similar loading rate. After doubling the OLR from 2 to 4 kg VS m^{-3} d^{-1} less methane was extracted per added VS, leading to a 16-26% decrease in specific methane yields, thus leaving more untapped methane potential being left in the residues.

The post-methanation potential of the digestates, if completely recovered, would in northern climatic conditions correspond to 0.9-2.5 m^3 CH_4 t^{-1} ww of digestate and up to 12-31 % of total methane production, the highest levels following co-digestion of manure with straw. If the post-storage tanks were maintained at 20 or 35 °C throughout the year, a post-methanation potential of 1.7-4.7 or 2.9-7.7 m^3 CH_4 t^{-1} ww of CSTR digestate, respectively, could be obtainable, corresponding to 21-43 and 35-56 % of total methane production.

Study of alkali-treatment reinforced the feasibility of co-digestion with substrate VS containing 30 % (VS) of crop and 70 % (VS) of manure at an OLR 2 kg VS m^3d^{-1} HRT 20 days. The concept of solids re-circulation with and without alkali treatment was proved not useful and resulted in stratification of reactor materials.

References

Amon, B., Kryvoruchko, V., Amon, T. & Zechmeister-Boltenstern, S. 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. Agr. Ecosyst. Environ. 112: 153–162.

Angelidaki, I. and Ahring, B.K. 1993. Thermophilic anaerobic digestion of livestock waste: the effect of ammonia. Appl. Microbiol Biotechnol 38: 560-564.

APHA. 1998. Standard methods for the examination of water and wastewater. 20^{th} ed. American Public Health Association, Washington DC, USA.

Callaghan, F. J., Wase, D. A. J., Thayanity, K. & Forster, C. F. 2002. Continuous co-digestion of cattle slurry with fruit and vegetable wastes and chicken manure. Biomass Bioenergy 22: 71–77.

Clemens, J., Trimborn, M., Weiland, P. & Amon, B. 2006. Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. Agr. Ecosyst. Environ. 112: 171–177.

Fan, L. T., Gharpuray, M. M. & Lee, Y.-H. 1981. Evaluation of pretreatments for enzymatic conversion of agricultural residues. Biotechnol. Bioeng. Symp. 11: 29–45.

Finnish Government. 1998. VNp 219/1998 Regulation on limiting the concentrations of agriculture-derived nitrates in water bodies (in Finnish). Suomen Säädöskokoelma 1998(219): 909–913.

Finnish Standard Association. 1988. SFS 5504 Determination of chemical oxygen demand (COD_{Cr}) in water with closed tube method, oxidation with dichromate. 4 p., Finnish Standard Association, Helsinki.

Finnish Standard Association. 2002. SFS-EN 12457–4 Characterisation of waste. Leaching. Compliance test for leaching of granular waste materials and sludges. Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction). 27 p., Finnish Standard Association, Helsinki.

Fischer, J. R., Iannotti, E. L. & Fulhage, C. D. 1983. Production of methane gas from combinations of wheat straw and swine manure. Transactions ASAE 26: 546–548.

Fujita, M., Scharer, J. M. & Moo-Young, M. 1980. Effect of corn stover addition on the anaerobic digestion of swine manure. Agric. Wastes 2: 177–184.

Hashimoto, A. G. 1983. Conversion of straw-manure mixtures to methane at mesophilic and thermophilic temperatures. Biotechnol. Bioeng. 25: 185–200.

Hashimoto, A. G. 1986. Pretreatment of wheat straw for fermentation to methane. Biotechnol. Bioeng. 28: 1857–1866.

Hills, D. J. 1980. Biogas from a high solids combination of dairy manure and barley straw. Transactions ASAE 23: 1500–1504.

Hills, D. J. & Roberts, D. W. 1981. Anaerobic digestion of dairy manure and field crop residues. Agric. Wastes 3: 179–189.

Hobson, P. N. & Wheatley, A. D. 1993. Anaerobic digestion: Modern theory and practice. 269 p., Elsevier Applied Science, London.

Kaparaju, P. L. N. & Rintala, J. A. 2003. Effects of temperature on post-methanation of digested dairy cow manure in a farm-scale biogas production system. Env. Technol. 24: 1315–1321.

Kaparaju, P. & Rintala, J. 2005. Anaerobic co-digestion of potato tuber and its industrial by-products with pig manure. Res. Conserv. Recy. 43: 175–188.

Kaparaju, P., Luostarinen, S., Kalmari, E., Kalmari, J. & Rintala, J. 2002. Co-digestion of energy crops and industrial confectionery by-products with cow manure: Batch scale and farm-scale evaluation. Wat. Sci. Technol. 45: 275–280.

Lehtomäki, A., Viinikainen, T.A. and Rintala, J.A. Screening boreal energy crops and crop residues for methane biofuel production. Submitted.

Mata-Alvarez, J., Macé, S. & Llabres, P. 2000. Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. Biores. Technol. 74: 3–16.

Nordberg, Å. & Edström, M. 1997. Co-digestion of ley crop silage, straw and manure. In: Holm-Nielsen, J. B. (ed.), Proc. Workshop on the Future of Biogas in Europe 1997: 74–81. BioPress, Risskov Denmark.

Perstorp Analytical / Tecator AB. 1995. Determination of nitrogen according to Kjeldahl using block digestion and steam distillation. Tecator application note, Perstorp Analytical / Tecator AB.

Somayaji, D. & Khanna, S. 1994. Biomethanation of rice and wheat straw. W. J. Microbiol. Biotechnol. 10: 521–523.

Viinikainen, T., Lehtomäki, A., Alén, R. & Rintala, J. 2006. Effect of harvest time on the chemical composition of energy crops and crop residues intended for methane production by anaerobic digestion. Submitted.

Weiland, P. 2003. Production and energetic use of biogas from energy crops and wastes in Germany. Appl. Biochem. Biotechnol. 109: 263–274.

Weiland, P. 2006. Anaerobic digestion of agricultural waste and selected biomass. In: Proc. Venice 2006, Biomass and Waste to Energy Symposium, Venice, Italy, 29.11.-1.12.2006.

Weiland, P. & Hassan, E. 2001. Production of biogas from forage beets. In: van Velsen, A. F. M. & Vestraete, W. H. (eds), Proc. 9th World Congress on Anaerobic Digestion: 631–633. Technologisch Instituut, Antwerp.