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Prasad Kaparaju

Enhancing Methane Production in a Farm-scale Biogas Production System

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UNIVERSITY OF JYVÄSKYLÄ

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ABSTRACT

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Biogas technology with utilisation of biogas is increasingly applied in the agricultural sector to produce renewable energy and to minimise environmental emissions both resulting in reduction in greenhouse gas (GHG) emissions. The main objective of this thesis was to evaluate methods to enhance the methane production in a farm-scale biogas production system.

Semi-continuous digestion of pig and dairy cow manures produced methane yields (m^3 kg^{-1} volatile solids (VS)) of about 0.31 and 0.14 respectively at 2 kgVS m^{-3} d^{-1} loading rate, 30 d hydraulic retention time (HRT) and 6.0% feed VS while in batches yields were 0.14, and 0.36 m^3 kg^{-1} VS for dairy cow and pig and manures respectively. These yields were lower than the theoretical yield of 0.4 m^3 kg^{-1} VS reported for cow manure. Possible co-substrates to enhance the methane production were investigated. Methane yields (m^3 kg^{-1} VS) in batch assays were 0.14 to 0.35 for three different energy crops and 0.32-0.39 for confectionery by-products. On full-scale application, cow manure alone and co-digestion with energy crops produced 0.22 m^3 CH_4 kg^{-1} VS and co-digestion with confectionery by-products (20% of feed biomass) about 0.28 m^3 kg^{-1} VS. Laboratory co-digestion of pig manure with potato tuber or its industrial by-products (potato peel or potato stillage) at loading rate of 2 kg VS m^{-3} d^{-1} produced methane yields (m^3 kg^{-1} VS) of about 0.22 at 85:15 and 0.31 at 80:20 feed VS ratio (VS% pig manure to potato co-substrate) compared to 0.14 for pig manure alone. The batch incubation of digested materials from a farm biogas digester (35°C) and its associated post-storage tank indicated that both materials could still produce up to 0.20 m^3 kg^{-1} VS. The amount and rate was highly dependent on temperature. These results suggest that the untapped methane potential in the digested manure cannot effectively be recovered at temperatures prevailing in the post-storage tank (5-10°C) during the winter in the Northern latitude biogas production system while some methane could be recovered at during the spring. Batch assays showed that methane potential of digested materials incubated after a solid-liquid separation (>2, 1-2, 0.5-1, 0.25-0.5 and <0.25 mm) was evenly distributed depending upon the relative distribution of the fractions' in the digester material but not with post-storage tank material. The main difference was with the <0.25 mm fraction, which for the post-storage material had much lower methane yields than for the same fraction of digester material. On the other hand, fractionation was unfeasible for nitrogen management. Employing various post-treatment methods to improve the methane potential of >2 mm solid fraction of the digester material indicated that chemical treatment with or without thermal were slightly effective than other tested methods during the short-term (30-50 d) batch incubation. On the other hand, in long-term incubation (345 d), maceration, freeze/thaw and thermal treatments were the best treatments. Benefits of biogas technology in mitigating GHG emissions were mainly through replacing fossil fuel by biogas. In conclusion, the results indicate that methane production could be enhanced if co-digestion of manures with energy crops or industrial organic wastes and post-methanation of digested materials are included as a systems approach in a farm-scale biogas production system.

Key words: Anaerobic digestion; biogas; co-digestion; farm-scale; livestock; greenhouse gases; manure; methane; post-methanation; post-treatment; pre-treatment; renewable energy

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CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is a summary and discussion of the following articles and manuscripts, which are referred to by their Roman numerals in the text.

I Kaparaju, P.L.N. and Rintala, J.A. 2003. Farm-scale anaerobic digestion of swine and dairy cow manure as a measure to mitigate greenhouse gas emissions and produce renewable energy. (submitted).

II Kaparaju, P., Luostarinen, S., Kalmari, E., Kalmari, J. and Rintala, J. 2002. Co-digestion of energy crops and industrial confectionery wastes with cow manure: Batch-scale and farm-scale evaluation. Water Sci. Technol. 45(10) 275-280.

III Kaparaju, P.L.N. and Rintala, J.A. 2003. Farm-scale anaerobic co-digestion of potato tuber and its industrial by-products with pig manure. (submitted).

IV Kaparaju, P.L.N. and Rintala, J.A. 2003. Effects of temperature on post-methanation of digested dairy cow manure in a farm-scale biogas production system. Environ. Technol. (in press).

V Kaparaju, P.L.N. and Rintala, J.A. 2003. Effects of solid-liquid separation on recovering residual methane and nitrogen of a digested dairy cow manure. (submitted).

VI Kaparaju, P.L.N. and Rintala, J.A. 2003. The effects of post-treatment methods and temperature on the methane potential of >2 mm solid fraction of the digested cow manure. (submitted).

VII Kaparaju, P.L.N. and Rintala, J.A, Farm-scale biogas production systems with a view to enhance methane production: a review. (manuscript).

ABBREVIATIONS

AD	anaerobic digestion
AWMS	animal waste management system
CHP	combined heat and power
COD	chemical oxygen demand
CRM	confectionery raw material
CSTR	continuously stirred tank reactor
EC	European Commission
EURO	EURO Currency
EF	emission factor
EU	European Union
EUROSTAT	European Statistics from Statistical Office of the European Communities
GHG	greenhouse gas
GWP	global warming potential
HRT	hydraulic retention time
IBP	industrial by-products
IPCC	Intergovernmental Panel on Climate Change
kWh	kilowatt hour
Mtoe	Million tonnes of oil equivalent
SCOD	soluble chemical oxygen demand
SRT	solids retention time
SS	suspended solids
TCOD	total chemical oxygen demand
TKN	total kjeldahl nitrogen
TS	total solids
VFAs	volatile fatty acids
VS	volatile solids
VSS	volatile suspended solids

1 INTRODUCTION

1.1 Agriculture as source of renewable energy production and greenhouse gas emissions

There is a growing global interest to significantly reduce the anthropogenic emissions of greenhouse gases (GHG): mostly methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) and to promote sustainable development. Agricultural sector may play a significant role by producing renewable resources and by reducing its own emissions. Moreover, agriculture in European Union (EU-15) is considered as a key sector for the European strategy of doubling the share of renewable energies from 6 to 12% in gross energy demand in the EU by 2010 (EC 1997). The estimated potential for biomass substituting fossil fuels in EU is about 6.4 EJ a^{-1}, which is equivalent to 0.34 Pg a^{-1} of CO_2 derived fossil fuel emissions (Kaltschmitt et al. 1998). This is consistent with market projections for the EU by 2010 of 4 EJ a^{-1} (Grassi 1999) of which 3.1 EJ a^{-1} are in the heat sector, 0.8 EJ a^{-1} in power generation and <0.1 EJ a^{-1} in bioethanol/biomethanol markets. Agriculture in EU member States produces annually 0.4 Pg CO_2 equivalents, i.e. 10% of the anthropogenic GHG emissions and accounts for 43 and 56% of total EU's CH_4 and N_2O emissions respectively (EUROSTAT 2003). Livestock production centres especially, ruminants and mineral arable soils are the major sources of CH_4 and N_2O emissions respectively (Safley et al. 1992; EUROSTAT 2003). Anaerobic digestion (AD) with utilisation of biogas is increasingly recognised as a promising technology in the agricultural sector to produce renewable energy and to minimize environmental emissions (e.g. GHGs and odours). Both centralised and farm-scale applications have been considered and have their advantages and disadvantages. The economy of farm-scale biogas systems depends for example on the value of the energy produced from the biogas and the value of the digested material as fertilizer. In an attractive biogas energy markets (price of electricity, or biofuel production), the interest to maximize the amount of methane production and time of production is also growing in farm-scale production systems.

Renewable energy from energy crops, biomass from forest management (Kaltschmitt & Reinhard 1997), and animal manure, slurry and waste (Bates 2001) have the largest potential as future bioenergy sources. According to European Commission's White Paper on Renewable Energy Sources, the renewable energy potential through biogas exploitation (livestock production, sewage treatment, landfills) is 15 million tonnes of oil equivalent (Mtoe), agricultural and forest residues is 30 Mtoe and for energy crops is 45 Mtoe (EC 1997). Currently, the major biomass resource in many farm-scale biogas plants in distributed energy production systems is livestock manure i.e. pig and cow manures. In evaluating the potential and the effects of AD in different farms it has to be considered that the manures are rather inhomogeneous complex substrates and their characteristics vary between different species and also among the same animal species e.g. due to differences in feed, and/or due to the differences in manure management practices (Hobson & Wheatley 1993). Because of these variations also the feasibility of AD and methane potential may vary greatly as suggested in full-scale applications and laboratory studies. For instance, under careful monitoring of few selected farm-scale digesters, methane yields of 0.25-0.5 m^3 kg^{-1} volatile solids $(VS)_{\text{added waste}}$ for pig manure (3-8% total solids, TS) and 0.20-0.30 m^3 kg^{-1} $VS_{\text{added waste}}$ for cow manure (5-12% TS) were reported (Moller 2000). Correspondingly, the figures under optimum laboratory conditions were 0.29-0.37 m^3 kg^{-1} $VS_{\text{added waste}}$ (Hansen et al. 1998; Sommer et al. 2002) for swine manures and 0.11-0.24 m^3 kg^{-1} $VS_{\text{added waste}}$ for cow manure (Hansen et al. 1998; Sommer et al. 2002). Thus, in typical cow manure processing biogas digesters with 20 to 30 d hydraulic retention time (HRT) ca. 50% of theoretical methane yield for raw cow manure (0.4 m^3 kg^{-1} $VS_{\text{added waste}}$) is normally achieved. Up to 25% of the untapped methane potential is found in the digested particulate matter (biofibres) of the manure (Hartmann et al. 2000). Potential methods to improve the methane recovery from the manure (Fig. 1) are increasing the retention time of the manure in the digester, pre-treatment of the manure and/or substrate, co-digestion of manures with organic wastes of farm and/or industrial origin or methanation during the post-storage of the treated manure (post-methanation).

1.2 Enhancing methane production in a farm-scale biogas production

Anaerobic co-digestion of organic waste of farm origin e.g. manures with surplus crop and crop residues as well as with organic residues from food and other agro-industries and municipal waste sludges would offer a number of benefits for both farmer and industry by not only providing an on-site treatment of wastes but also form a source of renewable energy (Weiland & Hasan 2001; Braun et al. 2002). Apart from biotechnological advantages (Mata-Alvarez et al. 2000), such as overcoming the problem of maintaining a stable pH within the methanogenesis range during digestion of agro-industrial wastes (Brummeler & Koster 1990) or ammonia inhibition related to pure manure digestion (Angelidaki & Ahring 1993), co-digestion will improve the energy balance of the farm and also decrease considerably the investment costs per unit of energy. Indeed, co-digestion may even result in an energy surplus, providing additional income to the biogas plants from the sale of produced electricity or heat to local grid or community heating system or by storing the upgraded biogas as vehicle fuel (Brolin & Kättström 2000; Wellinger 2000). The surplus crop produced in agriculture and/or its organic residues created during industrial processing can thus form a source of renewable energy and aid in generating additional revenue and diversifying the agricultural activity (Nordberg 1996). However, the ratio of the feed components along with the optimum particle size of the substrates is of paramount importance in a co-digestion process.

Enhanced post-methanation is an attractive method to harvest the remaining methane potential of the digestate, as the storage capacity for livestock slurries in many European farms has been extended due to the legislation for the spread of slurry (Burton 1996). For instance, the slurry storage capacity in Finnish dairy farms has been extended from a few months to one year's slurry production. Thus, the methane obtained during the post-methanation of the digestate could be an additional biogas incentive. Post-digestion in covered slurry storage tanks, which may also be used for gas storages, will occur at ambient temperatures prevailing in the storage tanks and can vary with the climatic conditions. For example, the temperatures inside a partly sub-surface insulated storage tank in Finland can vary from ca. 5°C (several months) up to 20-25°C (few months). However, the ultimate methane production in the storage tank will depend on physical and biological factors such as ambient temperature, retention time, digested material retained in the storage tank as inoculum and the incoming digested material's characteristics. Therefore, processing of the substrate, manipulation of the conditions inside the storage tank and/or acclimatization of the microbial consortia to the prevailing environmental conditions could enhance methane production from the already digested manure.

In order to optimize the methane potential recovery and material and nutrient flow of the digested material - obtained either straight from the digester or from the associated digester's post-storage tank – physical separation of the material into various fractions (solids-liquid) with different properties could be performed. The high methane potential fraction could be used for energy extraction (e.g. by recycling to the digester) while the low methane fraction could be directed elsewhere. Correspondingly, the nutrient rich fraction could be directed for fertilising purposes. Previous studies on solid-liquid separation have shown to obtain an optimum feed stock for energy or nutrient extraction with different manures (Holmberg et al. 1983; Lo et al. 1983; Huijismans & Lindley 1984; Haugen & Lindley, 1988, Zang & Westerman 1997) and with fibres separated from the manure (Hartmann et al. 2000). However, studies on the effect of solid-liquid separation to recover the methane potential of an already digested manure have not been reported.

Previous attempts to fractionate digested manure into different fractions indicated that the methane potential of the liquid fraction (<0.25 mm) could apparently be recovered during the subsequent long storage in the post-storage tank whereas, the methane from the >2 mm fraction was found to be more difficult to recover and could form the remaining energy rich fraction of the digestate. Therefore, to further enhance the methane potential of the digested manure, the most after sought solution would be to increase the biodegradability of the energy rich solid fraction of digested manure by employing various post-treatment methods. Post-treatment of digested manure would not only further improve the digestion process by increasing the biodegradability and/or reducing the dilution of substrate but also fulfils the need of substantial reduction of solids and concentration of nutrients. Thus, the separated solids contain a majority of the nutrients that can be stored, stacked, and exported if required. However, the amount, quality, and nature of these products will depend on feedstock quality, digestion method and, type and the extent of the post-treatment refinement processes.

Several treatment methods such as physical, chemical and biological can be employed either before a primary digestion as pre-treatment (Angelidaki & Ahring 2000) or after the digestion as post-treatment. The aim of these treatments methods however remains the same, to destroy the lignocellulosic structure of the solid fractions so as to increase the specific area (Fan et al. 1982), soften the solids, facilitate access for bacterial entry, and/or release cellulose and hemicellulose material from these substrates. Such processes will not only enforce the treated materials to be exposed to the bacterial action but also improves the degradability and henceforth its methane potential. The effect of various treatment methods as pre-treatments on the fibres separated from untreated manure to enhance the methane potential have been demonstrated successfully (Angelidaki & Ahring 2000; Hartmann et al. 2000). However, the effect of post-treatment to increase the methane potential of an already digested manure has not been reported.

Biomethanation is a biological process dependent on temperature. The optimum process temperatures are 20-45°C for the mesophilic process and 45-60°C for the thermophilic process (Madigan et al. 2000). However, methanogenesis can also occur at low temperatures (<20°C) under psychrophilic conditions (Safley & Westerman 1992). Recently, the possible digestion of raw cow and pig manures under extreme temperature conditions, both at low (5-20°C) and high (55-82°C) temperatures along with the advantages of low temperature digestion has been demonstrated Nozhevnikova et al. 1999). However, the effect of post-methanation of digested materials sampled from digester (35°C) and post-storage tank (5-10°C) as such at temperatures ranging from 5 to 55°C was never studied before.

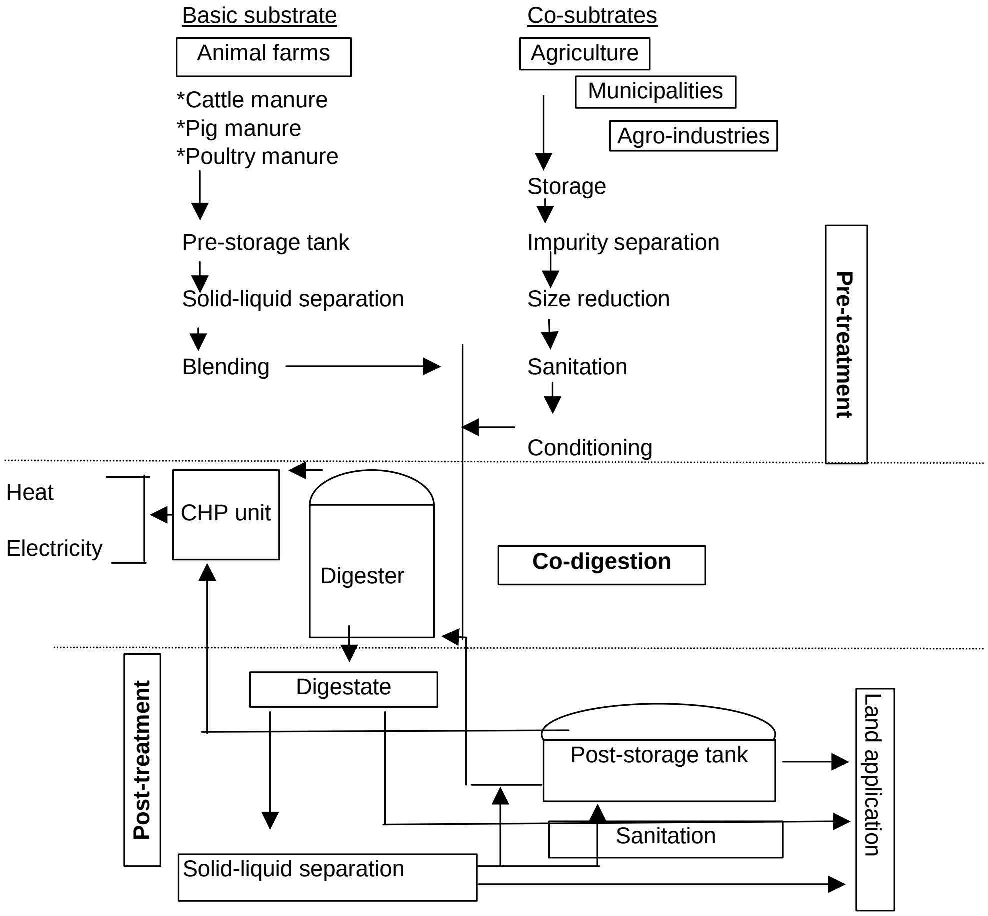

FIGURE 1 Potential concept of on-farm anaerobic digestion of manures and industrial by-products (VII).

2 OBJECTIVES

The main objective of this thesis was to evaluate methods to enhance methane production in a farm-scale biogas production system. The biological methane production potential of livestock manures were first investigated with and without inoculation in batch assays at 35°C (I). Anaerobic co-digestion and post-methanation were investigated as possible approaches to enhance methane production (II-VI). Co-digestion of various confectionery by-products and energy crops along with the effects of particle size reduction and crop maturity (vegetative and flowering stage) on methane production of the energy crops were evaluated in laboratory study and compared to the results obtained on full-scale application (II). The effect of the feed component ratio of manure co-digested with energy crops or industrial by-products was further evaluated in a laboratory semi-continuous digestion (III). The effects of temperature (IV), solid-liquid separation (V) and post-treatment methods (VI) on post-methanation of digested materials sampled from a farm digester and the associated post-storage tank were investigated in laboratory batch experiments. The energy balance and potential greenhouse gas (GHG) emissions that could be avoided through adoption of on-farm anaerobic digestion were also estimated for the studied farms (I). The role of anaerobic digestion in mitigating GHG emissions and producing renewable energy with emphasis on enhancing methane production in a farm-scale biogas production system was reviewed (VII).

3 MATERIALS AND METHODS

3.1 Substrates, feed and inocula

3.1.1 Manures as such and prepared feed

The characteristics of the studied manures are shown in the Table 1. Two different dairy cow manures as well as swine manures (pig and sow) were used as substrates (I). Cow manures were procured from two separate 70 cow unit dairy farms (Halsua and Laukaa, Finland). Pig manure (TS 7.4%) was obtained from a pig farm (Halsua, Finland) consisting of 100 fattening pigs with an annual piglet production of 1,500 while, sow manure (TS 1.1%) was procured from a sow farm (Halsua, Finland) rearing 210 sows and with a piglet production of 3,150 per year. The manure productions from these farms were 2,000 m^3 of cow manure, 800 m^3 of pig manure and 2,000 m^3 of sow manure per year. All substrates were stored at 4°C before use. Cow manure (8.7% TS) from Laukaa dairy farm was obtained in two consignments while, cow manure (7.8% TS) from Halsua dairy farm along with swine manures were obtained as a single consignment. Manures were collected from the pre-storage tank.

In the digester experiments (II), cow manure from Laukaa dairy farm was only used, as the chemical composition of the two cow manures was found similar, except for the slight difference in solids and chemical oxygen demand (COD) content. Swine manures were used as such, while feed was prepared once in a fortnight for cow manure (Laukaa dairy farm). Feed VS of cow manure was adjusted to be on par with that of pig manure (6% VS) by diluting with distilled water. Prepared feed had chemical composition of pH 7.6, TS 6.6%, VS 6%, total Kjeldahl nitrogen (TKN) 4 gl^{-1}, ammonium-nitrogen (NH_4^+-N) 1.4 gl^{-1}, COD soluble 4 gl^{-1}, COD total 56 gl^{-1} and was also stored at 4°C. Upon consumption, fresh feed was either prepared or drawn periodically from the storage (4°C). Feed prepared from different consignments was shown as "new feed" while feed drawn from stored material was designated as "feed change" in Figures 3-5. The characteristics of the substrates and inoculum were analyzed immediately upon arrival at the laboratory.

TABLE 1 Characteristics of farm animal manures (I).

Characteristics	Sow manure	Pig manure	Halsua cow manure	Laukaa cow manure
pH	7.2	6.7	7.2	7.1
Alkalinity (as $CaCO_3$; gl^{-1})	142	48	192	201
TS (%)	1.1	7.4	7.8	8.7
VS (% of TS)	69.1	81.8	82.1	85
Ash (% of TS)	30.9	18.2	17.9	15
TSS (%)	0.13	0.24	0.24	0.20
TKN (gl^{-1})	2.0	5.6	3.5	3.5
NH_4^+-N (gl^{-1})	1.4	2.9	1.2	1.4
NH_4^+-N/TKN (%)	70	52	34	40
TCOD (gl^{-1})	22	63	24	43
SCOD (gl^{-1})	11	29	8	4
SCOD/TCOD (%)	50	46	33	9
TCOD/VS (gCOD/gVS)	2.9	1.0	0.38	0.58

3.1.2 Energy crops

Energy crops viz. clover, grass hay and oats grown on the farm (Laukaa Farm, Leppävesi village, Jyväskylä, Finland) were harvested at a maturity stage corresponding to usual harvest for animal feed (II). For laboratory batch experiment, representative samples of energy crops were drawn from the farm and stored at 4°C (Table 2). To study the effect of harvest time on methane production potential, clover was harvested during the vegetative and flowering stage. In the farm-scale studies, energy crops were harvested and stored in field under plastic sheet.

Fresh potato tubers were purchased from a supermarket in Jyväskylä, Finland (III). The homogenised feed materials were stored separately in plastic boxes of 300 g capacity at –20±1°C (Table 3). Two days before each feeding, frozen feed was thawed at room temperature (20±1°C), and depending upon the required feed VS ratio, pig manure and potato waste were mixed before each feeding.

TABLE 2 Characteristics of the energy crops and confectionery by-products (II).

Substrates	pH	TS (%)	VS (%)	VS/TS	TKN (gl^{-1})
Energy crops					
Clover (vegetative)	7.8	18.7	16.9	0.90	3.1
Clover (flowering)	7.8	13.5	11.9	0.88	3.8
Grass hay	7.9	25.9	23.6	0.91	1.7
Oats	7.6	60.2	55.9	0.93	1.6
Confectionery by-products					
Chocolate	7.2	97.5	93.7	0.96	n.d
Black candy	8.2	84.6	78.3	0.93	n.d
CRM	6.1	89.1	89.0	1.0	n.d

n.d. not determined

3.1.3 Industrial by-products and feed

Confectionery by-products (Table 2) such as chocolate, black candy and confectionery raw material (CRM) were obtained from a confectionery factory (Panda Oy, Jyväskylä, Finland). The stock was stored at –20±1°C before use (II).

Potato peelings (the outer epidermal layer of potatoes) were procured from a peeling factory while potato stillage (which separates into a supernatant liquid and semi-solid upon standing) was obtained from an ancillary industry manufacturing glue for the paper industry in Finland (III). Similar to potato tuber, the homogenised feed materials of potato peel and stillage were also stored separately in plastic boxes of 300 g capacity at –20±1°C (Table 3). Two days before each feeding, frozen feed was thawed at room temperature (20±1°C), and depending on the required feed VS ratio, pig manure and potato waste were mixed before each feeding.

TABLE 3 Characteristics of potato peel, potato stillage and potato tuber (III)

Characteristics/ Substrates	Potato peel	Potato stillage	Potato tuber
pH	3.5	4.5	6.0
TS (%)	22.6	48.5	19.9
VS (%)	21.4	46.6	18.8
TKN (gl^{-1})	1.7	0.34	2.4
NH_4^+-N (gl^{-1})	<0.01	<0.01	<0.01
TCOD (gl^{-1})	235	600	210
SCOD (gl^{-1})	32	18	33
TCOD/VS (gCOD/gVS)	1.1	1.3	1.1

3.1.4 Anaerobically digested materials from a farm digester and post-storage tank

Anaerobically digested material consisting of digested cow manure with minor amounts of readily biodegradable industrial by-products (Table 4) was sampled from an on-farm biogas plant and post-storage tank (Laukaa farm, Finland) (IV-VI). During the study winter season, the 150 m^3 farm-scale mesophilic biogas digester was operated with high solids (ca. 10% TS) feed consisting of cow manure and industrial by-products. The feed and digested manure, respectively, were sampled as grab samples from pre-storage manure tank and digester (February) when the farm-scale digester had shown normal methane production ca. 100 m^3 d^{-1}. Digested material was also collected from a 1500 m^3 post-storage tank, which held digested manure at ambient temperature (ca. 5-25°C) up to 9-12 months; this tank was well insulated and partly below the soil surface. The post-storage tank was sampled during the spring (May), when the digested slurry after careful mixing was spread on agricultural land and when the tank contained digested manure produced from the previous August onwards. Upon arrival at the laboratory, assays were prepared immediately without any inocula addition. However, it is to be noted that the feed of the full-scale digester changes slightly depending upon the availability of materials and/or season, thus the characteristics of digested materials from either digester or post-storage tank cannot strictly be compared to that of feed.

3.1.5 Inocula

Two different anaerobically digested materials were used as inocula in the studies (I-III, VI). Mesophilically digested cow manure from an on-farm digester (Laukaa, Finland) was used as inoculum (I, II, VI).

Sludge from a mesophilic digester in the municipal sewage treatment plant (Jyväskylä, Finland) was used as inoculum in the study to investigate co-digestion of potato and its industrial by-products with pig manure (III).

3.2 Pre- and post-treatment methods

3.2.1 Pre-treatments of energy crops (particle size reduction)

Fresh samples of energy crops viz. clover, oats and grass hay were chopped to ca. 0.5, 1 and 2 cm size particles with stainless steel knife (II). In farm-scale studies, the harvested energy crops stock was mechanically ground with a meat grinder to particle size of 2 cm and mixed with manure before feeding to farm digester (II). The potato tubers were communised to less than 5 mm in size using a Retsch Mill blender (Germany) (III).

TABLE 4 Characteristics of feed and digested materials sampled from a farm digester (35°C) and the associated post-storage tank (5-10°C) before and after solid-liquid separation (IV, V).

Characteristic /Substrate	pH	TS (%)	VS (%)	TKN (gl^{-1})	NH_4^+-N (gl^{-1})	NH_4^+-N /TKN (%)	TCOD (gl^{-1})	SCOD (gl^{-1})	TCOD /VS (gCOD gVS^{-1})
Feed	7.0	6.9	5.6	2.9	1.9	63.5	75	15	1.3
Digester material	7.7	6.0	4.6	3.6	2.1	57.1	50	8	1.1
Post-storage tank material	7.4	5.7	4.4	3.4	2.0	59.6	56	7	1.3
Solids sizes for digester material									
>2 mm	8.2	10.1	8.6	4.2	1.7	41.3	81	11	0.94
1-2 mm	9.0	9.2	7.7	3.0	1.4	44.7	95	12	1.2
0.5-1 mm	8.8	8.4	6.9	3.7	1.8	48.6	73	10	1.6
0.25-0.5 mm	8.9	7.3	5.8	3.6	1.6	46.3	81	10	1.4
<0.25 mm	8.2	4.2	2.9	3.7	2.2	60.0	47	12	1.6
Solids sizes for post-storage tank material									
>2 mm	8.1	11.5	9.6	3.7	2.0	54.7	72	12	0.75
1-2 mm	8.3	9.8	8.3	3.4	1.8	54.7	88	11	1.1
0.5-1 mm	8.4	8.8	7.3	3.3	1.5	47.1	94	12	1.2
0.25-0.5 mm	8.5	8.2	6.6	3.0	1.5	51.5	97	11	1.5
<0.25 mm	8.1	3.9	2.7	3.0	2.1	69.7	36	12	1.3

3.2.2 Solid-liquid separation of digested materials

Solids separation was performed in parallel set-ups with digested material drawn as grab samples from farm digester (35°C) as well as from post-storage tank (5-10°C) (V). This process was performed after a brief storage of materials at 4°C for 2-3 d. The solids (material retained on sieve) were separated by allowing a sample of homogenized material to pass through a sequence of four aluminum sieves with mesh sizes of 2, 1, 0.5 and 0.25 mm (Oy Scanteknik Ab, Finland). Solid-liquid separation was carried out manually by brushing the material gently over the sieve with nylon brush. This process may have altered the physical structure of the material as solids had to be separated from the digested material with a little force. The fractionation process lasted for ca. 1-2 d with each material. Fractions remaining in each sieve and the one leaving the smallest sieve were collected and weighed to obtain the weight/weight of each fraction and were denoted as >2.0, 1-2, 0.5-1, 0.25-0.5 and <0.25 mm respectively. The separated solids and liquid fractions were stored immediately at 4°C before further use (Table 4).

3.2.3 Post-treatment of >2 mm solid fraction of the digested material

The effect of different treatments on characteristics and methane potential of the >2 mm solids fractions was studied by employing a range of post-treatment methods (VI). The post-treatments employed in this study included mechanical maceration, exposure to high temperatures (thermal treatment) or to a freeze/thaw cycle, incubation in sodium hydroxide (NaOH) chemical treatment with or without a thermal treatment. Similarly, the effect of an aeration process on the digested manure as such was also evaluated. Description regarding to the procedure adopted for each post-treatment methods employed in this study were described in the Table 5. Treatments were performed in 120 ml glass bottles in triplicate. For each treatment, 40 ml of >2 mm solids were used. No pH adjustment (back to neutral) was carried out prior to start of treatments. The characteristics of the solids before and after the treatment are presented in Table 6.

TABLE 5 Studied post-treatment methods performed on the largest solids fraction (>2 mm) separated from a mesophilically digested cow manure (VI).

Treatment	Method	Any adjustments or remarks
Post-treatments		
Maceration	Mechanical maceration using kitchen blender (Braun, Germany)	Solids of <1 mm.
Freezing and thawing	Solids were frozen for 24 h at –20°C and then left to thaw at 20°C for 4 h.	--
Thermal	Static incubation at 80°C for 3 h in incubator.	--
Chemical treatment	NaOH at the rate of 40 g kg^{-1}VS incubated statically at 20°C for 48 h.	Treated material pH adjusted immediately to 7-7.5 with 10 ml of 5 M hydrochloric acid (HCl).
Chemico-thermal treatment	Chemical and thermal treatments mentioned above were performed in a sequence.	Treated material pH adjusted immediately to 7-7.5 with 10 ml of 5 M HCl.
Aeration	One litre of digested material was aerated using aquarium air pumps (Rena air pump, France) maintained at oxygen flow rate of 2 ml O_2 l^{-1} of material h^{-1} for 1 d at 20°C.	Treated material pH adjusted immediately to 7-7.5 with 5 M HCl.

TABLE 6 Characteristics of feed, digested material (full-scale digester operated at 35°C) and the >2 mm solid fraction separated from the digested material before and after employing various post-treatment methods (VI).

Characteristic /Substrate	pH	TS (%)	VS (%)	TKN (gl^{-1})	NH_4^+-N (gl^{-1})	NH_4^+-N /TKN (%)	TCOD (gl^{-1})	SCOD (gl^{-1})	TCOD/VS (gCOD gVS^{-1})
Feed	7.0	6.9	5.6	2.9	1.9	63.5	75	15	1.3
Digester material	7.7	6.0	4.6	3.6	2.1	57.1	50	8	1.1
Aerobic	9.1	6.8	5.3	3.7	1.5	40.8	66	13	1.2
Post-treatments of digester material (solids >2 mm)									
>2 mm solids as such	8.2	10.1	8.6	4.2	1.7	41.3	81	11	0.94
Thermal	7.9	10.5	8.9	3.5	1.8	51.4	80	12	0.89
Chemical	9.2	8.9	7.4	2.9	1.3	46.8	49	9	0.66
Chemico-thermal	8.9	8.4	6.9	3.0	1.9	40.3	54	15	0.78
Freezing and thawing	8.1	10.7	9.2	3.8	1.2	50.4	73	11	0.79
Maceration (<1 mm)	8.8	7.7	6.2	3.6	2.2	59.7	80	19	1.3
Inoculum (<0.25 mm)	8.2	4.2	2.9	3.7	2.2	60.0	47	12	1.6

3.3 Assays and reactors studies

3.3.1 Biochemical methane production potential assays

The batch studies to assay the methane potential of different manures and the effect of inoculation on methane yields (I) and to study the methane potential of energy crops or industrial by-products (II) were conducted in duplicate two litre (l) glass bottles. To each assay, substrate and inoculum were added at the rate of 6.9 gVS each (VS_{waste} to $VS_{inoculum}$ ratio of 1) (I). One litre (17 gVS l^{-1}) of inoculum was added to each substrate (volumes adjusted to have 51 gl^{-1} VS for all energy crops and 25.8 gl^{-1} VS for all confectionery by-products) resulting in VS_{waste} to $VS_{inoculum}$ ratios of 3 for energy crops and 1.5 for confectionery by-products (II). Total working volume was adjusted to 1.5 l with distilled water. Bottles were flushed with nitrogen/carbon dioxide gas mixture (80/20%) before sealing with rubber stopper. Assays were incubated at 35±1°C and each bottle was shaken by hand once in a day throughout the weekdays (Monday through

Friday). Assays without added substrate were assayed to evaluate the performance of inoculum alone (I and II).

3.3.2 Post-methanation experiments

The batch experiments to study the effect of temperature (IV), solid-liquid separation (V) and post-treatments (VI) on the methane potential of the digested material sampled from farm digester (IV, V, VI), post-storage tank (IV, V) and laboratory continuously stirred tank reactors (CSTRs) (III) were carried out in duplicate 120 ml glass bottles. To each bottle, 60 ml of thoroughly mixed material was transferred as such (III, IV, V) or after adjusting the pH to neutral with 10 ml of 5 M HCl in assays subjected to chemical, chemico-thermal and aeration post-treatments (VI). Assays were prepared immediately at 20°C without any inocula addition (III, IV, V) or by adding to each treated assay (40 ml), 20 ml of inoculum (<0.25 mm) (VI). The blank assays contained 20 ml of inoculum and 40 ml of distilled water (VI). The methane productions from blanks were subtracted from those of the samples (VI).

Assays were sealed immediately with butyl rubber stoppers and aluminium crimps. The sealed bottles were then flushed with nitrogen/carbon dioxide (70/30) gas mixture for 3 min. Further 0.5-1 ml of 0.25 gl^{-1} of sodium sulphide ($Na_2S\ 7H_2O$) was injected into the bottles in order to ensure optimum anaerobic conditions. Treated assays were incubated in duplicate at 5, 10, 15, 20°C and at 35 and 55°C as reference temperature (IV, VI) and at 35°C (III, V). In the final stage of the experiments, the temperature of one of each pair of replicate assays was increased to 35°C from the previously incubated temperatures of 5-20°C (IV, VI).

3.3.3 Semi-continuous digester experiments

The digester experiments were carried out in identical CSTRs with a total capacity of 5 l and a liquid capacity of 4 l (I) and 3.5 l (III) at 35±1^{o}C. Digesters were mounted separately on a mechanical stirrer, stirring continuously at 200 rpm. The outlets provided at the top of the each digester were used for feeding, withdrawing digestate and for collecting biogas.

Digesters were inoculated on day 1 with 3.8 l of mesophilically digested dairy cow manure (I) and 3.4 l of mesophilically digested sewage sludge (III). The substrates used for semi-continuous digester studies were cow manure from Laukaa dairy farm, pig and sow manures (I) while the substrates used in co-digestion experiment with pig manure were potato tuber, potato peel and potato stillage (III).

After inoculating on day 1, semi-continuous feeding was generally initiated on day 8, when the methane content in the biogas reached 50%. Digesters were usually syringe-fed below the liquid level on every weekday (Monday through Friday). Prior to each feeding, a volume about 10% less than the feed volume was removed with syringe to maintain a constant digester volume. Feed was withheld temporarily between 53 and 61 (I) and between 12 and 26 (II) days of operation. On day 62, 250 ml of distilled water was added to each digester in order to restore the desired working volume before daily feeding could resume (I).

Sow manure was fed at a loading rate of 0.38 kgVS m^{-3} d^{-1} (feed VS 0.77%) and HRT of 20 d (I). While digesters treating pig manure and cow manure (Laukaa farm) were operated with same loading rate (2.0 kgVS m^{-3} d^{-1}), feed VS (6.0%) and HRT (30 d) (I).

3.3.4 Farm biogas plant

Farm biogas plant is a vertical steel digester (150 m^3 capacity, liquid volume 120 m^3), operated at 35–37°C with central mechanical stirring system (II). The feed was prepared every week or on alternate week in the feed tank by feeding the well-mixed cow manure from the pre-storage tank (760 m^3 capacity) to a feed tank where energy crops/confectionery by-products were mixed periodically. The feed is generally pumped to the digester from the feed tank 2-3 times per day with a total average amount of ca. 6 m^3 d^{-1}. HRT was 22 d. Digested material leaves the digester, and enters the post-storage tank (1500 m^3). The specifically designed slurry post-storage tank has a dome shaped soft top membrane and function as gas storage, capable to hold biogas, amount of one week's consumption and collect biogas (annually on average ca. 10% additional methane, methane production varies e.g. according to temperature) produced from the already digested material in the post-storage tank (retention time varying from 1 week to 9 months). The biogas thus produced, is led to the biogas combined heat and power (CHP) generator.

3.4 Analyses, calculations, energy equivalents and conversion factors

3.4.1 Chemical analyses

pH was measured using Metrohm, 744 pH meter immediately after each sampling to avoid pH fluctuations due to CO_2 losses. Total alkalinity (TA), ammonium nitrogen (NH_4^+-N), TS and VS were analyzed according to Standard Methods (APHA 1998). Total Kjeldahl nitrogen (TKN) was determined using a Kjeltec System 1002 Distilling unit (Perstop Analytical/Tecator AB 1995). Before distillation, the samples were digested with digester 2006 (Tecator AB). Chemical oxygen demand, total (TCOD) and soluble (SCOD) were analysed according to Finnish Standards (Finnish Standards Association 1988). The SCOD and NH_4^+-N samples were filtered with glass fibre filter paper (Φ90 mm, GF50, Schleicher & Schuell). Biogas volume, methane volume and methane content in biogas (analysed with a

Perkin Elmer Autosystem XL gas chromatograph with a flame-ionisation detector) were analysed as described by Salminen et al. (2000).

3.4.2 Statistical analysis

Statistical analysis was performed using SPSS procedure (SPSS version 11.0 for Windows 2001). A one way analysis of variance (ANOVA) test was carried out (VI). When this analysis indicated a significant difference, F statistic was subjected to pair-wise and complex comparisons of Tukey test.

3.4.3 Calculations

Loading rate (kgVS m^{-3} d^{-1}) and HRT in the digester studies were calculated based on actual daily feed additions (I, III). Specific methane yields (m^3 kg^{-1} $VS_{\text{added waste}}$) in the digester were calculated on weekly methane production and added VS amount.

Specific- and ultimate-methane yields (m^3 kg^{-1} $VS_{\text{added waste}}$) in batch studies were calculated as the cumulative methane (ml) produced per g VS added (II-V) and before employing the treatments (VI) and expressed at 30-50 d (III-VI) and after 250-340 d of incubation respectively (IV-VI).

The un-ionised fraction of the ammonium-nitrogen (determined as described elsewhere (Perstop Analytical Tecator AB 1995) was calculated by the following equation:

$$F_{NH3} = (1 + 10^{(pK_w - pK_b - pH)})^{-1} \tag{i}$$

The values of the dissociation constant of water (K_w) and the ionisation constant of free-ammonia nitrogen (K_b) obtained from literature (Lide 1997) were pK_b = 9.25 and pK_w = 13.995 at 25°C and calculated to be pK_b = 4.733 and pK_w = 13.684 at 35°C.

Global Warming Potential (GWP) for the studied livestock type and manure management systems was estimated based on the methodology and default parameters recommended by Intergovernmental Panel on Climate Change (IPCC 1996). The GWP (over a 100 year period) of CH_4 and N_2O for an equivalent mass of CO_2 are 21 and 310 times respectively.

Total annual CH_4 emissions from domestic livestock (Gg) were calculated as the sum of emissions from enteric fermentation and manure management. The CH_4 emission from enteric fermentation (Mg a^{-1}) was obtained by multiplying the number of animals (1000s) with CH_4 emission factor for enteric fermentation (kg $head^{-1}$ a^{-1}). While CH_4 emissions from manure management (Mg a^{-1}) were calculated as the number of animals (1000s) times CH_4 emission factor for manure management (kg $head^{-1}$ a^{-1}). The emissions factors for enteric fermentation and manure management are 81 and 6 kg CH_4 $head^{-1}$ a^{-1} for dairy cattle and 1.5 and 4 kg CH_4 $head^{-1}$ a^{-1} for swine respectively.

Total annual N_2O emission (Gg) was obtained as nitrogen excretion (Nex) per animal waste management system (AWMS; kgN a^{-1}) times emission factor (EF_3) for AWMS (kg N_2O-N kgN^{-1}) multiplied by factor (44/28) x 10^{-6}.

Where, Nex per AWMS (kgN a^{-1}) is the number of animals (1000s) multiplied by Nex (kg $head^{-1}$ a^{-1}) and fraction of manure N per AWMS (%/100; fraction). Nex (kg $head^{-1}$ a^{-1}) values are 70 for dairy cattle and 20 for swine. EF_3 for anaerobic lagoon AWMS is 0.001. Ratio to convert N_2 to N_2O-N is 44/28.

The nitrogen use efficiency (amount of N available for plants in 100 kg applied N) for undigested and digested manure is 35-43% and 70-100% respectively (Klinger 1999). The amount of inorganic fertilizer that could be saved due to the increased efficiency of the digested manure was determined by multiplying the difference in efficiencies (70-35 = 35%) with the total N content in the digestate. Considering conversion factor of 2%, the N_2O emission from applied N fertilizer (t) was thus calculated as the quantity of N fertilizer (t) applied times 0.02. Literature shows values ranging from 0.25 to 2.25% (IPCC 1997). A carbon tax of 40 EURO t^{-1} of CO_2 produced was used throughout the study (IPCC 2001).

The GWP (over a 100 year period) of CH_4 and N_2O for an equivalent mass of CO_2 are 21 and 310 times respectively (IPCC 1996).

3.4.4 Energy equivalents and conversion factors

Energy equivalents were calculated as per the values referred by (ETSU 1997).

One cubic metre of biogas in a CHP unit would produce 1.7 kWh of electricity and 2 kWh of heat. To produce 1 MWh of electricity from coal, 0.8684 t of CO_2 is generated (IPCC 1996). To produce 1 kg N as inorganic fertilizer, 2 kg of mineral oil is needed (Klinger 1999). The energy value of 1 t of oil is 12 MWh.

4 RESULTS AND DISCUSSION

4.1 Anaerobic digestion of manures

4.1.1 Biochemical methane potential of livestock manures with and without inoculation

The methane production rate and yield of dairy cow, pig and sow manures was investigated in batch assays (122 d) at 35°C with and without addition of mesophilically digested cow manure (I). Manures incubated with acclimatized inocula produced specific methane yields (m^3 kg^{-1} $VS_{added\ waste}$) of 0.13-0.16, 0.36 and 0.54 for dairy cow, pig and sow manures respectively (Table 7). However, pig manure followed by cow manures would give more methane per ton of material than the studied sow manure. These specific methane yields (m^3 kg^{-1} $VS_{added\ waste}$) were in agreement to the yields of 0.11-0.24 reported for cow manure (Zeeman 1991; Hansen et al. 1998; Francese et al. 2000; Moller 2000; Sommer et al. 2002) and 0.30 (Hansen et al. 1998); 0.32 (Moller 2000; Sommer et al. 2002); 0.50 ±0.05 (Hashimoto et al. 1981) reported for swine manures in laboratory batch digestion at 35°C. Manures incubated as such on the other hand also produced specific methane yields (m^3 kg^{-1} $VS_{added\ waste}$) of 0.08-0.07 for cow manures, 0.26 for pig and 0.27 for sow manures which indicates the potential for GHG emissions under optimal conditions, if not recovered. Ability for manures to produce methane without inoculation also suggests that farm-scale biogas plants can be started without the use of acclimatized inocula. However, incubation of manures as such would result in delayed methanation and low methane yields (Fig. 2). The probable reason for delayed methanation is due to the time required for the complex, mixed bacterial population to transform into a highly effective flora and due to the lack of sufficient numbers of pertinent bacteria at all critical stages of fermentation (Chen & Hashimoto 1996).

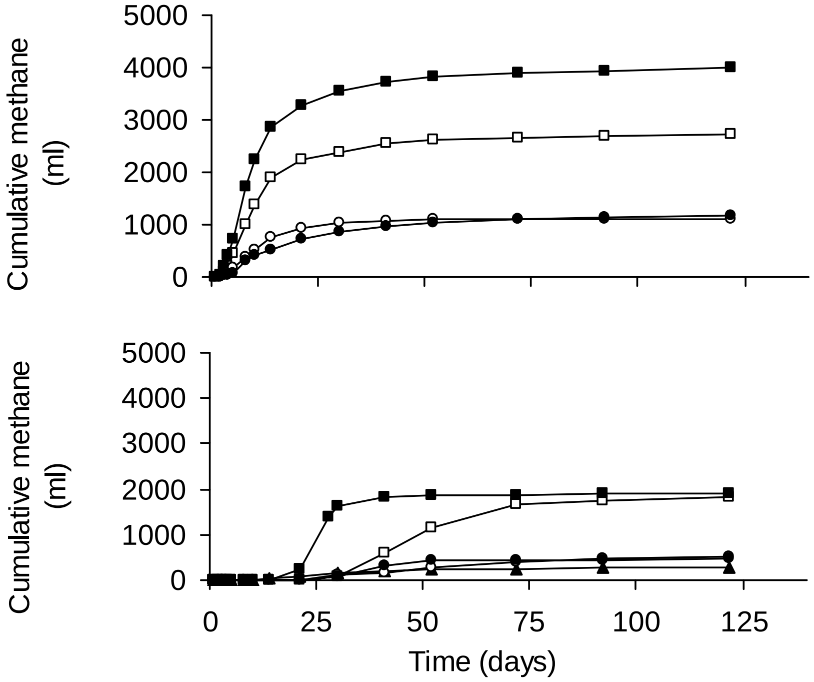

FIGURE 2 Cumulative methane production of manures incubated in batch assays at 35±1°C with mesophilically digested cow manure used as inoculum (above; inoculum methane extracted from the samples) and without inoculum (below). Inoculum ▲; pig manure □; sow manure ■; Halsua cow manure ○ and Laukaa cow manure • (I).

TABLE 7 Specific methane yield from various farm animal manures digested in batch assays with and without inoculum (mesophilically digested cow manure) at 35±1°C (I).

Treatment	Specific methane yield[1]					
	Without inoculum	With inoculum	Without inoculum	With inoculum	Without inoculum	With inoculum
	(m^3 kg^{-1} TS)		(m^3 kg^{-1} VS)		(m^3 t^{-1} of waste)	
Inoculum (control)	--	0.03	--	0.04 (0.004)	--	1.9 (0.017)
Sow manure	0.19 (0.03)	0.35 (0.03)	0.27 (0.04)	0.54 (0.03)	2.1 (0.32)	4.1 (0.16)
Pig manure	0.18 (0.02)	0.29 (0.02)	0.26 (0.03)	0.36 (0.03)	15.9 (0.17)	21.5 (0.16)
Halsua cow manure	0.06 (0.005)	0.14 (0.01)	0.08 (0.03)	0.13 (0.04)	4.9 (0.43)	8.4 (0.08)
Laukaa cow manure	0.06 (0.009)	0.17 (0.009)	0.07 (0.01)	0.16 (0.04)	4.9 (0.74)	11.9 (0.04)

[1] methane yield of inoculum subtracted and values in parentheses are standard deviation.

4.1.2 Semi-continuous anaerobic digestion of manures

The performance of semi-continuous digestion of dairy cow and swine manures obtained from different farms was investigated in laboratory CSTRs at 35°C with an aim to design full-scale application (I). Anaerobic digestion was feasible with loading rate up to 2 kg VS m^{-3} d^{-1}, feed VS of 6% and HRT of 30 d as methane production in most runs responded exponentially to feeding and no increased trend in digestate SCOD was noticed (Figs. 3-5). The present study and previous studies suggest that digesters treating dairy cow and pig manure in CSTR-systems at 35°C could be operated at a loading rate of 2 kgVS m^{-3} d^{-1} and HRT of 30 d. Literature indicates that this loading rate seems to be optimum than the any other published data of 1.8 to 4.2 kgVS m^{-3} d^{-1} for cow manure (see e.g. Bruke 2001) and 1 to 4 kgVS m^{-3} d^{-1} for pig manure (reviewed by Boopathy 1998) digested in CSTR over a long period. The mean specific methane yields for pig manure (Fig. 3) ranged from 0.30 to 0.32 m^3 kg^{-1} $VS_{added\ waste}$ (Table 8). A similar performance was also noticed with cow manure (Fig. 4), except that the specific methane yields during the same periods were 50-55% of those obtained with pig manure. Specific methane yield for sow manure (Fig. 5) operated at 0.38 kgVS m^{-3} d^{-1}, feed VS of 0.77% and HRT of 20 d ranged between 0.14 and 0.19 m^3 kg^{-1} $VS_{added\ waste}$. Methane yields obtained in semi-continuous digestion were comparable to the yields of 0.11-0.24 m^3 kg^{-1} VS fed reported for cow manure in laboratory studies at 35°C (Zeeman 1991; Hansen et al. 1998; Francese et al. 2000; Sommer et al. 2002). For instance, Zeeman (1991) has reported a methane yield of 0.168 m^3 kg^{-1} $VS_{added\ waste}$ for dairy cow slurry digested in CSTR at 30 d HRT and 35°C. However, the yields obtained for cow manure in the present laboratory study were significantly lower than the yields of 0.20-0.25 m^3 kg^{-1} VS fed reported in farm-scale digestion (Baader et al. 1984; Moller 2000). Unlike for cow manure, methane yields achieved for sow (0.14-0.19 m^3 kg^{-1} $VS_{added\ waste}$) and pig manures (0.30-0.32 m^3 kg^{-1} $VS_{added\ waste}$) can be compared to the yields of 0.25 and 0.30 m^3 kg^{-1} VS fed reported during the full-scale digestion of sow and pig manures respectively (Pind 2001). This study suggests that basic data such as manure characteristics and its methane potential and management practices are essential while designing farm biogas plants. Further, information pertaining to one farm can also be considered as a benchmark for designing biogas plants on farms with similar farm configuration. For instance, methane yields achieved for dairy cow manures procured from different farms, which had only little variation in manure characteristics, produced similar specific methane yields (0.13-0.16 m^3 kg^{-1} $VS_{added\ waste}$) in batch experiments.

The faster and higher specific methane production noticed for swine manures than dairy cow manure could be due to the difference in the amount of readily available SCOD and/or volatile fatty acids (VFAs, not measured). For instance, swine manures (38-42%) in this study had a higher ratio of SCOD/TCOD than cow manures (7%) suggesting a faster methane production potential for former than latter substrates. In addition, the higher VS, fat and anaerobically degradable dissolved organic components and lower water content and carbon to nitrogen ratio generally noticed in swine manures than in cow manure (Zeeman 1991; Steffen et al. 1998) makes swine manures as better substrates for methanogenesis than cow manures (Zeeman 1991; Husted 1994). Further, hydrolysis of compounds such as cellulose, hemicellulose when constituted with lignin are usually difficult-to-digest and are present in a higher proportion in cow manure (Zeeman 1991) and are considered limiting factor for methanation as proved experimentally by Noike et al. (1985), as also suggested by the potential for methane production during post-digestion (IV). The fact that cow manure is a product of partially digested material from the rumen is also considered as the reason for higher methane yields by pig manure than cow manure (Zeeman 1991). Finally, manures from different animals probably contain different species of anaerobic bacteria, which may be better adapted or acclimatized to inhibitive components.

TABLE 8 Loading rate, HRT, methane yield and methane content (values in parentheses are standard deviation) in the biogas produced during selected periods of semi-continuous digestion of sow, pig and cow manures in CSTR at 35±1°C (I).

Digester	Loading rate (kgVS m^{-3} d^{-1})	HRT (d)	Days of operation	Methane yield		Methane content (%)
				(m^3 kg^{-1} VS$_{\text{added waste}}$)	(m^3 t^{-1} feed)	
Sow manure	0.38	20	14-45	0.14 (0.1)	1.08	48-50 (8)
			97-115	0.19 (0.07)	1.46	50 (6)
Pig manure	2.0	30	14-45	0.30-0.32 (0.03)	18-19	56-58 (6)
			97-115	0.25 (0.07)	15	57 (5)
Cow manure	2.0	30	14-45	0.13-0.16 (0.02)	7.8-9.6	50-54 (6)
			97-115	0.11 (0.03)	6.6	47 (8)

The NH_4^+-N concentrations (Table 9) in the digesters reached from an initial 1.3 gl^{-1} to as high as 3.9 gl^{-1} (final values) in pig manure (Fig. 3), from 1.4 to 2.2 gl^{-1} in cow manure digester (Fig. 4) and from 1.2 to 1.6 gl^{-1} in sow manure digester (Fig. 5). The NH_4^+-N levels in this study were similar to those reported during the mesophilic digestion of cow manure (Sanchez et al. 2000) and pig manure (Angelidaki & Ahring 1993) in CSTR but never reached the levels of >4 gl^{-1}, considered to cause inhibition in cattle manure digestion (Angelidaki & Ahring 1993). Moreover, the corresponding free-ammonia values 0.12-0.14 gl^{-1}; pH 7.6) for sow manure, 0.20 gl^{-1} (pH 7.8) for cow manure and 0.35 gl^{-1} (pH 7.8) for pig manure) in this study were much lower than the values of 0.70 gl^{-1} for cattle manure (Angelidaki & Ahring 1993) and 1.1 gl^{-1} for swine manure (Hansen et al. 1998) needed to introduce severe ammonia inhibition. Thus, the underline mechanism for the successful operation of the digesters despite noticing a gradual accumulation of NH_4^+-N could be due to a slow adaptation of the methanogens to these concentrations over a long period of time. Previous studies also have shown that digestion process can be adapted without any reduction in methane yields at an NH_4^+-N concentration of 4 gl^{-1} for cattle manure (Angelidaki & Ahring 1993) and 6 gl^{-1} for pig manure (Hansen et al. 1998). Contrastingly, for an unadapted methanogenic culture, ammonia inhibition can commence at concentrations of 1.5-2.5 gl^{-1} (Angelidaki & Ahring 1993).

TABLE 9 Characteristics of digestates (day 133) sampled during semi-continuous digestion of sow, pig and cow manures in CSTR at 35°C (I).

Characteristics	Sow manure	Pig manure	Cow manure
pH	7.6	7.7	7.5
TS (%)	0.74	5.1	4.3
VS (%)	0.38	4.2	3.2
Ash (% of TS)	48.6	12.5	25.9
TKN (gl^{-1})	1.9 (1.3)	5.8 (5.5)	3.8 (3.9)
NH_4^+-N (gl^{-1})	1.6 (1.1)	3.9 (4.4)	2.2 (2.8)
NH_4^+-N/TKN (%)	82	68	57
SCOD (gl^{-1})	2.19	6.21	2.31

Note: values in parentheses are data analysed at the end of 60 unfed days.

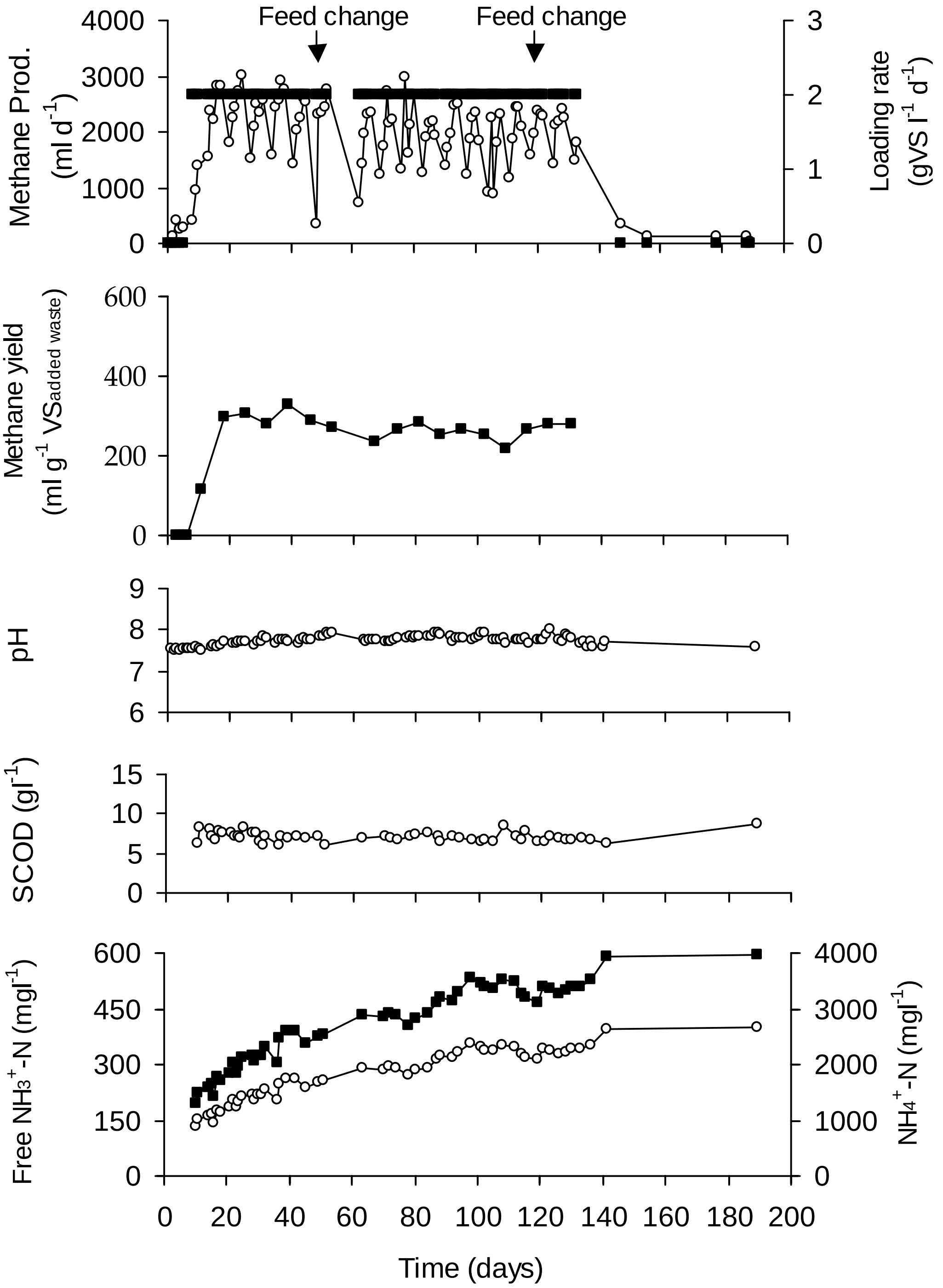

FIGURE 3 Mesophilic digestion of pig manure in CSTR: (a) Loading rate ■; methane yield ○, (b) Specific methane yields ■ (c) pH, (d) SCOD, (e) Free ammonia-nitrogen (NH_3^+-N; ○) and ammonium-nitrogen (NH_4^+-N; ■) concentration in the digestate (I).

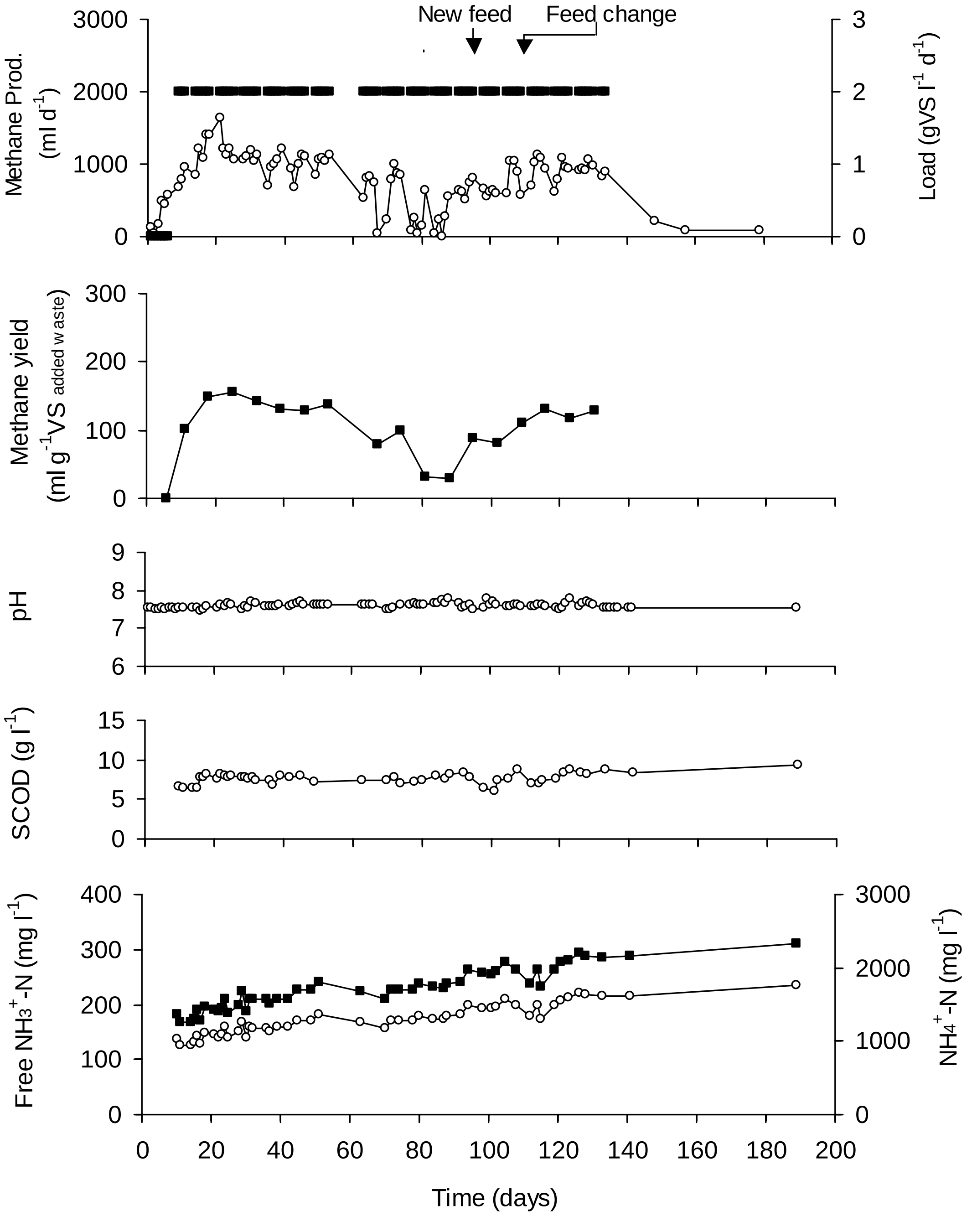

FIGURE 4 Mesophilic digestion of dairy cow manure in CSTR: (a) Loading rate ■; methane yield ○, (b) Specific methane yields ■ (c) pH, (d) SCOD, (e) Free ammonia-nitrogen (NH_3^+-N; ○) and ammonium-nitrogen (NH_4^+-N; ■) concentration in the digestate (I).

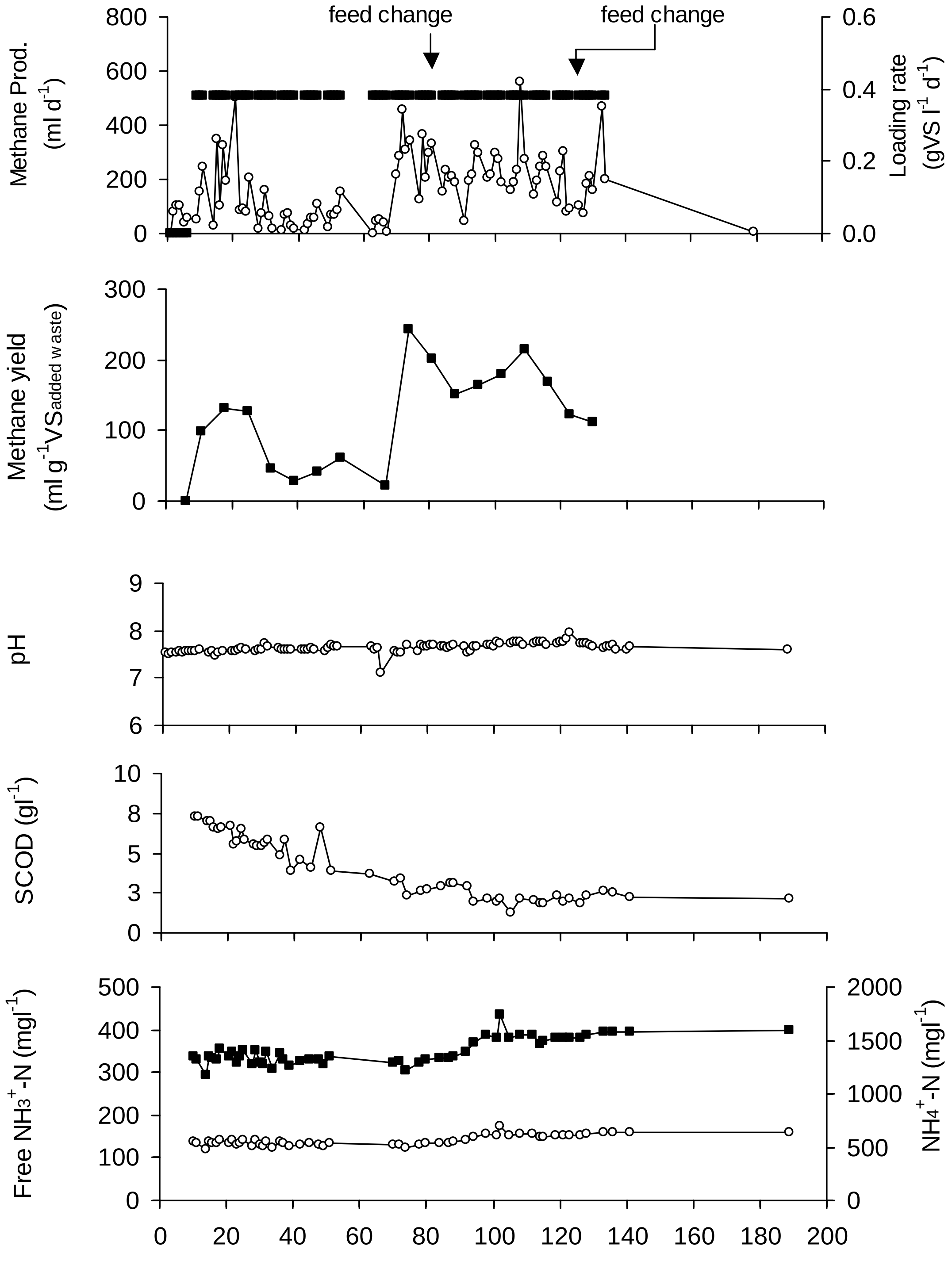

FIGURE 5 Mesophilic digestion of sow manure in CSTR: (a) Loading rate ■; methane yield ○, (b) Specific methane yields ■ (c) pH, (d) SCOD, (e) Free ammonia-nitrogen (NH_3^+-N; ○) and ammonium-nitrogen (NH_4^+-N; ■) concentration in the digestate (I).

4.2 Anaerobic co-digestion

4.2.1 Evaluation of energy crops and confectionery by-products as potential co-substrates

The use of various energy crops and confectionery by-products as possible co-substrates for manure co-digestion was evaluated in batch experiments (155 d) at 35°C using mesophilically digested cow manure as inocula (II). Methane production in all assays was delayed by 1-3 d and accounted for prolonged time (Fig. 6). For the studied co-substrates, methanation was first noticed in grass hay followed by clover, black candy, chocolate, confectionery raw material (CRM) and oats. By day 22 (corresponding HRT of farm digester), ca. 70 to >95% and 83 to 95% of the ultimate methane yields was realized for energy crops and confectionery by-products respectively (Table 10). Among the confectionery by-products, highest specific methane yield (m^3 kg^{-1} VS) was produced by black candy (0.39) followed by chocolate (0.37) and CRM (0.32) corresponding to methane yields of 284-346 m^3 t^{-1} of by-product. While grass hay produced the highest specific methane yield per kgVS followed by oats and clover whereas, per ton of material oat had the highest yield (Table 10).

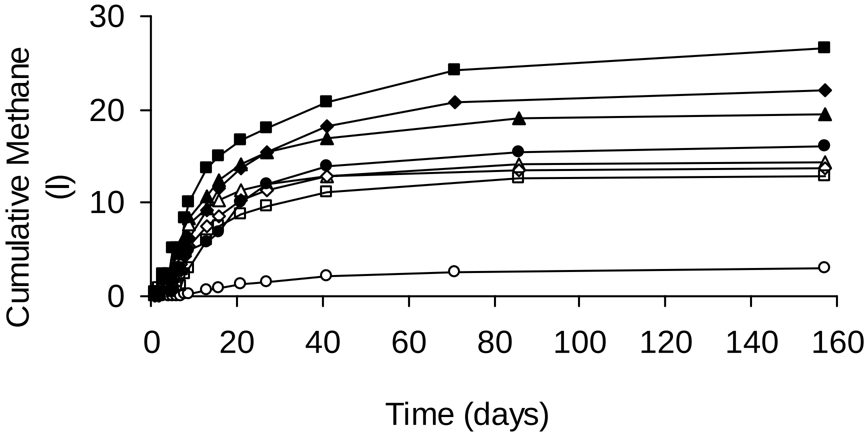

FIGURE 6 Mean cumulative methane production from energy crops: clover (2 cm, vegetative, ▲), clover (2 cm, flowering, ●), grass hay (1 cm ■), oats (0.5 cm ♦) and confectionery by-products: chocolate (◊), black candy (Δ) and confectionery raw material (□) co-digested with digested cow manure, control (○) under batch assays at 35°C.

TABLE 10 Specific methane yields, pH, soluble chemical oxygen demand (SCOD) for various energy crops and confectionery by-products with digested cow manure as inoculum in batch assay at 35°C (II).

Substrate	Particle size	pH (final)	SCOD (final)	Specific methane yield[1]			Methane yield on Day 22 to ultimate yield[1]
	(cm)		(gl^{-1})	(m^3 kg^{-1} TS)	(m^3 kg^{-1} VS)	(m^3 t^{-1} of material)	(%)
Energy crops							
Clover (flr.)	2	7.69	7.6	0.12	0.14 (0.01)	16.7	90.6
Clover (veg.)	2	7.61	5.9	0.19	0.21 (0.02)	35.5	98.6
	1	7.61	5.4	0.13	0.14 (0.02)	23.7	96.8
	0.5	7.62	5.6	0.18	0.20 (0.02)	33.8	97.4
Grass hay	2	7.46	8.3	0.25	0.27 (0.03)	63.7	79.3
	1	7.48	8.4	0.32	0.35 (0.02)	82.6	73.3
	0.5	7.48	8.3	0.29	0.32 (0.02)	75.5	83.8
Oats	2	7.44	6.7	0.23	0.25 (0.02)	139	70.0
	1	7.43	7.2	0.23	0.25 (0.02)	139	72.4
	0.5	7.47	7.6	0.24	0.26 (0.03)	145	77.0
Confectionery by-products							
Chocolate	--	7.54	6.1	0.36	0.37 (0.03)	346	90.4
Black candy	--	7.44	6.6	0.36	0.39 (0.03)	305	94.6
CRM	--	7.42	4.6	0.32	0.32 (0.03)	284	83.5
Inoculum	--	7.41	6.3	0.11	0.18 (0.01)	3.0	41.7

[1] methane yield of inoculum subtracted; values in parentheses are standard deviation.

4.2.2 Effect of particle size reduction as pre-treatment and crop maturity on methane production of energy crops

The effects of particle size (2, 1 and 0.5 cm) and crop maturity (vegetative and flowering stage) on methane yields of energy crops were investigated in batch experiments (155 d) at 35°C (II). The effects of particle size were different for different energy crops (Table 10). For oats no effect was observed, whereas, 1 cm size was optimal for grass hay and least optimal for clover. The methane yields were ca. 10-30% higher at optimal particle sizes as compared to the least optimal ones. This response of particle size reduction on methane production in grass hay might be due to a lower lignin content in grass hay than compared to clover and oats (Moore 1958). Sharma et al. (1988) while testing five particle sizes (0.088, 0.40, 1, 6 and 30 mm) reported an increase in methane yields with decrease in particle size. The increase in biogas was 4-10% when the particle sizes were 0.088 and 0.4 mm for raw materials like wheat straw, rice straw, and Bermuda grass (Sharma et al. 1988). Stage of the crop also influenced the methane yields. For the same particle size (2 cm), clover harvested during the vegetative stage produced 33% higher methane yield than when harvested during the flowering stage indicating that the lignin content in the crop increases with crop maturity. These results also indicate that the anaerobic digestibility is highly correlated with the lignin content in the plants and the hydrolysis of lingo-celluloses is generally dependent on the lignin to cellulosic ratio (Scharer & Moo-Young 1979). Shiralipour & Smith (1985) demonstrated that the age of Napier grass at harvest time influenced the methane yields as young tissues produced more methane than the old tissues, probably because younger tissues are less lignified. However, studies by Pouech et al. (1998) showed that crop maturity was weakly influential on methane yields for wheat, clover and ray-grass.

4.2.3 Co-digestion of potato tuber and its industrial by-products with pig manure in CSTR

Effects of the change in feed component ratio of pig manure to potato co-substrates (potato tuber, potato stillage and potato peel) on process performance in a semi-continuous co-digestion was evaluated in CSTR at 35°C (II). Co-digestion of pig manure and potato waste at 90:10 feed component ratio (loading rate of 2 kgVS m^{-3} d^{-1}; HRT of 23-32 d) resulted in a sharp decrease in pH from 8.1 to 7.1 and cessation of methane production within 4 days of operation. Therefore, feeding was temporarily withheld for a fortnight in an attempt to restore process stability. Upon attaining stable methane production (50% methane content), feeding was resumed at the same loading rate of 2 kgVS m^{-3} d^{-1} (44 d HRT) but with pig manure alone (days 22-32). Feeding with pig manure alone produced a stable methane production in the respective digesters. For the different co-digestions, methane production during days 22-32 ranged between 0.13 and 0.15 m^3 kg^{-1} $VS_{\text{added waste}}$ (methane content of 61-63%). On observing normal digester performance, co-digestion was once again resumed on day 33 with a loading rate of 2 kgVS m^{-3} d^{-1}, HRTs of 39 d and feed VS ratio of 85:15 (pig manure to potato waste) and continued for 58 d (Table 11). Operating the digesters at this loading rate, feed VS ratio was increased to 80:20, and co-digestion was continued for a further 33 days at HRTs 26-27 d (from days 92-123) and for 42 days at HRTs 25-26 (from day 124 to day 165). From days 166 to 194, the loading rate was increased from 2 to 3 kgVS m^{-3} d^{-1} (HRT 38-39 d) without changing the feed VS ratio of 80:20 (pig manure to potato waste).

The effect of waste proportion in the feed mixture on process performance appears to be important. Loading rate of 2 kgVS m^{-3} d^{-1} and feed VS of up to 15-20% of potato waste was found feasible for anaerobic co-digestion (Figs. 7-9). The higher specific methane yields (m^3 kg^{-1} $VS_{\text{added waste}}$) of 0.21-0.24 and 0.30-

0.33 obtained at 85:15 and 80:20 feed ratio (VS% pig manure to VS% potato waste) respectively than 0.13-0.15 m^3 kg^{-1} VS $_{\text{added waste}}$ achieved on digestion of pig manure alone (100:0 feed ratio) was apparently due to a higher methane potential for potato co-substrates than pig manure. However, it should be noted that the runs were only 1.3 to 1.6 HRTs, which are quite short for achieving stable conditions.

TABLE 11 Loading rate, feed VS ratio and methane production of potato peel, potato stillage and potato tuber co-digested with pig manure in CSTR at 35±1°C (III).

Load (kgVS m^{-3} d^{-1})	Feed ratio (VS %)		HRT	Days	Methane yields (m^3 kg^{-1} VS $_{\text{added waste}}$)	Methane yields (m^3 t^{-1} of feed)	Methane content (%)
	Pig manure	Potato peel	(d)				
2	90	10	32	1-6	0.01 (0.1)	3.2	8 (6)
2	100	--	44	22-32	0.15 (-)	10.3	63 (2)
2	85	15	39	33-91	0.24 (0.04)	16.7	60 (3)
2	80	20	27	92-123	0.33 (0.03)	23.1	62 (3)
2	80	20	26	124-165	0.33 (0.02)	22.8	62 (3)
3	80	20	39	166-194	0.30 (0.05)	30.9	63 (2)
	Pig manure	Potato stillage					
2	90	10	23	1-6	0.01 (0.2)	1.0	9 (7)
2	100	--	44	26-32	0.13 (-)	9.2	61 (3)
2	85	15	39	33-91	0.23 (0.03)	15.3	60 (4)
2	80	20	26	92-123	0.31 (0.07)	21.3	60 (2)
2	80	20	25	124-165	0.33 (0.02)	23.0	60 (1)
3	80	20	38	166-194	0.30 (0.04)	31.0	61 (2)
	Pig manure	Potato tuber					
2	90	10	34	1-6	0.01 (0.3)	0.7	7 (6)
2	100	--	44	26-32	0.13 (-)	9.0	61 (1)
2	85	15	39	33-91	0.21 (0.02)	14.6	63 (4)
2	80	20	27	92-123	0.30 (0.08)	21.3	61 (3)
2	80	20	26	124-165	0.33 (0.08)	22.8	60 (2)
3	80	20	39	166-194	0.28 (0.03)	29.1	58 (4)

Note: values in parentheses are standard deviation.

The high methane potential achieved by co-digestion of potato waste was probably due to the high anaerobic degradability ca. 90-100% of the starch, the main component of potato waste (Stewart et al. 1984). For comparison Stewart et al. (1984) reported a methane yields of 0.426 m^3 kg^{-1} VS $_{\text{added waste}}$ on continuous digestion of potato waste (peel and rejects) at a loading rate of 2.5 kgVS m^{-3} d^{-1} in a 20 l CSTR at 35°C and 20 d HRT. Weiland (1993) reported successful digestion of potato pulp (18-21% TS) or potato thick stillage (14-18% TS) with a 50-70% degradation and biogas yields of 300-500 m^3 per ton of dry matter. Whereas, the ultimate biodegradability reported for potato peel in a 37-85 d (35°C) batch digestion at a substrate to inoculum ratio of 0.8 was 86-91% (Kang & Weiland 1993). Nevertheless, co-digestion in the present context should be considered as a process for simultaneous treatment of two different waste streams and as a solution to the problems of ammonia inhibition generally encountered during pig manure digestion and "souring" of readily acidifying potato waste which is basically low in pH. The successful operation at the feed VS ratios of 80-85 to 15-20 (pig manure to potato wastes) could be due to synergy between pig manure and potato waste by the release of ammonia, pig manure provided the necessary buffering (Wilkie et al. 1986; Angelidaki & Ahring 1993) to counterbalance the potential of rapid accumulation of VFA produced from the highly degradable potato waste. Compared to effects of feed component ratio, loading rate seems have less effect on process performance. Under similar feed VS ratio of 80:20 (pig manure to potato waste), increasing the loading rate from 2 to 3 kgVS m^{-3} d^{-1} resulted in yield decrease from 0.30-0.33 to 0.28-0.30 m^3 kg^{-1} VS $_{\text{added waste}}$ (Figs. 7-9).

The study also revealed that co-digestion of potatoes and its industrial by-products with pig manure, if performed under identical process conditions such as same total feed VS, loading rate, HRT, and feed VS ratio would result in similar process performance (such as quality of digestate, NH_4^+-N and SCOD concentrations and trends, pH and methane production). Moreover, methane per ton of feed was found to be similar with the three co-substrates even though the chemical composition of potato stillage was slightly different to that of potato peel or potato tuber (Table 3).

TABLE 12 Characteristics of digestates sampled on day 154 (beginning of post-treatment expt.) and at the end of (day 194) the semi-continuous co-digestion of potato peel, potato stillage, potato tuber with pig manure in CSTR at 35°C (III).

Digested material/ Characteristic	Potato peel		Potato stillage		Potato tuber	
	Day 154	Day 194	Day 154	Day 194	Day 154	Day 194
pH	7.8	7.9	7.8	7.8	7.8	7.8
TS (%)	3.5	4.4	3.9	3.7	4.0	4.2
VS (%)	2.5	3.1	2.8	2.7	3.0	3.1
TKN (gl^{-1})	4.9	5.1	4.5	4.7	4.6	4.7
NH_4^+-N (gl^{-1})	3.4	3.3	3.1	3.5	2.9	3.4
NH_4^+-N /TKN (%)	69	65	69	74	63	72
SCOD (gl^{-1})	7.7	8.0	8.5	9.1	7.0	7.4

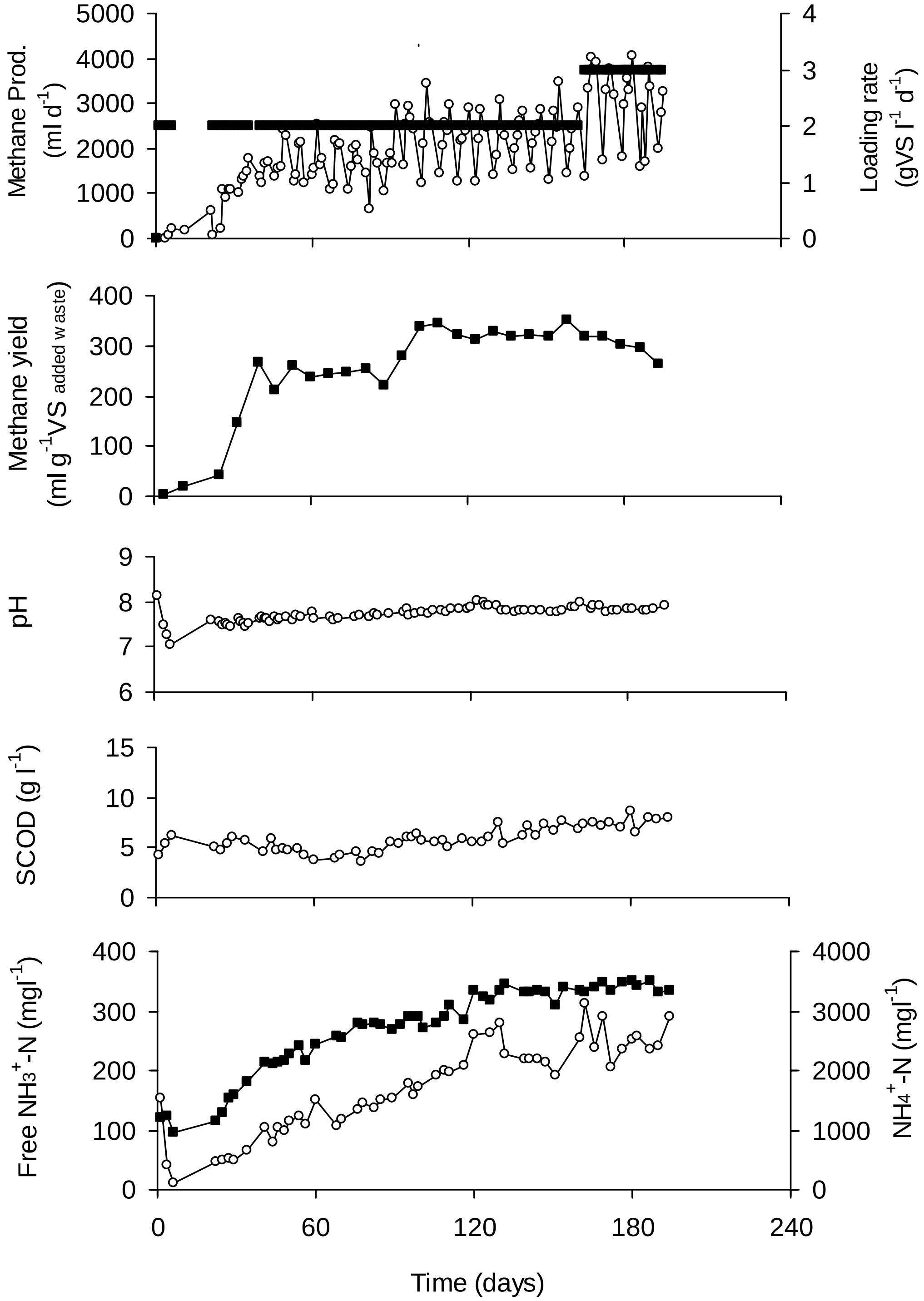

FIGURE 7 Co-digestion of potato peel with pig manure at 35°C in CSTR: (a) ■ Load, ○ methane yield, (b) ■ specific methane yields per gram volatile solids, (c) pH, (d) soluble chemical oxygen demand (SCOD), (e) ○ free ammonia-nitrogen (NH_3^+-N;) and ■ ammonium-nitrogen (NH_4^+-N) concentration in the digestate (III).

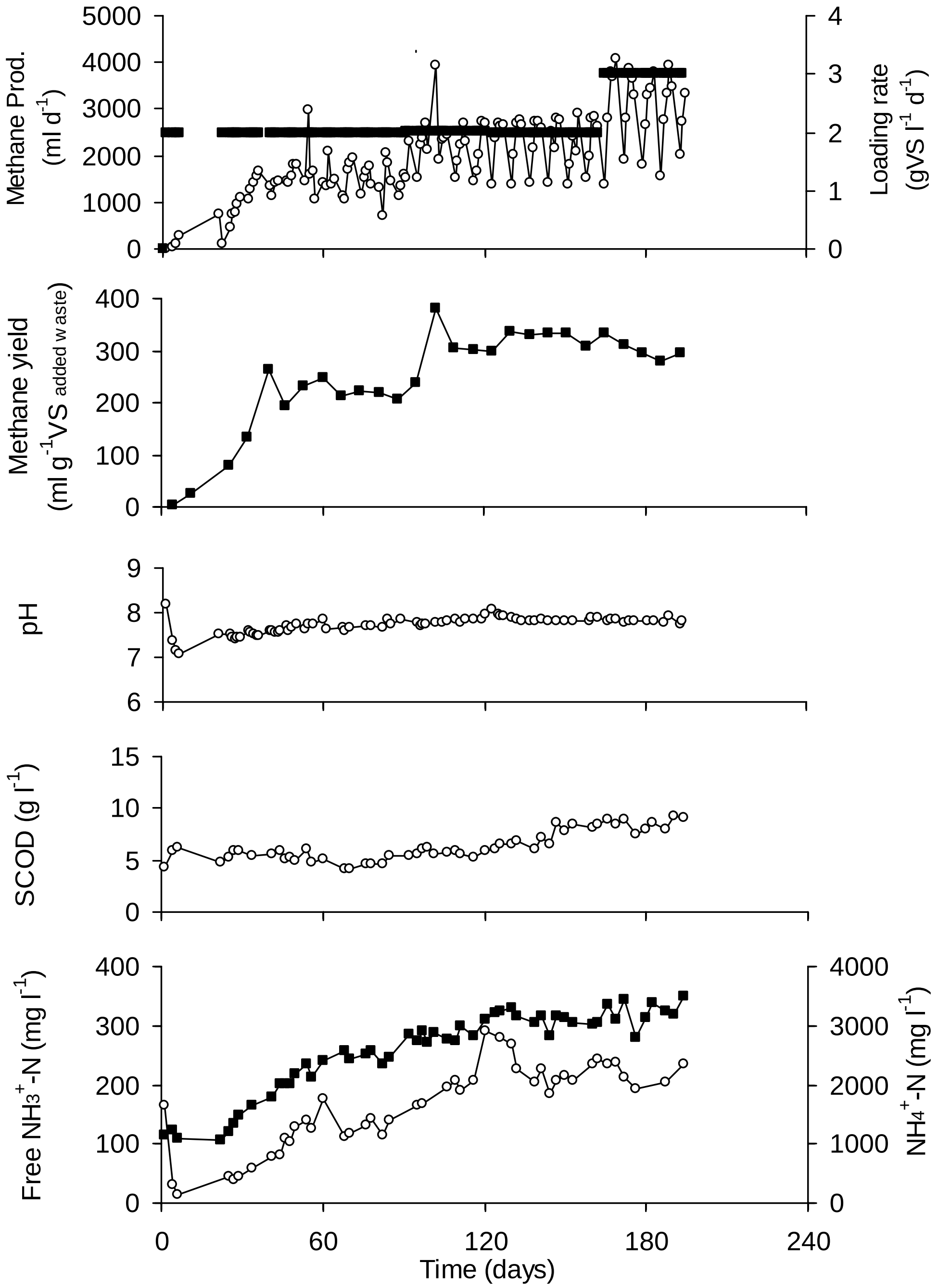

FIGURE 8 Co-digestion of potato stillage with pig manure at 35°C in CSTR: (a) ■ Load, ○ methane yield, (b) ■ specific methane yields per gram volatile solids, (c) pH, (d) soluble chemical oxygen demand (SCOD), (e) ○ free ammonia-nitrogen (NH_3^+-N;) and ■ ammonium-nitrogen (NH_4^+-N) concentration in the digestate (III).

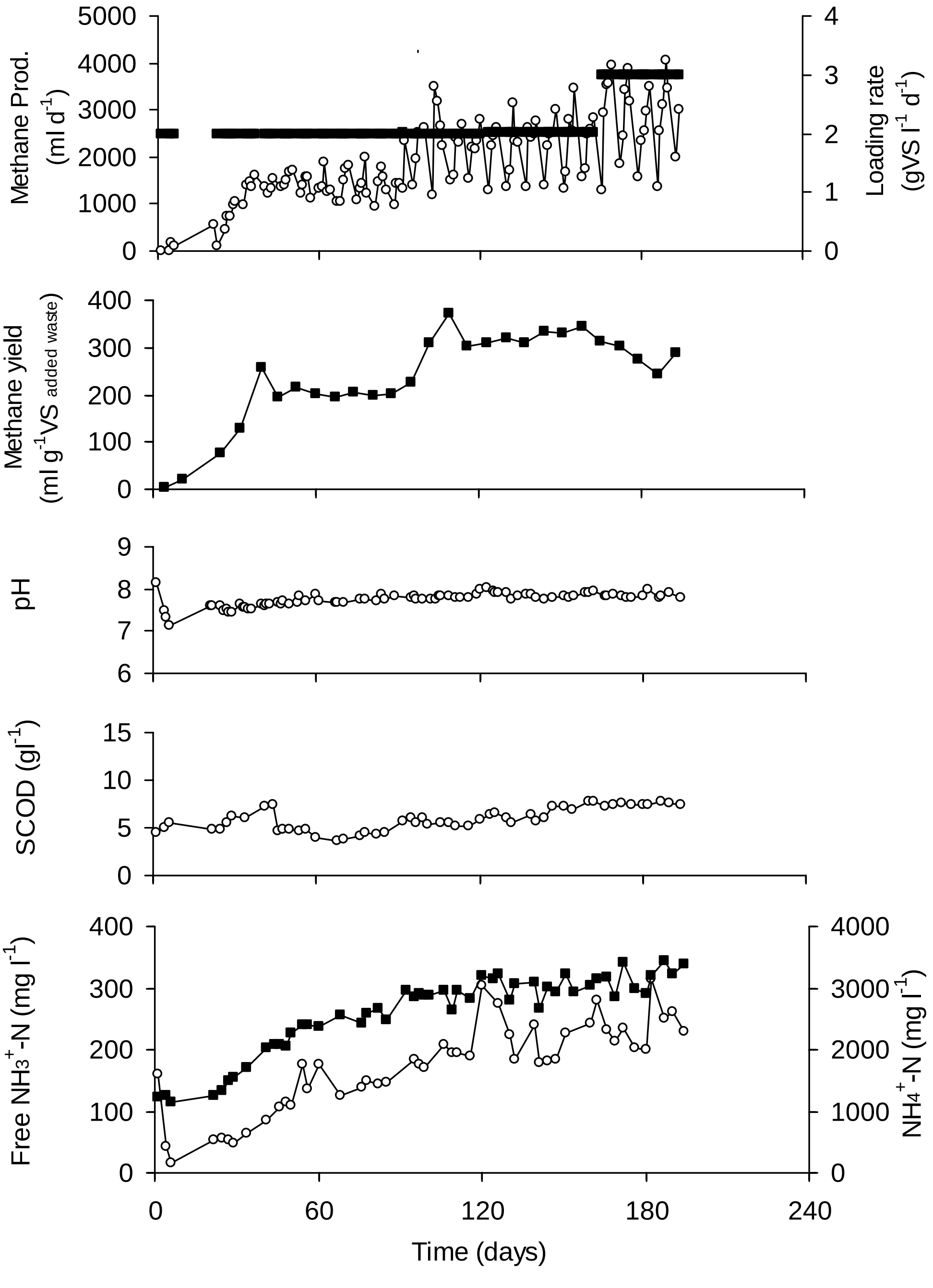

FIGURE 9 Co-digestion of potato tuber with pig manure at 35°C in CSTR: (a) ■ Load, ○ methane yield, (b) ■ specific methane yields per gram volatile solids, (c) pH, (d) soluble chemical oxygen demand (SCOD), (e) ○ free ammonia-nitrogen (NH_3^+-N;) and ■ ammonium-nitrogen (NH_4^+-N) concentration in the digestate (III).

One ton of potatoes when co-digested with 12-15 m^3 of pig manure would produce 328 m^3 of methane. Thus, 5248 m^3 of methane would be generated from one ha of potatoes (@ 16 t of potatoes per hectare). In this way, the amount of energy that could be generated from one hectare potato harvest (tubers) would be equivalent to 51 MWh a^{-1} of heat or 6.3 MWh a^{-1} of electricity. Similarly, for the starch industry, 0.9 MWh a^{-1} electricity or 7.1 MWh a^{-1} heat could be generated when a ton of potato stillage is co-digested with 30 m^3 of pig manure.

4.2.4 Full-scale co-digestion of energy crops and/or industrial confectionery by-products with cow manure in a farm biogas plant

The feasibility of full-scale co-digestion of energy crops and/or confectionery by-products was evaluated in a farm-scale biogas plant (II). Digester has been in operation since 1998. Co-digestion with energy crops and/or confectionery by-products was taken up in spring 2000 (Fig. 10). During this period, the digester showed reliable performance with both co-substrates, confectionery by-products and energy crops. Approximately 40 to 50% of VS were degraded with <100-200 mg l^{-1} of volatile fatty acids (data not shown) and 0.6-1.7 gl^{-1} of NH_4^+-N concentration in digestate. Digestion of cow manure alone produced an average specific methane yield of 0.22 m^3 kg^{-1} $VS_{\text{added waste}}$. Addition of confectionery by-products increased the specific methane yield to about 0.28 m^3 kg^{-1} $VS_{\text{added waste}}$ whereas, with energy crops methane yield was about similar to that obtained from cow manure alone (ca. 0.21 m^3 kg^{-1} $VS_{\text{added waste}}$). The plant produced about 150 m^3 d^{-1} biogas (55-58% CH_4 content) per 6 m^3 biomass in co-digestion of confectionery by-products and cow manure. Without confectionery by-products, that amount of manure yielded about 85 m^3 of biogas. These figures also include biogas from the post-storage tank. The reason for higher biogas yields upon co-digestion of manure with confectionery by-products than manure alone was due to the fact that confectionery by-products are easily degradable and have higher methane potential than manure or energy crops (see previous section 4.2.1). Previous experiences on full-scale co-digestion at 30-33°C also showed an immediate increase and doubling in biogas yields after 60 h of addition of pure fat to cattle slurry at feed VS ratio of 20 to 80% respectively with 74% VS degradation (Amon et al. 1998). In that study, the mean methane yields (over a period of 3 d after the addition) with and without fat addition amounted 54 and 31.3 m^3 h^{-1} respectively. These results and those from existing full-scale application suggests that co-digestion of organic wastes with agricultural manures would enhance the methane yields in a farm-scale biogas system. However, the composition and amount of the added organic wastes should be appropriate to avoid process failure, low biogas quality and operational hazards.

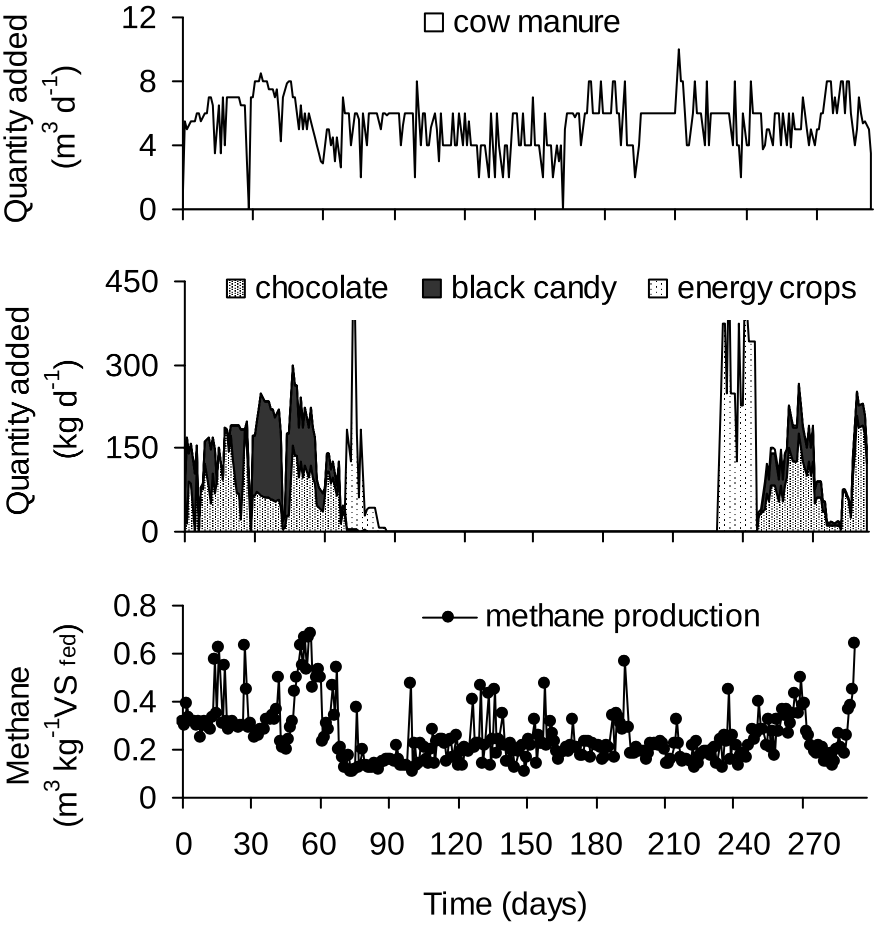

FIGURE 10 The added amounts of cow manure (a), energy crops and confectionery by-products: chocolate and black candy (b) and the methane production (c) during the mesophilic co-digestion in a farm-scale digester (Day 0 = 6.2.2000) (II).

4.3 Post-methanation

The effects of post-methanation to recover the remaining methane potential of the digested materials sampled from a laboratory CSTR (I, III) and, full-scale farm digester and its associated post-storage tank (IV-VI) were investigated in laboratory batch experiments.

4.3.1 Post-methanation of digested materials: effect of temperature

The effect of temperature on the digested materials sampled from an on-farm digester (35°C) and digester's associated post-storage tank (5-10°C) was studied in batches at 5, 10, 15 and 20°C and as reference at 35 and 55°C (IV). Long-term incubation of materials as such produced specific methane yields (m^3 kg^{-1}

VS$_{\text{added waste}}$) of 0.20-0.26 at 35-55°C and 0.085-0.09 at 10-20°C for digester material (345 d) and 0.16-0.21 at 35-55°C, 0.053-0.087 at 15-20°C and 0.026 at 10°C for post-storage tank material (250 d). At 5°C, both materials produced less than 0.005 m^3 kg^{-1} VS$_{\text{added waste}}$ (Table 13). The lower methane potential of the post-storage tank material compared to that of the digester material at all temperatures indicates the occurred methanation in actual farm biogas production conditions in Finland.

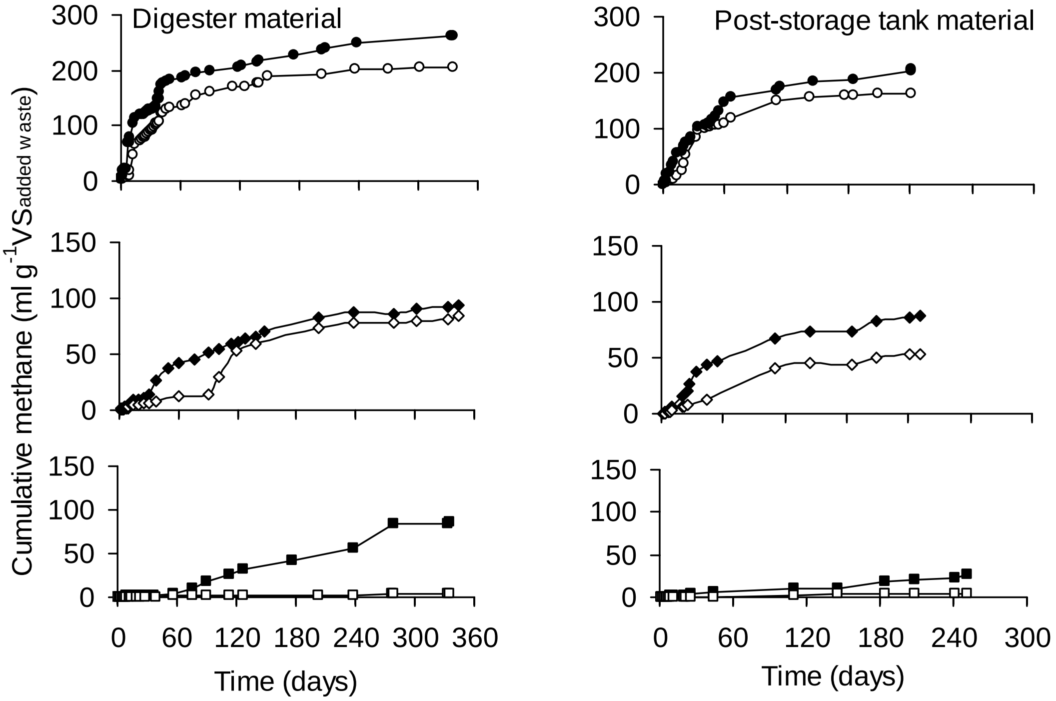

FIGURE 11 Cumulative methane production of digested cow manure obtained from mesophilic farm-scale digester and post-storage tank incubated at ● 55, ○ 35, ♦ 20, ◊ 15, ■ 10 and □ 5°C (IV).

The highest methane potentials obtained at 35°C could be considered as the maximum obtainable methane potential from these materials. These yields can be compared to the obtainable yields from farm digester (0.22 m^3 kg^{-1} VS$_{\text{added waste}}$), the source of the experimental material (II), or in full-scale digestions (0.20-0.24 m^3 kg^{-1} VS$_{\text{added waste}}$) reported for raw dairy cow manure (Moller 2000). The high methane yields along with the long periods of methane production and the high final SCOD values (Table 15) were apparently due to the fact that both materials contained relatively high solids (ca. 6% TS) and the solids' degradation was rather slow (Table 4). The high solids in the digested materials were due to the use of high solids feed in the studied farm. Further, it was assumed that the high methane production from the already digested material was probably observed because in the farm-scale biogas digester, methane had been recovered largely from the readily degradable part of cow manure and co-substrate, industrial by-products (20% of the total feed biomass).

TABLE 13 Mean specific methane yields (standard deviation in parentheses) of digested materials sampled from a mesophilic farm digester (35°C) and post-storage tank (5-10°C) incubated at various temperatures (IV).

Temp. (°C)	Specific methane yields (m^3 kg^{-1} $VS_{\text{added waste}}$)						
	Digester material				Post-storage tank material		
	After 250 d	After 345 d	After 345 d (m^3 t^{-1} material)	Relative methane compared to 35°C (%)	After 250 d	After 250 d (m^3 t^{-1} material)	Relative methane compared to 35°C (%)
55	0.201 (0.05)	0.204 (0.01)	9.3 (0.02)	77.8	0.164 (0.06)	7.2 (0.06)	79.6
35	0.240 (0.05)	0.262 (0.06)	12.0 (0.05)	100	0.206 (0.06)	9.0 (0.05)	100
20	0.088 (0.02)	0.093 (0.03)	4.2 (0.03)	35.5	0.087 (0.03)	3.8 (0.02)	42.2
15	0.079 (0.01)	0.085 (0.02)	3.9 (0.02)	32.4	0.053 (0.01)	2.2 (0.01)	25.7
10	0.057 (0.009)	0.085 (0.02)	3.9 (0.01)	32.4	0.026 (0.05)	1.1 (0.06)	12.6
5	0.003 (0.0006)	0.003 (0.0009)	0.13 (0.0007)	1.1	0.005 (0.001)	0.22 (0.001)	2.4

The effect of temperature on methane potential was significant. With both materials, the achieved potentials were less than 50% at 20°C and even less than 10% at 5°C of those achieved at 35°C. The higher final SCODs at decreasing temperatures suggest that hydrolysis was not the limiting step in the methanation at lower temperatures (Table 15). Previous studies on the influence of ambient temperatures on digestion of raw manure showed no methane production during the semi-continuous digestion of pig manure in a CSTR at 15°C (20 d HRT), whereas at 20°C the methane production reached almost 66% of the value produced at 30°C (van Velsen 1981). Similarly, no methane was produced from a liquid fraction of separated raw cattle manure when incubated in batches for 20 d at 10 and 15°C and methane produced at 20°C was only 37% of that produced at 30-35°C (Hawkes et al. 1984). On the other hand, in a study on the effect of temperature (15-40°C) and detention time ranging from 10 to 150 d on dairy cow slurry digested in a CSTR-system, a specific methane of 0.168 m^3 kg^{-1} VS at 35°C (30 d HRT) with no gas production from the un-inoculated dairy cow slurry at temperatures <15°C was reported (Zeeman

1991). However, for practical application of anaerobic manure treatment, a minimum temperature of 15°C was suggested (Nozhevnikova et al. 1999).

TABLE 14 Effect of an increase in digestion temperature from ≤20 to 35°C on methane yield of digested materials (IV).

Previous Temp. (°C)	Digester material			Post-storage tank material		
	Before $(m^3\ kg^{-1}\ VS_{added\ waste})$	After[a] $(m^3\ kg^{-1}\ VS_{added\ waste})$	Increase in methane yield at 35°C (%)	Before $(m^3\ kg^{-1}\ VS_{added\ waste})$	After[a] $(m^3\ kg^{-1}\ VS_{added\ waste})$	Increase in methane yield at 35°C (%)
20	0.090	0.114 (0.093)	21.0	0.083	0.117 (0.087)	29.1
15	0.080	0.108 (0.085)	26.0	0.050	0.094 (0.053)	46.8
10	0.083	0.125 (0.085)	33.6	0.021	0.080 (0.026)	73.8
5	0.003	0.061 (0.003)	95.1	0.005	0.075 (0.005)	93.3

[a] After values are after 40 days of incubation at 35°C. Values in parentheses are the methane yields of the single samples incubated at original temperatures.

When the materials incubated for 345-days at temperatures ≤20°C were shifted to 35°C, methane production was rapidly stimulated (lower final SCODs) indicating the ability of the mesophiles to increase their methanogenic activity after a temperature increase to 35°C (Table 14). An inoculum acclimatized at 10°C for 5 months was also found to be effective at 10°C and grew well with much higher methane production rates at 30°C than at the pre-incubated temperature of 10°C (Nozhevnikova et al. 1999). Both these results suggest that the bacteria in general could acclimatize to low temperatures and can produce methane linearly with increase in temperature (Sutter & Wellinger 1985; Kettunen & Rintala, 1997; Nozhevnikova et al. 1997). However, it should be emphasised that the microbial consortia acclimatised to low temperatures are not true psychrophiles but are psychrotrophs, mesophiles that could grow at low temperatures. This is because a true psychrophile will not survive temperatures higher than the temperatures optimum for their growth. The temperature optima for the growth of these microorganisms could vary from 25 to 30°C for psychrotrophs (Morita 1974; Russel 1990; Nozhevnikova et al. 2001) or 20 to 40°C for psychrotolerant organisms (Madigan et al. 2000), which is 5-10°C lower than those for the known mesophilic methanogens.

The short lag and the high methane yield at 55°C indicate that the presence of thermophilic or thermotolerant type of bacteria in the materials. For instance, material from a mesophilic digester can be used to start-up a thermophilic digester (Lepisto & Rintala 1995). The reason for the lower methane yields at 55 than at 35°C even during the long incubation periods is not clear but it could be assumed that more energy is needed for the maintenance and growth of bacteria at 55 than at 35°C (Madigan 2000). On the other hand, the high final SCOD values at 55°C suggest that more solids were probably degraded to SCOD than at 35°C, and that the produced SCOD was apparently not available for the methanogens (Table 15). These results however contradict the methane yields generally observed during raw manure digestion, where higher methane yields are often reported at 55 than at 35°C (e.g. Mackie & Bryant 1995).

TABLE 15 Final SCOD values of digester material and post-storage material incubated at 5-55°C for 345 and 250 days respectively (IV).

Substrate/ Temp. °C	Final SCOD (gl^{-1}) [a]					
	55	35	20	15	10	5
Digester material	8.8 (0.02)	4.2 (0.02)	6.3 (0.004)	7.1 (0.007)	6.7 (0.006)	8.7 (0.03)
Post-storage material	8.0 (0.02)	4.9 (0.02)	5.0 (0.01)	6.2 (0.01)	6.5 (0.01)	7.3 (0.04)
After Temp. increase from ≤20 to 35°C (40 d)						
Digester material	--	--	5.3 (0.04)	6.2 (0.04)	6.2 (0.04)	5.8 (0.007)
Post-storage tank material	--	--	5.1 (0.007)	5.4 (0.04)	6.1 (0.03)	4.8 (0.05)

[a] Values in parentheses are the standard deviations.

The results suggest that in a farm-scale digestion process up to 0.008-0.04, 0.04-0.07 and 0.05-0.07 $m^3\ kg^{-1}\ VS_{added\ waste}$ of methane can be recovered at 15 and 20 °C from the post-storage tank after 30, 90 and 180 days of incubation respectively. This would mean that in a farm-scale digestion system, an additional 30% methane compared to that normally obtained by full-scale digestion of manure could be achieved during the 6 months' storage of digested material. On the other hand, the methane yields that could be obtained at 15-20°C were only about 26-42% of the yields achieved at 35°C (final values). Thus, the untapped methane potential of high solids digested manure can partly be recovered in the digester's post-storage tank at ambient temperatures prevailing during the winter in a Northern latitude biogas production system. As ambient temperatures in the post-storage tank increase with day length from winter to summer, a progressive rise in methane production rates can be expected as methanogenic activity increases. However, the methane is not recovered when the demand and the market value for electricity would be at the highest (winter time), and thus use of this methane for electricity generation is not the most economically efficient option. The energy value of the methane could be recovered most efficiently if the produced methane could be used as biofuel, for which the demand and value is much more independent of the season. Alternately, longer HRTs should be applied in the digester operations.

4.3.2 Post-methanation of digested materials: effect of solid-liquid separation on recovering methane and nitrogen

The feasibility to optimize the methane and nitrogen recovery by solid-liquid separation of materials sampled from farm biogas digester (35°C) and post-storage tank (5-10°C) was studied as such in batches at 35°C (V). With both materials and all fractions, methane production started rapidly (Fig. 12) and continued even for several months with many fractions (Fig. 13). Only the methane production of the <0.25 mm fraction of the post-storage tank material started slowly and remained low giving the lowest specific, volumetric and ultimate methane yields. Opposite was true for the same fraction of the digester material, whose methane production increased exponentially after ca. 15 d delay and resulted in the highest specific and ultimate methane yields. However, the slower methane production rates in all fractions compared to the digester material as such suggest that hydrolysis in case of solid fractions >0.25 mm and methanogenesis in case of liquid fraction (<0.25 mm) might be the rate limiting steps. Moreover, the separation process had also exposed the fractions to the air and might have inhibited some of the methanogens (Haugen & Lindley 1988).

In long-term incubation, specific methane yields of 0.16-0.18 and 0.41 m^3 kg^{-1} VS $_{\text{added waste}}$ respectively were produced for solids (>0.25 mm) and liquid fraction (<0.25 mm) indicating that the digester material still had high ultimate methane potential in both solids and liquid fraction. While with post-storage tank material, specific methane yields of 0.13-0.16 and 0.05 m^3 kg^{-1} VS $_{\text{added waste}}$ was obtained suggesting that the remaining methane potential of the digested material after storing for several months in post-storage tank at low temperatures (5-10°C) was mainly available in the solids than in liquid fraction. Thus, the feasibility to recover the remaining methane potential from segregated fractions in a farm-scale biogas production system may be significantly different for digested material coming straight from a farm-scale digester or a post-storage tank. The ultimate specific methane yields obtained in the present study can be compared to the methane yields of 0.22 m^3 kg^{-1} $VS_{\text{added waste}}$ normally reported for raw cow manure in full-scale digestion (Hartmann et al. 2000; Moller 2000) or to the theoretical methane yield of 0.40 m^3 kg^{-1} $VS_{\text{added waste}}$ for cow manure (Hartmann et al. 2000). Hartmann et al. (2000) reported a biogas potential (50 d) of 0.266-0.284 m^3 kg^{-1} VS for the separated liquid (<0.7 mm) of raw manure which was found to be much higher than the fibres' (<0.5 mm) biogas potential of 0.105-0.156 m^3 kg^{-1} VS.

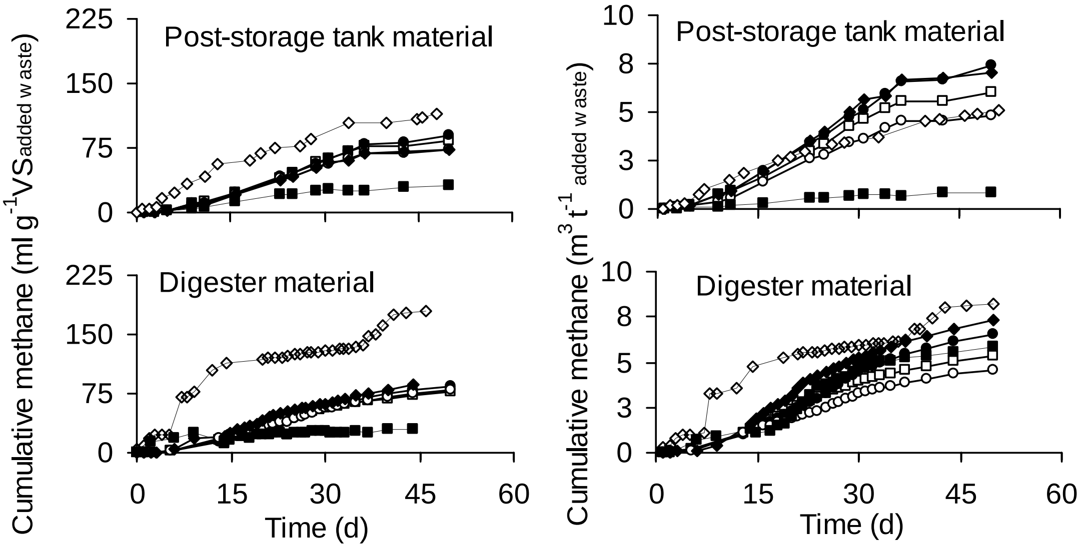

FIGURE 12 Cumulative methane potential of ♦ digested material as such and various fractions of digested material: ◊ >2 mm, ● 1-2 mm, □ 0.5-1 mm, ○ 0.25-0.5 mm and ■ <0.25 mm incubated as such at 35°C during the initial 50 d of incubation (V).

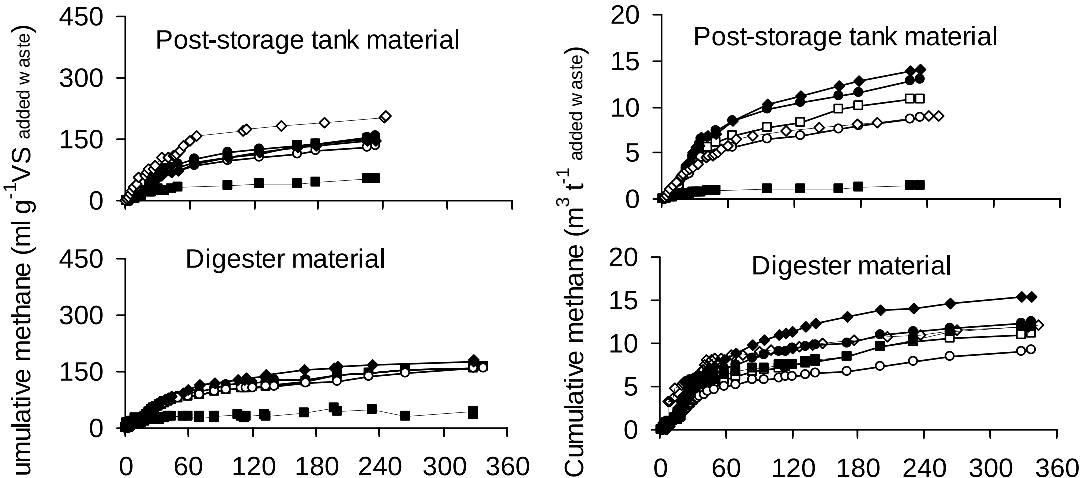

FIGURE 13 Cumulative methane potential of ♦ digested material as such and various fractions of digested material: ◊ >2 mm, ● 1-2 mm, □ 0.5-1 mm, ○ 0.25-0.5 mm and ■ <0.25 mm incubated as such at 35°C after 350 d of incubation (V).

The specific methane yields obtained during the initial 30–50 d by all fractions larger than 0.25 mm of digester material was about 0.056-0.085 m^3 kg^{-1} $VS_{added\ waste}$ (volumetric methane yield 3.2 to 7.3 m^3 t^{-1}; Table 17) which was ca. 34-52% of the ultimate methane yields (0.16-0.18 m^3 kg^{-1} $VS_{added\ waste}$). Similarly, the specific methane yields during the same period for fractions larger than 0.25 mm of post-storage tank material was 0.055-0.092 m^3 kg^{-1} $VS_{added\ waste}$, which was ca. 39-63% of the ultimate methane yield (0.13-0.16 m^3 kg^{-1} $VS_{added\ waste}$). Further, the methane potential (m^3 t^{-1} of material) obtained for each fraction of digester material was about the same to its relative distribution in the material, only the >2 mm fraction had ca. 10% higher specific methane yield than its weight (26.5%). This means that separation of digester material into various fractions would divide the material about equally both in volume and methane potential (Table 16). For instance, a screen with 2 mm pore diameter would divide the digester material into two fractions: 26.5% oversized and 73.5% undersized material and the methane potentials would be ca. 4.1 and 8.6 m^3 respectively (Table 18). On the other hand, use of the 0.25 mm sieve would produce a 60.5% undersized and 39.5% oversized materials with methane potentials of 7.2 and 5.5 m^3 respectively. However, segregation of the digester material into various fractions may not help in obtaining a fraction which could produce methane at a much faster rate as the methane production rate from the digester material as such was found to be slightly higher than that of the >2 mm fraction (highest methane per ton of individual fraction).

For the post-storage tank material, the liquid fraction (<0.25 mm) showed significantly lower methane production than its' solid fractions and than the same fraction of the digester material. This means that use of all fractions larger than 0.25 mm, which constitutes 33.1% of the total material weight, would result in producing 82% of the total methane potential (Table 16). On the other hand, the SCODs were about the same for the different fractions of the post-storage material and digester material. This suggests that most of the methane from the solid fractions of the post-storage material was from solids, and that the composition of SCODs might be different in post-storage tank and digester materials. It is therefore presumed that a major part of the SCOD of the digester material had been methanized during the long storage of the digested slurry (ca. 9 months) in the post-storage tank. However, one must note that the solids in the present study were not washed with water after the solid-liquid separation process. Therefore, the SCOD from the solid fractions was assumed to be derived primarily from the loosely bounded water held to these solid particles. The amount of this water in a particular fraction is however thought to vary with the surface area of that fraction. Upon dilution with water to determine the SCOD, this loosely bound water was therefore released. This explains the reason why the solids also contained same amount of SCOD similar to that of the liquid fraction, which was analysed without further dilution.

TABLE 16 Percentage distributions of the various fractions in the digested manure along with their chemical composition with respect to their distribution and methane yields after 30 and 50 days of incubation and ultimate methane yields (250-340 d) (V).

Solids size	Distribution (%)	TS (%)	VS (%)	TKN (%)	NH_4^+-N (%)	TCOD (%)	SCOD (%)	Methane (%)		
								30 d	50 d	Ultimate
Digester material										
>2 mm	26.5	42.5	46.4	29.7	23.1	35.5	25.2	28.2	31.3	32.1
1-2 mm	3.6	5.3	5.6	2.9	2.4	5.7	3.7	3.3	3.8	3.5
0.5-1 mm	5.4	7.2	7.6	5.2	4.8	6.5	4.7	4.3	4.7	4.7
0.25-0.5 mm	4.0	4.6	4.7	3.8	3.3	5.4	3.5	2.6	3.0	2.9
<0.25 mm	60.5	40.4	35.7	58.5	66.3	47.0	62.9	61.6	57.2	56.7
Post-storage material										
>2 mm	18.1	34.5	37.2	21.2	18.2	25.5	18.2	48.0	51.8	49.5
1-2 mm	5.4	8.8	9.6	5.8	5.0	9.3	5.0	12.2	12.9	13.7
0.5-1 mm	5.6	8.2	8.8	5.8	4.3	10.3	5.6	11.3	11.0	11.9
0.25-0.5 mm	4.0	5.4	5.7	3.7	3.0	7.6	3.7	6.4	6.2	6.9
<0.25 mm	66.9	43.2	38.7	63.5	69.6	47.2	67.4	22.2	18.1	18.0

Mass balance of the solid-liquid separation revealed that the digested materials coming straight from digester and post-storage tank mainly contained more of <0.25 mm (60-67%), and >2 mm fractions (18-26%) while the remaining 13-15% was made up of fractions ranging between 0.25 and 2 mm (Table 16). This would suggest that the solids coming from the biogas digester had not been significantly hydrolysed even during 9 months period in practical ambient conditions occurring in post storage tank. In a similar study Hartmann et al. (2000) compared the distribution of five solid fibre sizes only (>4 mm, 2-4 mm, 1-2 mm, 0.5-1 and <0.5 mm) in raw manure to that of the digested manure after the materials were first passed through a tested separation unit (brush sieve of 5 mm and a screw press) and noticed that the digested manure contained more of the fractions 2-4 and 1-2 mm with a slight decrease in the smallest fibres <0.5 mm.

TABLE 17 Mean specific and volumetric methane yields after 30 and 50 d of incubation from the various fractions of digester (35°C) and post-storage tank (5-10°C) materials at 35°C (V).

Fraction	Specific methane yield ($m^3\ kg^{-1}\ VS_{added\ waste}$)		Volumetric methane yield ($m^3\ t^{-1}$)		Methane yield of different fractions in whole material ($m^3\ t^{-1}$)	
	30 d	50 d	30 d	50 d	30 d	50 d
Digester material						
Digester material as such	0.130 (49)	0.179 (68)	6.0	8.2	--	--
>2 mm	0.061 (34)	0.085 (47)	5.3	7.3	1.4	1.9
1-2 mm	0.058 (35)	0.085 (52)	4.4	6.5	0.16	0.23
0.5-1 mm	0.057 (35)	0.078 (48)	3.9	5.4	0.21	0.29
0.25-0.5 mm	0.056 (35)	0.079 (49)	3.2	4.6	0.13	0.18
<0.25 mm	0.173 (42)	0.202 (49)	5.0	5.9	3.0	3.5
Post-storage tank material						
Post-storage tank material as such	0.085 (41)	0.115 (55)	3.7	5.1	--	--
>2 mm	0.063 (43)	0.092 (63)	6.1	8.8	1.1	1.6
1-2 mm	0.062 (39)	0.089 (56)	5.1	7.4	0.28	0.40
0.5-1 mm	0.063 (42)	0.083 (55)	4.6	6.0	0.26	0.34
0.25-0.5 mm	0.055 (41)	0.072 (54)	3.6	4.8	0.15	0.19
<0.25 mm	0.028 (54)	0.031 (60)	0.76	0.84	0.51	0.56

Note: Values in parentheses are percentage yields to the ultimate methane yields.

Mass balances also indicated that separation of digested material into individual fractions would result in equal distribution of TKN and NH_4^+-N concentrations along the different fractions except for the >2 mm fraction which had slightly more TKN (Table 16). It should be noted that the NH_4^+-N in the solid fractions is mainly concentrated in the liquid phase surrounding the solid particles. Thus, the amount of NH_4^+-N in the individual fraction will depend upon the ratio of solids to the liquid phase. Separation of digester material with a screen pore diameter of 2 mm sieve would result in an oversized fraction (26.5%) containing 29.7% of TKN and 23.1% of NH_4^+-N, while the undersized fraction (73.5%) would contain 70.3% of TKN and 76.9% of NH_4^+-N concentrations. Similarly, use of the 0.25 mm sieve would produce an undersized fraction (60.5%) with 58.5% of TKN and 66.3% of NH_4^+-N whereas the oversized fraction (39.5%) would contain the rest (Table 16). These results suggest that sieving will not benefit in fractioning the digested material into a nitrogen rich or poor fraction. This is in agreement with the observation made by Moller et al. (2000) who reported that the mechanical screen separators were less effective in separating manures into a liquid fraction and a dry-matter and nutrient-rich fractions (total phosphorus and nitrogen) than decanting centrifuges, which happen to retain considerable amount of total phosphorus and only small fraction of total nitrogen. However, in their study the authors observed that the decanters were noticed to have higher efficiencies when treating anaerobically digested cattle and pig manures than untreated manures.

TABLE 18 Ultimate mean specific and volumetric methane yields for various fractions of solids and liquid separated from the digested manure sampled from digester (35°C) and post-storage tank (5-10°C) incubated as such in batches at 35°C (V).

Fraction	Ultimate specific methane yield ($m^3\ kg^{-1}\ VS_{added\ waste}$)	Ultimate volumetric methane yield ($m^3\ t^{-1}$)	Methane yield of different fractions in whole material ($m^3\ t^{-1}$)
Digester material			
Digester material as such	0.262 (0.06)	12.0	--
>2 mm	0.179 (0.05)	15.4	4.1
1-2 mm	0.162 (0.05)	12.5	0.45
0.5-1 mm	0.161 (0.04)	11.1	0.60
0.25-0.5 mm	0.159 (0.04)	9.2	0.37
<0.25 mm	0.410 (0.11)	11.9	7.2
Post-storage tank material			
Post-storage tank material as such	0.206 (0.06)	9.0	--
>2 mm	0.146 (0.05)	14.0	2.5
1-2 mm	0.157 (0.05)	13.0	0.70
0.5-1 mm	0.149 (0.05)	10.9	0.61
0.25-0.5 mm	0.133 (0.04)	8.8	0.35
<0.25 mm	0.051 (0.02)	1.4	0.92

Note: Values in parentheses are standard deviation.

The present results show that solid-liquid separation would not effectively recover the remaining methane potential of the digester material but will recover a part of methane from post-storage tank material through post-methanation. However, it should be noted that the methane potential of the separated fractions would depend on how the fractionation is performed. Keeping in view the above prerequisite, the overall manure digestions' in farm-scale biogas plants could be increased if the feed is either retained for longer time in the digester or the separated solids from post-storage tank material are recycled to digester to ensure a more extensive digestion. Any screen with a pore diameter measuring between 2 and 0.25 mm could be employed in a full-scale solid-liquid separation unit. If facilities are available, digested material from the post-storage tank could be fractioned before it is being pumped out for the agriculture use. Hartmann et al. (2000) were also in similar opinion and found that recirculation of fibres with or without maceration from reactor would enhance methane potential to a small extent. However, separation of fibres with the tested separation unit (5 mm brush sieve and screw press) was found to be inefficient in terms of recovering the biogas potential from the fibres as most of the organic material was lost in the liquids that left the separation unit.

4.3.3 Post-methanation of >2 mm solid fraction of digested material: effect of post-treatment methods and temperature on recovering methane

The feasibility of thermal, chemical, chemico-thermal, mechanical maceration and freezing and thawing treatment methods to enhance the methane recovery of the >2 mm solids fraction of digester material along with aeration of digested material as such was investigated at 5-55 °C in batch assays (VI). The effect of post-treatment methods on the methane potential of the treated solids varied with incubation time and temperature. With all treated materials, significant methane production started immediately at 35°C and after 30 d at 55°C (Fig. 14). On the other hand, significant methane productions at 20, 15 and 10°C were noticed only after 20, 90 and 250 d of incubation respectively. Methane production rate at 5°C however remained low even after 350 days of incubation (Fig. 15). Increase in temperature to 35°C for 40 d after a 6 months incubation at ≤20°C resulted in higher methane yields. The increase in the methane yields was more drastic at 5-10°C than at 15-20°C. However, the increase in methane yields after a raise in temperature from ≤20 to 35°C was much more visible in solids subjected to chemical treatment with or without thermal treatment than any other studied treatments. Statistical analyses (Table 19) based on ultimate methane yields of the >2 mm solids fraction showed a significant difference in mean specific methane yields between the treatments, across the temperatures (Fig. 16) and their interactions (all at <0.1% level of confidence). However, pair wise and complex comparisons using Tukey test revealed that thermal, chemical, chemico-thermal and freezing/thawing treatments were not significantly different from each other (data not shown). Similarly, no significant difference was noticed between maceration and chemical treatments. Correspondingly, the effect of aeration was found to be significantly different from other treatments.

The mean specific methane yields (ml g^{-1} $VS_{\text{added waste}}$) obtained during 30-50 d of incubation of treated solids (with added inocula) were 46-109 at 35-55°C, 2-28 at 15-20°C, 0.7-2 at 10°C and 0.3-0.8 at 5°C. These yields were 29-60%, 5.5-59%, 4.7-5.7% and 30% of the ultimate methane yields achieved at 35-55, 15-20, 10 and 5°C respectively. Methane yields achieved in a short-term (30 d) post-digestion indicated that at 35-55°C chemico-thermal and chemical treatment out performed the effect of maceration and thermal treatment. Whereas at 20°C, chemical treatment followed by maceration and thermal treatments were relatively effective than chemico-thermal treatment. On the other hand at 5-10°C, the effect of thermal treatment and maceration was found to be more pronounced than chemical treatment with or without a thermal treatment. The effect of a freeze/thaw cycles however remained more or less the same with increase in incubation time but improved slightly with decrease in temperature from 55 to 5°C, while aeration was identified as the least effective post-treatment methods at all tested temperatures. All treatments at >20°C showed to follow more or less the same trend as that of assays incubated for 30 and 50 d. Whereas at <20°C, thermal treatment and maceration were found to be the most effective treatment methods after 30 and 50 d incubation period respectively.

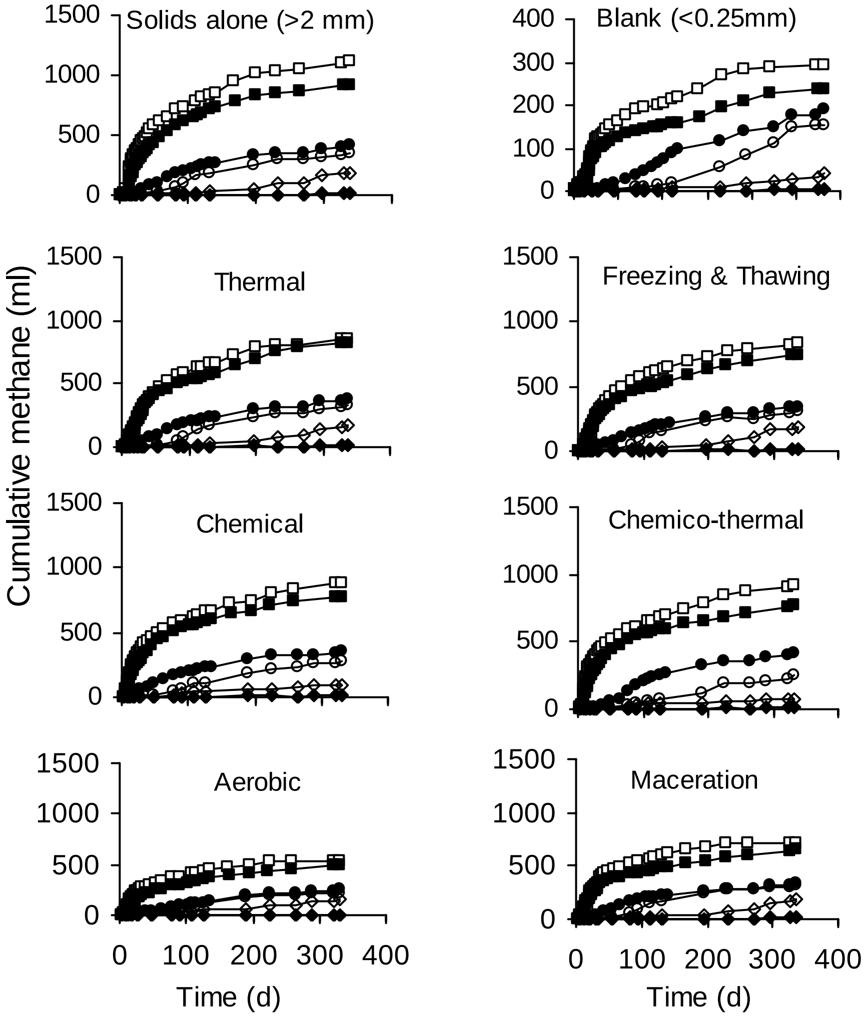

FIGURE 14 Cumulative methane potential of the solid fraction (>2 mm) of the digester manure before and after various post-treatments and blank (<0.25 mm) at temperatures: □ 55, ■ 35, ● 20, ○ 15, ◊ 10, ♦ 5°C (V).

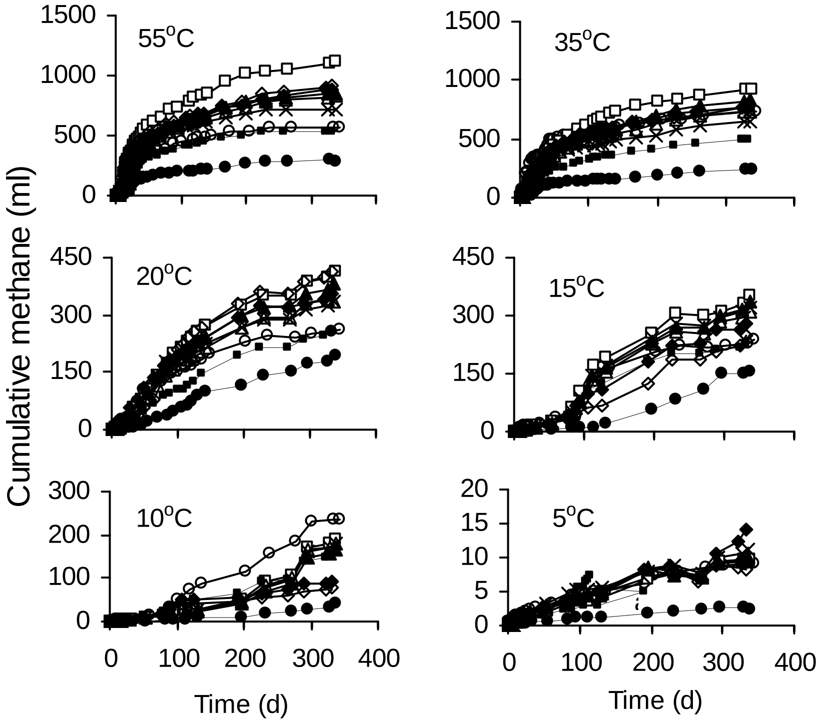

FIGURE 15 Cumulative methane potential of the solid fraction (>2 mm) incubated at 5-55°C after various post-treatments: □ >2 mm solids as such; ■ aerobic; ○ digester manure as such; ● blank (<0.25 mm), ♦ chemical; ◊ chemico-thermal; ▲ thermal; Δ freezing and thawing; x maceration (V).

The ultimate methane yields (350 d) achieved for treated solids compared to untreated solids were only 57-85% at 55°C, 67-97% at 35°C, 48-76% at 20°C and 39-81% at 15°C indicating that treated materials had even lower ultimate methane yields at 15-55°C (39-97%) than untreated material. Whereas at 5 to 10°C, all treatments with the exception of chemical with or without a thermal treatment resulted in an increase in methane potential at 5°C (100-150%) and 10°C (29-100%). However, it must be noted that the absolute methane yields were several folds at higher temperatures compared to those at 10 and 5°C. The slight increase in methane yields of treated solids at 35°C during 30-50 d digestion suggest that the methane potential of solids can be improved through a short-term active full-scale digestion at 35°C. On the other hand the increase in ultimate methane yields at 5-10°C or increase in methane yields when assays incubated for 345 d at ≤ 20°C were shifted to 35°C for 40 d (Table 22), suggest that more methane could be recovered if the biodegradability of solids is improved before a post-storage (5-10°C).

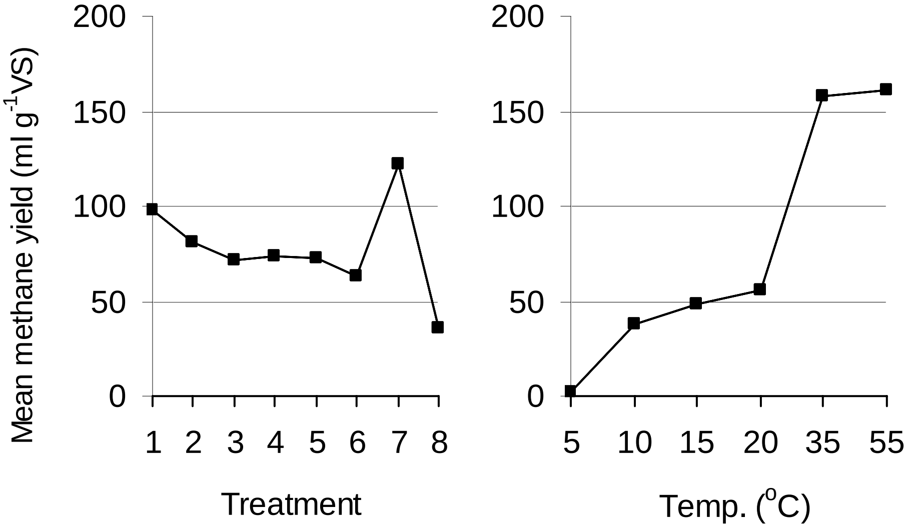

FIGURE 16 Methane potential of >2 mm fraction incubated at 5-55°C after various post-treatments: 1 >2 mm solids as such; 2 thermal; 3 chemical; 4 chemico-thermal; 5 freezing and thawing; 6 maceration; 7 digester manure as such and 8 aerobic treatment (VI).

TABLE 19 Analyses of variance showing the effects of various post-treatments, temperature and their interactions on the methane potential of the >2 mm fraction of the mesophilically digested cow manure incubated in batches at temperatures 5-55°C (VI).

Source	df	F	Sig.
Corrected Model	47	190.5	.000
Intercept	1	11523.6	.000
TEMP	5	1419.7	.000
	7	151.8	.000
TREAT			
TEMP x TREAT	35	22.6	.000
Error	48		
Total	96		
Corrected Total	95		

a R Squared = 0.995 (Adjusted R Squared = 0.989)

The comparison of the methane yields of the treated with untreated assays in this study cannot be not strictly justified as untreated material was assayed as such whereas treated material was assayed with inoculum. Several reasons could be attributed for this yield difference for e.g. added inoculum may have influenced the digestion process. Nevertheless, the main reasons for lower ultimate yields of the treated solids than untreated solids should indicate the nature of the solubilized molecules and/or formation of refractory compounds due to Maillard reactions (Muller 2000) occurring between solubilized compounds leading to the formation of complex or toxic compounds (Tanaka et al. 1997) or loss of readily degradable material during the treatments, whose effects could have been seen better at higher temperatures, where methanogenesis is generally very active. Another possible reason could be the disturbance of the microbial activity associated in solid fraction, due to the treatment, which is absent for the un-treated fraction. The reason for the different effects of the treatments at different temperatures and incubation time might be due to differences in hydrolysis of treated solids induced by various post-treatments and/or limitations in conversion of solubilized COD to methane or involvement of potentially inhibitory compounds in the subsequent several steps of anaerobic degradation. For instance, Kostyukovsky and Marounek (1995) reported the formation of coloured compounds, which are complex and very difficult to degrade even by rumen microorganisms. On the other hand, studies showing an increase in methane yields after employing some of the tested treatments either on fresh manure or on the fibres separated from the manure as pre-treatments are well documented (Angelidaki & Ahring 2000; Hartmann et al. 2000; Bonmati et al. 2001). These studies were mostly conducted at one temperature (e.g. at 35 or 55°C) in batch experiments with retention times of 45 to 60 d using thermophilic inoculum (Angelidaki & Ahring 2000), for 50 d using thermophilic inoculum (Hartmann et al. 2000) or for 80 d using sewage sludge (Bonmati et al. 2001). On the other hand, the effect of maceration with or without chemical treatment in semi-continuous digestion in CSTR was evaluated at 55°C (Angelidaki & Ahring 2000). On comparison with the above studies, the present study evaluated the effects of various post-treatments at different temperature range (5-55°C) and under both short-term (30-50 d) and long-term (350 d) incubations. Thus it appears that the effects of treatments is different for solids separated from an already digested manure as the nature (amount and number of solids) and the chemistry (COD, nitrogen) of the organic matter used in the present study is comparatively different from the materials used in the above mentioned experiments.

The increased effect of a thermal treatment over other tested post-treatment methods either at ≤20°C in short-term (30-50 d) or at 15, 20 and 35 °C in long-term (350 d) incubations could be due to better methanation rates induced by thermal process as a result of increased organic matter solubilization due to accelerated hydrolysis of organic matter and thereby its availability to the microorganisms (Bonmati et. al. 2001). This effect was evident from the slight increase in SCOD (Table 6). However, previous studies have shown that besides incubation temperature, manure characteristics may also affect the effects of a thermal treatment. For instance, Bonmati et al. (2001) reported an enhancement in methane yields from 347 to 557 l kg^{-1} VS for fresh pig slurry with low ammonia to TKN ratio (ca. 50%) and ammonia content (1.3 gl^{-1}) after a thermal process of 80°C and 3 h contact time while with an old pig slurry with high ammonia to TKN ratio (69%) and high ammonia content (3.6 gl^{-1}) the methane yields decreased from 96.1 to 67.7 l kg^{-1} VS. The decreased yields in the latter treatment was mainly attributed to generation of ammonia during the thermal process which in turn resulted in an increased pH and thereby affected the methanation rates due to free-ammonia inhibition (Clark & Speece 1989).

TABLE 20 Mean specific methane yields after 30 and 50 d of incubation of the >2 mm fraction of the mesophilically digested cow manure before and after various post-treatments in batches at 5-55°C (VI).

	Specific methane yields, ml g^{-1} VS $_{\text{added waste}}$ ^{2}											
Incubation time	30 days						50 days					
Temp.,°C	55	35	20	15	10	5	55	35	20	15	10	5
Treatments												
>2 mm solids as such	82	61	11	2.7	0.74	0.25	112 (52)	85 (48)	20 (25)	5.5 (8)	1.6 (4)	0.41 (21)
Thermal[1]	49	48	11	2.9	1.0	0.44	80 (49)	83 (48)	25 (46)	4.2 (7)	1.9 (5)	0.64 (31)
Chemical[1]	78	61	21	1.9	0.73	0.35	100 (58)	95 (61)	28 (59)	4.4 (12)	1.5 (10)	0.47 (14)
Chemico-thermal[1]	88	65	8	2.0	0.76	0.38	109 (60)	96 (63)	13 (20)	3.7 (13)	1.4 (12)	0.55 (33)
Freezing and thawing[1]	46	47	10	2.5	0.87	0.32	75 (48)	71 (49)	21 (50)	4.5 (9)	1.7 (4)	0.58 (27)
Maceration[1]	56	51	11	3.9	0.90	0.38	87 (70)	75 (63)	16 (40)	6.5 (13)	2.3 (5)	0.76 (30)
Aeration[1]	39	27	7	1.3	0.35	0.09	48 (69)	38 (52)	10 (55)	3.3 (15)	1.05 (3)	0.23 (16)

[1] Methane yield of blank excluded from sample.

[2] Values in parentheses are the percentage methane production with respect to ultimate methane potential.

The observed high methanation rate from chemically treated solids with or with out a thermal treatment than other treatments in this study is due to the ability of bases such as NaOH to cause some degree of de-lignifications of the cellulosic structures and affect solids' degradation through swelling/dissolving of the cellulose and thereby its hydrolysis (Fan et al. 1982; Hobson & Wheatley 1993). On the other hand, the increase in ultimate methane yields by 25-35% for the combined effect of chemical and thermal treatment over chemical treatment alone is attributed to the increased SCOD solubilization (Tanaka et al. 1997; Delgenes et al. 2000). However, the lower methane yields noticed at ≤20°C than at >20°C for chemical treatment with or without a thermal treatment might be due to the limitation in the conversion of the solubilized SCOD to methane. This is explained by the fact that in chemically treated solids, hydrolysis of organic matter was not anymore a rate-limiting step but it was the solubilization of molecules that might have limited the digestion process. On the other hand, with additional heating, COD solubilization was enhanced, but the conversion of the solubilized COD to methane did not improve. These observations are in accord to the statement reported by Penaud et al. (2000) that thermal heating emphasised alkaline solubilization but did not improve the biodegradability rates of a microbial biomass. Nevertheless, the observed no improvement in methane yields in solids treated with NaOH with or without thermal treatment over untreated solids in the present study suggests that the effect of chemical treatment might also be dependent upon the lignin content (McMillan 1994) and type of lignocellulosic materials treated (Millet et al. 1976), dosage and incubation temperature (Penaud et al. 1999). Pavlostathis & Gossett (1985) reported greater than 100% increase in methane yield from wheat straw pre-treated with 500 g NaOH /kg TS for 24 h at room temperature (26±2°C) compared with untreated wheat straw. While, Angelidaki & Ahring (2000) reported a 13 and 23% increase in methane potential of the treated fresh cattle manure over untreated manure at a dosage of 20 and 40 g kg^{-1} VS of NaOH respectively.

The low methane yields after a freeze/thaw cycle at all incubated temperatures suggests that hydrolysis may be the rate limiting step as indicated by the unchanged SCOD content (Table 6). Nevertheless, earlier studies have shown that exposure of lignocellulosic substances to freeze/thaw cycles in general would disrupt the material substantially resulting in increased surface area and/or affect enzymatic reaction through removal of cell contents and consequently cellulose hydrolysis (Park et al. 2002). The reason for low methane yields after a freeze/thaw cycle might be that the number of cycles was less or the duration of the treatment was short to impart substantial impact on the solids degradation. However, previous studies on the effect of freezing on fermentation of fresh samples of manure pre-cooled in ice and samples frozen (-10°C) for one day and then defrosted showed no significant difference in the total methane production or generation (Gonzalez-Avalos & Ruiz-Suarez 2001). On the other hand, samples frozen for two or more days required several days of fermentation to achieve production levels similar to those initially shown by fresh samples indicating that the original methanogenic bacterial population was diminished significantly by freezing.

The lowest methane yields achieved at temperatures >20°C for macerated solids suggests that solids with relatively high ammonia content incubated as such without any pH adjustment might have resulted in ammonia inhibition compared to some treated solids, whose pH was adjusted to neutral prior to digestion. On the other hand, the highest methane yields obtained at temperature ≤15°C indicate the relief of ammonia inhibition and possible conversion of the easily available SCOD to methane and/or due to use of smallest particle size. This is due to the fact that the problem of free ammonia related inhibition generally noticed in mesophilic and thermophilic digestion is less prevalent at psychrophilic digestion (Masse et al. 2003). Angelidaki &

Ahring (1994) also found that reducing the temperature from 55 to 35°C when the ammonia loading rate was high resulted in increased stability within the process along with increased biogas yields. The high ammonia and SCOD concentrations coupled with a decrease in solids content could be the result of maceration and/or subsequent solid-liquid separation performed on the macerated solids. Use of low speed macerator may not have affected solids' physical destruction due to already smaller particle size but might have damaged the surfaces of the solids to some extent releasing the degradable cellulose and hemicellulose into the liquid fraction (Hartmann et al. 2000). On the other hand, sieving the macerated solids through 1 mm sieve might have transferred significant amount of ammonia and SCOD to the filtrate containing <1 mm solids fraction. Nevertheless, Hartmann et al. (2000) while using the fibres separated from manure reported that the biogas potential of larger fibre fractions (>1 mm) was enhanced from 155 to 185 ml g^{-1} $VS_{\text{added waste}}$ while the smallest fibres (<0.5 mm) were unaffected (from 157 to 154 ml g^{-1} $VS_{\text{added waste}}$) by a high speed macerator (900 rpm).

TABLE 21 Ultimate mean specific methane yields after 350 d of incubation of the >2 mm fraction of the mesophilically digested cow manure before and after various post-treatments in batches at 5-55°C (VI).

	Specific methane yields, ml g^{-1} VS $_{\text{added waste}}$					
Temperature, °C	55	35	20	15	10	5
>2 mm solids as	215	179	85	68	37	2
such	(7.3)	(12.2)	(9.2)	(0.71)	(0.04)	(0.05)
Treatment methods^{1,2}						
Thermal^{1a}	163	172	55	55	37	2
	(23.3)	(4.1)	(6.5)	(5)	(1.1)	(0.007)
Chemical^{1ba}	171	156	47	36	15	3.4
	(13.4)	(0.93)	(1.2)	(0.76)	(0.76)	(0.25)
Chemical +	181	154	65	27	11	1.6
thermal^{1a}	(15.1)	(13)	(2.8)	(1.2)	(3.1)	(0.098)
Freezing and	158	146	42	46	40	2.1
thawing^{1a}	(8.6)	(12.5)	(4.9)	(0.85)	(0.82)	(0.03)
Maceration^{1b}	124	119	41	49	41	2.5
	(1.7)	(3.9)	(14.7)	(0.25)	(3.2)	(0.06)
Digested manure	204	262	93	84	85	3.3
as such	(12.3)	(4)	(0.0)	(7.0)	(0.71)	(0.14)
Aerobic^{1c}	70	73	18	21	33	1.4
	(8.8)	(1.3)	(4.5)	(0.66)	(5.1)	(0.01)

[1] Methane yield of blank excluded from samples; values in parentheses are standard deviation.

[2] Tukey HSD Based on Type III Sum of Squares. Harmonic Mean Sample Size = 12.0

Alpha =0.05. Treatments that share the same alphabet are not significantly different.

The lower methane production from the aerated material compared to digested material as such at all temperatures and under both short- and long-term digestion suggest that the process could have been inhibited by the presence of inhibitor or toxic substances (Bonmati & Flotats 2003), inhibit/destroy anaerobes or that aeration degraded biologically degradable material. The loss of ammonia (28%) without any change in TKN in the present study suggests that aeration has resulted in organic matter volatization. Lau et al. (1992) reported no difference in TKN content of swine waste upon composting at different O_2 flow rates of 0.2 to 1 l min^{-1} kg^{-1} VS. Ammonia has volatilised apparently because of high pH generated as the organic acids were oxidised to carbonates and bicarbonates. The increased pH after aeration process in the present was however neutralised with HCl addition before incubation. Salminen et al. (2001) also reported a 30% loss of ammonia concentration but noticed a significant decrease in SCOD and ca. 10% decrease in TS and VS during a 6-h aerobic post-treatment of a mesophilically digested poultry slaughterhouse waste aerated at the oxygen flow rate of >2 ml O_2 l^{-1} material h. Thus, aeration process may not be an appropriate technology to enhance the methane yields of digested manure but can be recommended as a post-treatment for total ammonia removal. Bonmati & Flotats (2003) also reported that air stripping of pig slurry as pre-treatment resulted in lower methane production rates than the untreated slurry but recommended it as post-treatment for complete removal of ammonia without pH adjustment of digested slurry.

TABLE 22 Effect of an increase in temperature from pre-incubated temperature of 5-20ºC to 35ºC on methane yields of >2 mm fraction of the mesophilically digested cow manure (VI).

	Specific methane yields, ml $g^{-1}VS_{added\ waste}$													
Treat.	>2 mm solids as such		Thermal		Chemical		Chemical + thermal		Freezing + thawing		Maceration		Aeration	
Temp., ºC	Before	After[1]	Before	After[1]	Before	After[1]	Before	After[1]	Before	After[1]	Before	After[1]	Before	After[1]
20	77	98 (91)	47	68 (50)	44	74 (46)	64	86 (67)	37	63 (38)	29	46 (31)	14	31 (15)
15	60	82 (67)	42	62 (51)	32	72 (37)	16	59 (26)	38	58 (45)	43	71 (48)	19	38 (21)
10	33	75 (37)	35	81 (38)	19	73 (15)	8.6	48 (9)	41	85 (41)	36	73 (39)	37	63 (36)
5	1.8	44 (1.9)	1.9	52 (2.1)	1.7	55 (3.6)	2.1	67 (1.6)	1.9	55 (2.2)	2.1	53 (2.5)	1.1	34 (1.4)

[1] After values are after 40 d of incubation at 35ºC. Values in parentheses are the methane production of the single sample incubated at original temperatures.

4.3.4 Post-methanation of digested materials sampled from a laboratory CSTR

Methane that could be recovered from digested materials at the end of semi-continuous digestion of manures alone (I) or during the stable co-digestion period of pig manure with potato waste (III) was quantified for 60 days at 35°C. Methane recovered from the unfed digesters operated semi-continuously with manures for 133 d (pig and dairy cow @ 2 kg VS m^{-3} d^{-1} loading rate; 20 d HRT and feed VS 6% and sow manure @ 0.38 kg VS m^{-3} d^{-1} loading rate; 20 d HRT and feed VS 0.77%) was respectively, 0.108, 0.067 and 0.003 m^3 of methane kg^{-1} $VS_{\text{in the digester}}$ (I). These results suggested that digesters treating pig and dairy cow manure still contain some undigested solids. The low methane yields from digester fed with sow manure were probably due to a high TS, VS and SCOD removals. The TS and VS removals at the end of the semi-continuous digestion of manures were 18.7 and 42.4% for sow manure compared to 26.4 and 26.7% for pig manure and 34.7 and 42.9% respectively for cow manure. On the other hand, the SCOD in digesters treating pig and cow manures stabilized between 7 and 8 gl^{-1} (Table 9) while in digester fed with sow manure decreased sharply from 8 to 2 gl^{-1} within 90 d and reached 2 gl^{-1} at the end of semi-continuous digestion (133 d).

In another study with the digested materials (Table 12) sampled (day 154) during the stable semi-continuous co-digestion of pig manure and potato waste, methane production started immediately and continued even after 60 days of incubation (III). The specific methane yields of 0.12-0.15 m^3 kg^{-1} $VS_{\text{added waste}}$ achieved during a 60 d post-digestion (Table 23) suggested that digested materials still contained some degradable material. It is assumed that the high methane production from the already digested material probably occurred because during semi-continuous co-digestion more methane had been recovered from the readily degradable potato waste than from the pig manure.

The results from both these post-methanation studies suggest that in a farm-scale digestion system, some additional methane could be obtained during the 9 to 12 months' storage of digested slurry, which is generally required as a concomitant restriction on the season for slurry application on agricultural lands. Digested materials sampled from a farm digester had produced even up to 0.26 m^3 of methane per kg $VS_{\text{added waste}}$ was obtained at 35°C (IV) indicating the importance of measures to recover remaining methane potential of digestates. However, methane recovery at prevailing actual ambient winter temperatures of 10°C or less was very slow. On the other hand, to optimize methane production in a typical co-digestion process on a farm-scale level involving manure and industrial organic wastes, digestions should be performed with either long HRTs or substrate retention times (SRTs) or alternatively compulsory post-storage of the digested materials with or without solids separation should be adopted. Post-methanation, typically at ambient temperatures, is possible as the storage capacity for livestock slurries in many European farms has been extended due to the legislation for the spread of slurry (Burton 1996) e.g. the slurry storage capacity in Finnish dairy farms has been extended from a few months to one year's production (II). Bates (2001) has stated that emissions from the digestate materials removed from the digester due to further decomposition may be avoided if covered and produced gas is recovered.

TABLE 23 Mean specific methane yields (standard deviation in parenthesis) obtained on post-digestion of the digested materials sampled (day 154) during co-digestion of pig manure with potato peel, potato stillage and potato tuber in CSTR at 35°C (VI).

	Specific methane yields after 30 and 60 days			
	(m^3 kg^{-1} $VS_{added\ waste}$)		(m^3 t^{-1} of material)	
Digestate	30 d	60 d	30 d	60 d
Potato peel	0.09 (0.03)	0.12 (0.04)	1.6	2.2
Potato stillage	0.11 (0.04)	0.15 (0.05)	1.7	2.4
Potato tuber	0.09 (0.04)	0.13 (0.04)	1.4	1.9

4.4 The effects of anaerobic digestion on energy production and the possible greenhouse gas emissions reduction in a farm-scale biogas production system

The effects of anaerobic digestion (AD) on energy production and the possible greenhouse gas (GHG) emissions that could be avoided through adoption of AD were calculated (I). The actual manure productions in the typical Finnish dairy, sow and pig farms were 2000, 2000 and 800 m^3 a^{-1} respectively. Based on the full-scale design along with the operational conditions and methane yields from the study, an energy equivalent of 78, 94 and 51 MWh of heat and 66, 80 and 43 MWh of electricity per annum could be generated in a CHP unit on dairy, sow and pig farms respectively. Thus, from the energy balance (Table 24), dairy farm can be self-sufficient or even supply small quantities of electricity (2 MWh a^{-1}) or heat (37 MWh a^{-1}). On the other hand, if the present sow farm (which is quite typical in Finland, but due to rapid changes in agriculture, the size of the farm is increasing) could avoid dilution of manure e.g. by reducing the water usage for flushing and with 6-7% VS, up to 69-78% and 76-86% of farm's electricity and heat requirements respectively could be met through on-farm AD.

The opportunity to use the biogas plants to produce electricity and heat rather than heat alone seems to be influenced also by the market price for the electricity e.g. selling prices in Finland are 0.06 and 0.015 EURO kWh^{-1} in winter and summer respectively, and are low compared to prices in Germany (0.1023 EURO kWh^{-1}, Nicklas & Lehn 2003). Calculations based on the present green electricity selling price in Finland indicate that although the produced methane could be used when the market value for electricity would be at the highest (winter time), the biogas production from manure alone would less beneficial. However, the inclusion of the gates fees and/or sale of treated material may internalize some more economical benefits to the farm-scale digestion.

The estimated reduction in CO_2 emissions if this produced electricity was displaced from coal-fired power station was 58, 69 and 37 Mg of CO_2 emissions per year for dairy, sow and pig farms respectively. This saved or avoided CO_2 emissions from the farm's methane production would be worth a carbon tax (@ 40 EURO t^{-1} of CO_2 equivalent) of 2309, 2765 and 1497 EURO a^{-1} respectively for dairy, sow and pig farms. Similarly, a carbon tax worth 1359, 1626 and 880 EURO could be saved for mitigating 34, 41 and 22 Mg of CO_2 emission on substituting the heat produced from coal with a renewable source and should be considered important in the context of its economical and environmental benefits and the extent of its use, especially in Nordic countries. Both these results indicate that the technical mitigation of CH_4 emissions from manure management would differ with and without adoption of AD and/or the energy substituted for fossil fuel use and on the value of reduced GHG emissions. Previous studies have shown that income received from digestate sales can have a significant influence on the cost-effectiveness for commercial farms e.g. with an installed capacity of 50 m^3 and a minimum livestock of 50 cattle or 500 pigs (Bates & Meeks 1999). Thus, it is clear that the economic effects of farm-scale biogas plants are not only dependent on the investment cost, energy potential but also on energy markets and sale of end products as well as the potential implementation of carbon taxes. Furthermore, technological developments such as the recent application of farm-scale biogas upgrading and using the upgraded biogas as vehicle/traffic fuel for own vehicles or sold for public transport could significantly affect the economics and environmental impacts of farm-scale AD (Wellinger 2000).

Based on the N content in the digestate, the estimated quantity of inorganic N fertilizer that could be potentially saved on dairy, sow and pig farms was 2394, 1197 and 1462 kg a^{-1} respectively. The reduction in this amount of inorganic fertilizer would be worth 449-898 EURO a^{-1} (considering @ 375 EURO t^{-1} of inorganic fertilizer. This reduction in fertilizer use on respective farms would also reduce N_2O emissions by 24-48 kg a^{-1}. Although this does not seem like a large quantity, but the high GWP of N_2O (310 times that of CO_2) means that this is worth annually 594 EURO for dairy farm, 297 EURO for sow farm and 362 EURO for pig farm. Further, the energy saved by the annual reduction in inorganic fertilizer production was estimated to be 207, 103 and 126 GJ a^{-1} for dairy, sow and pig farm respectively. This is equivalent to a reduction of 25 to 50 Mg of CO_2 equivalent per annum and worth significantly a value of ca. 998 to 1996 EURO a^{-1}.

The estimated GHG emissions (CH_4 and N_2O) from manure management were 137, 59 and 29 Mg of CO_2 equivalent per annum for dairy, sow and pig farms respectively, which probably could be avoided if AD is properly applied. Further, emissions from the digested materials due to further decomposition may also be avoided to a certain extent if the post-storage tank is covered and the produced CH_4 is recovered. Meeks & Bates (1999) have reported a 20-50%

reduction in CH_4 emissions from manure management in small farms and up to 50-70% in centralized AD plants or farms that have provision to recover the CH_4 that is generated during the storage of manures. This study also shows that enteric fermentation was the major route of CH_4 emission on dairy farm (93%) while emissions on swine farms were predominately due to manure management (73%). The obvious high CH_4 emission through enteric fermentation in dairy farms than in swine farms is due to the fact that 90% of the CH_4 produced by the methanogenic bacteria in the rumen is released through normal animal respiration and eructation while the remainder is released as flatus (DOE/EIA 1996). The calculated low N_2O emissions from raw manures in the present study also suggest that the impact of N_2O emissions from anaerobically treated manure would be much less than the N_2O produced from an equivalent raw manure, although this is unproven (Bates 2001). The main contribution of AD to this problem is through increased efficiency of the slurry as fertilizer, which can reduce the use of inorganic fertilizer and the associated GHGs emissions. On the other hand, the effect of AD on NH_3 emissions though is not known but the fact that the released NH_3 can be contained in the closed tanks rather than in open storage is beneficial (Burton et al. 1993). For instance, a shift towards anaerobic rather than aerobic storage of manure can reduce N_2O emission by a factor 10 (Kroeze & Mosier 1999). However, the decrease in pH upon digestion can result in a higher NH_3 loss when the digestate is land-spread, although research shows that ammonia volatization depends more on how long the slurry remains on the applied surface before incorporation in to the soil, than it does on whether the slurry has been digested (Tipping 1996). Both these results indicate that the technical mitigation of GHG emissions from manure management would differ with and without adoption of AD and/or the energy substituted for fossil fuel use.

The reductions in CO_2 and N_2O emissions from the produced renewable energy and, reduced fertilizer production and use suggests that major GHG emissions reductions from AD applications may be obtained also from other sources than replacement of fossil fuel by direct biogas use. Their importance vary from reduced GHG emissions through replaced fossil fuel consumption followed by reduced emissions due to manure management (sow farm) and from fertilizer use and production (dairy and pig farm). It should be emphasized that the savings on fertilizer use would also reduce N_2O emissions. While the total energy saved due to the annual reduction in inorganic N fertilizer production suggests that considerable amount of CO_2 emissions could be avoided each year on the studied farms. When applying carbon tax (@ 40 EURO t^{-1} of CO_2 equivalent) for the different methods to mitigate the GHG emissions, the main value for dairy farm would be from decreased emissions from manure management while the reduced GHG emissions form electricity production would provide the highest income for pig and sow farms (Table 25). Thus, by adopting AD, farms could not only produce renewable energy and meet their nutrient requirements but also offset the GHG emissions associated with these activities. However, it must be noted that the present calculations on GHG effects are mainly suggestive as the calculations are based on theoretical rather than practical basis. These calculations rely on many assumptions that the whole manures produced on these farms is collected and digested anaerobically, farmers will decrease their use of inorganic fertilizer according to the increase in efficiency of the digested materials and the N_2O emissions rates from soil (see e.g. Bates 2001). Moreover, several factors e.g. energy required for erecting the buildings and digester and in manufacturing the associated equipments, and the emissions associated with transportation and production of the employed raw materials etc were not taken into account in the present calculations.

TABLE 24 Design for full-scale biogas plants with energy- and global warming potential from the studied farms (I).

Parameters	Cow farm	Sow farm	Pig farm
Digester Design			
[a]Number of adult animals (at once)	70	210	100
[a]Number of young animals (at once)	30	3150	1500
[a]Manure production (m^3 a^{-1})	2000	2000	800
[1]Pre-storage tank capacity (m^3)	700	700	280
[b]Feed VS (%)	7.5	7.0	6.0
[b]Loading rate (kgVS m^{-3} d^{-1})	2.0	2.0	2.0
[b, 2]Digester capacity (m^3)	200	190	65
[3]Feed rate (m^3 d^{-1})	4.4	4.4	1.8
[4]Retention time (d)	38	35	30
[b] CH_4 yields (m^3 d^{-1})	53	58	32
[5]Post-storage tank capacity (m^3)	2000	2000	800
[b] **Farm Energy Production with AD**			
CH_4 from digester (m^3 a^{-1})	19200	21280	11520
[6]CH_4 from post-storage (m^3 a^{-1})	1920	2128	1152
Total CH_4 from digester and post-storage tank (m^3 a^{-1})	**21120**	**23408**	**12672**
[7] CHP- Heat (MWh a^{-1}) and	78	94	51
CHP-Electricity (MWh a^{-1})	66	80	43
[8] CO_2 emission from coal (Mg CO_2 a^{-1}) -			
-To produce equivalent electricity	58	69	37
-To produce equivalent heat	34	41	22
[a] **Farm Energy Consumption (digester heating + farm requirement)**			
Heat consumption (MWh a^{-1})	41	123	58
Electricity consumption (MWh a^{-1})	51	115	55
Farm Energy Balance with AD			
Electricity (MWh a^{-1}) and	+2.1	-51	-20
Heat (MWh a^{-1})	+37	-29	-7.7
Energy economics per annum (selling prices in EURO)			
[9]Heat sales (@ 0.03 € kWh^{-1}) and	1120	-870	-231
[10]Electricity sales (@ 0.015 € kWh^{-1}) or	31	-770	-304
[11]Electricity sales (@ 0.06 € kWh^{-1}) or	125	-3078	-1217
[12]Electricity sales (@ 0.10 € kWh^{-1})	209	-5130	-2028

[a]Data supplied by farmers; [b]Data from this study; [1]based on 35% of annual manure production; [2](daily manure prod x VS)/loading rate; [3](loading rate x working vol.)/(VS% x 1000); [4]working vol. (80% of digester capacity)/daily feed rate; [5]legislation capacity for 9-12 months slurry production (Al Seadi 2000); [6]CH_4 recovered @10% active digester annual production (II); [7]see materials and methods (ETSU 1997); [8]see materials and methods for emission factors (IPCC 1996); [9]selling price in Finland; Selling price during [10]summer and [11] winter in Finland; [12]Selling price in Germany (Nicklas & Lehn 2003).

Table 24…contd.

Parameters	Cow farm	Sow farm	Pig farm
[13]**Global Warming Potential (IPCC)**			
[d] Enteric fermentation (kg CH_4 a^{-1})	6075	765	375
[e] Manure management (kg CH_4 a^{-1})	450	2040	1000
[f] Total CH_4 emissions from livestock (kg CH_4 a^{-1})	*6525*	*2805*	*1375*
[g]CO_2 equivalent (kg of CO_2 a^{-1})	137025	58905	28875
Total N_2O emissions from livestock (kg N_2O a^{-1})	0.01	0.06	0.03
[h]CO_2 equivalent (kg of CO_2 a^{-1})	2.6	17.4	8.5
[i] Total emissions in CO_2 equivalent (Mg of CO_2 a^{-1})	137	58.9	28.9
[j] CH_4 emissions from manure management (%)	6.9	72.7	72.7
Reduction in N_2O emission per annum from reduced fertilizer use			
[b] Analysed TKN in digestate (kg m^{-3})	3.8	1.9	5.8
[14]Total N in digested slurry (kg a^{-1})	6840	3420	4176
[15]Inorganic N equivalent of undigested manure (kg a^{-1})	2394	1197	1462
[16] Inorganic N equivalent of digestate (kg a^{-1})	4788	2394	2923
[17]Saved application of inorganic N (kg a^{-1})	2394	1197	1462
[18] Money saved (EURO a^{-1})	898	449	548
[19] N_2O emission avoided (kg a^{-1})	48	24	29
CO_2 equivalent (Mg of CO_2 equivalent a^{-1})	15	7	9
Reduction in CO_2 emissions per annum reduced fertilizer production			
Saved application of inorganic N (kg a^{-1})	2394	1197	1462
[20] Electricity saved in production of inorganic N (MWh a^{-1})	57	29	35
Reduction in CO_2 emission (Mg a^{-1})	50	25	30

[13](IPCC, 1996); f = (d + e); i = (g + h); j = (e/f)*100; [14]@90% of total manure (ETSU 1997); [15,16,17] refer materials and methods (Klinger 1999). [18]assumed @ 375 EURO t^{-1} N; [19]refer materials and methods (IPCC 1997); [20]refer materials and methods;

TABLE 25 The economics of reduced GHG emissions[1] by adoption of AD in the studied farms (in EURO) (I).

GHG source	Dairy farm	Sow farm	Pig farm
Replaced fossil energy			
- Heat	1358	1626	880
- Electricity	2309	2764	1496
Reduced inorganic fertilizer			
- production	882	441	538
- consumption	1996	998	1218
Manure management	5481	2356	1155
Total (EURO)	12026	8185	5287

[1]assumed carbon tax @ 40 EURO t^{-1} of CO_2 produced (IPCC 2001);

5 CONCLUSIONS

The results obtained from the present study indicate that in a farm-scale biogas production system methane production could be enhanced if co-digestion of manures with energy crops or industrial organic wastes and post-methanation of digested materials are included as a systems approach.

Farm manures as such would produce methane, a potential GHG, if not recovered. Acclimatized inocula would fasten and increased the methane production, although digestion could also be started successfully without inoculation. Cow manures were found to be more benefited from inoculation than pig or sow manures. This study also revealed that under similar process conditions viz. same loading rate (2 kgVS m^{-3} d^{-1}), HRT (30 d) and feed VS (6.0%), pig manures would be better substrates than dairy cow manures producing specific methane yields (m^3 kg^{-1} $VS_{added\ waste}$) of 0.30-0.32 for pig manure and 0.13-0.16 for dairy cow manure.

Results from batch, semi-continuous and farm-scale studies suggested that energy crops and confectionery by products could be considered as potential co-substrates to be digested with manures. Especially, confectionery by-products showed potential for highly enhanced methane yields compared to digestion of cow manure alone. Energy crops could also be used as co-substrates Pre-treatment of energy crops by reducing particle size (2, 1 and 0.5 cm) did not influence methane yields in oats while, 1 cm particle size seems to optimal for grass hay and least optimal for clover. Energy crops harvested during vegetative stage resulted in higher methane yields than those harvested during the flowering period. However, the proportion of waste in a co-digestion process appears to be important e.g. feed VS in co-digestion of pig manure and potato waste may contain up to 15-20% of potato waste. Similarly, specific methane yields and process performance for potato tuber would be similar to those of its industrial by-products when co-digested with pig manure under identical process conditions such as total feed VS, loading rate and feed

VS ratio. Application of co-digestion technology of safe industrial by-products such as confectionery by-products or potato industrial by-products in the farm-scale biogas digesters will offer a number of benefits for both farmer and industry by not only generating on-farm renewable energy but also enabling treatment of waste for industry.

Post-digestion of digested materials sampled from laboratory CSTRs during semi-continuous digestion/co-digestion or during full-scale digestion from farm digester and its associated post-storage tank indicated that the digested materials still contained some degradable material and would produce an appreciable amount of methane during post-methanation. During the long-term incubation, the effect of post-methanation and temperature on methane yields of digested materials sampled from farm digester and post-storage tank indicated that highest methane potentials were obtained at 35°C, and could be considered as the maximum obtainable methane potential from these materials. The lower methane potential of the post-storage tank material compared to that of the farm digester material indicates the occurred methanation in actual farm biogas production conditions in Finland. During the long term incubation (250-345 d), the effect of temperature on methane potential of digested materials (farm digester or post-storage tank) was significant as the achieved potentials for both materials were less than 50% at 20°C and even less than 10% at 5°C of those achieved at 35°C. Increase in temperature after incubated for 345 d at temperatures ≤20°C to 35°C, improved methane production. Thus, these results suggest that the untapped methane potential in the digested manure cannot effectively be recovered at temperatures prevailing in the post-storage tank (5-10°C) during the winter in the Northern latitude biogas production system. Nevertheless, as the ambient temperature in post-storage tank increases e.g. with increase in day length, an increase in methanogenesis can be expected.

The results from separation of digested materials into solids and liquid fractions to optimize the methane and nitrogen recovery showed that materials obtained from farm biogas digester (35°C) and post-storage tank (5-10°C) would differ significantly. Although digester material found to contain high methane potential, its methane potential cannot effectively be recovered as separation of the material would distributes its methane potential equally depending upon the distribution of its' fractions. On the other hand, only a part of the methane potential could be recovered from the post-storage tank material. This study also showed that the digester material had high ultimate methane potential both in solids and liquid fraction while the methane potential of the material from post-storage tank was mainly concentrated in the solids. Separation of digested material into a nitrogen rich or poor fraction would not be feasible as both TKN and NH_4^+-N were equally distributed along the segregated fractions in both materials. Thus, separation of digested materials into solids and liquid fractions to recover methane may be feasible only with post-storage tank material but not with digester material. On the other hand, nitrogen management would not be feasible with neither material.

The effect of post-treatments and temperature on post-methanation to recover the remaining methane potential of >2 mm fraction of the digested manure indicated that at 5-20°C maceration or thermal treatments and at 35-55°C chemical treatment with or without a thermal treatment would improve the methane yields to a smaller extent. However, the feasibility of the tested treatment methods in a full-scale application needs further evaluation.

The feasibility of on-farm AD process through estimating energy production on the studied dairy, sow and pig farms indicated that dairy farm can be self sufficient in electricity and heat requirements and even sell surplus energy to local grid or heating system. While the benefits of adoption of AD process on mitigating GHG emissions was mainly through replacing fossil fuel consumption followed by reduction in emissions due to manure management (sow farm) and from fertilizer use and production (dairy and pig farm). This study also suggested that AD of farm manures offers both treatment of the manures and, produces carbon dioxide neutral methane from renewable sources and aid in reducing GHG emissions due to replacement of fossil fuels, manure management and inorganic fertilizer use and production.

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YHTEENVETO

Biokaasuteknologiaa pidetään maataloudessa lisääntyvässä määrin lupaavana tekniikkana tuottaa uusiutuvaa energiaa ja minimoida päästöjä ympäristöön. Eduista molemmat vähentävät kasvihuonekaasujen päästöjä. Tämän tutkielman päätavoite oli arvioida menetelmiä, jotka tehostaisivat metaanintuottoa tilakohtaisessa biokaasuntuotantojärjestelmässä.

Puolijatkuvatoimisessa anaerobisessa käsittelyssä sianlannan ominaismetaanintuotto oli 0,30–0,32 m^3 kg^{-1} orgaaninen aine (VS)$_{\text{lisätty jäte}}$ ja lehmänlannan (maitokarja) 0,13–0,16 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$, kun kuormitus oli 2 kgVS m^{-3} d^{-1}, viipymä 30 d ja lisätyn jätteen VS 6,0 %. Emakkosikalan lannan metaanintuotto oli 0,14–0,19 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$, kun kuormitus oli 0,38 kgVS m^{-3} d^{-1}, viipymä 20 d ja lisätyn jätteen VS 0,77 %. Sen sijaan panoskokeissa metaanintuotot olivat lehmänlannalla 0,13–0,15, sianlannalla 0,36 ja emakonlannalla 0,54 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$. Tuotot olivat matalampia kuin lehmänlannan teoreettinen metaanintuotto 0,4 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$. Mahdollisia yhteiskäsiteltäviä materiaaleja tutkittiin metaanintuoton tehostamiseksi tilakohtaisissa biokaasuntuotantojärjestelmissä. Energiakasvien ominaismetaanintuottoa arvioitiin panoskokeissa. Heinän (partikkelikoko <1 cm) metaanintuotto oli 0,35 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$, kauran (0,5 cm) 0,26 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$, kasvuvaiheen apilan (2 cm) 0,21 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$ ja kukkivan apilan (2 cm) 0,14 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$. Makeisten valmistuksen sivutuotteiden ominaismetaanintuotot olivat puolestaan 0,32–0,39 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$. Täydenmittakaavan biokaasuprosessissa pelkkä lehmänlanta tuotti metaania 0,22 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$. Makeisjätteen (20 % lisätystä jätteestä) ja lannan yhteiskäsittely lisäsi metaanintuottoa, joka oli noin 0,28 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$. Lannan ja energiakasvien yhteiskäsittelyssä metaanintuotto vastasi pelkän lehmänlannan käsittelyä. Puolijatkuvatoiminen sianlannan ja perunan tai sen teollisten sivutuotteiden (kuoret tai tärkkelysliete) yhteiskäsittely kuormituksella 2 kgVS m^{-3} d^{-1} tuotti metaania 0,21–0,24 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$, kun lisätyn jätteen VS suhde (VS % sianlantaa ja perunaa) oli 85:15, ja 0,30–0,33 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$, kun VS suhde oli 80:20. Pelkän sianlannan metaanintuotto oli 0,13–0,15 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$. Kun kuormitus nostettiin 3 kgVS m^{-3} d^{-1} (lisätyn jätteen VS suhde 80:20), metaanintuotto oli 0,28–0,30 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$. Panoskokeet anaerobisesti käsitellyillä materiaaleilla tilakohtaisesta biokaasureaktorista (35 °C) sekä sen jälkivarastointisäiliöstä (varastointi korkeintaan 9 kk ympäröivässä lämpötilassa) osoittivat, että pitkäaikaisessa inkuboinnissa (345 d) reaktorin materiaali tuotti metaania yhä 0,20–0,26 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$ 35–55 °C:ssa ja 0,085–0,09 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$ 10–20 °C:ssa. Jälkivarastoitu materiaali tuotti 250 d:ssa 0,16–0,21 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$ 35–55 °:ssa, 0,053–0,087 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$ 15–20 °C:ssa, 0,026 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$ 10 °C:ssa ja alle 0,005 m^3 kg^{-1} VS$_{\text{lisätty jäte}}$ 5 °C:ssa. Metaanintuotto aiemmin 5-20 °C:ssa (9 kk) inkuboiduissa panoskokeissa kasvoi, kun lämpötila nostettiin 35 °C:een (40 d), mistä voidaan päätellä, että ympäröivä lämpötilan noustessa loppukeväällä metaanintuotto jälkivarastointisäiliössä kasvaa. Panoskokeissa tutkittiin anaerobisesti käsiteltyjen materiaalien metaanintuottoa kiinteän faasin ja nesteen erotuksen jälkeen (>2; 1-2; 0,5–1; 0,25–0,5 ja <0,25 mm). Reaktorin materiaalin metaanintuotto jakautui tasaisesti riippuen eri fraktioiden suhteellisesta jakautumisesta materiaalissa. Samaa ei havaittu jälkivarastointisäiliön materiaalissa. Suurin eroavaisuus havaittiin fraktiossa <0,25 mm, jonka metaanintuotto jälkivarastointisäiliön materiaalilla (0,03 m^3 kg^{-1} $VS_{\text{lisätty jäte}}$ (0,8 m^3 t^{-1}) 30–50 d:n jälkeen ja 0,05 m^3 kg^{-1} $VS_{\text{lisätty jäte}}$ 250 d:n jälkeen) oli pienempi kuin reaktorin materiaalin (0,20 m^3 kg^{-1} $VS_{\text{lisätty jäte}}$ (5,9 m^3 t^{-1}) 30–50 d:n jälkeen ja 0,41 m^3 kg^{-1} $VS_{\text{lisätty jäte}}$ 250 d:n jälkeen). Fraktiointi ei tosin mahdollista typen hallintaa, sillä sekä kokonais- että ammoniumtypen pitoisuudet olivat jakautuneet yhtäläisesti eristetyissä fraktioissa molemmissa materiaaleissa. Erilaisten jälkikäsittelyjen käyttö reaktorin materiaalin >2 mm kiinteän fraktion metaanintuoton parantamiseksi osoitti, että kemiallinen käsittely (40 g NaOH kg^{-1} VS) yhdessä tai ilman lämpökäsittelyä (3h 80 °C) oli hieman tehokkaampi kuin muut tutkitut menetelmät lyhytaikaisissa (30–50 d) panoskokeissa. Metaanintuotto oli tällöin 0,061–0,096 m^3 kg^{-1} $VS_{\text{lisätty jäte}}$ 35 °C:ssa. Toisaalta pitkäaikaisissa (345 d) panoskokeissa pehmentäminen (hidasnopeuksinen sekoitin), pakastus/sulatus (24 h -20 °C ja 4 h 20 °C) ja lämpökäsittelyt olivat parhaat tuottaen metaania 0,002–0,0025 m^3 kg^{-1} $VS_{\text{lisätty jäte}}$ 5 °C:ssa ja 0,037–0,041 m^3 kg^{-1} $VS_{\text{lisätty jäte}}$ 10 °C:ssa. Biokaasuteknologian edut kasvihuonekaasupäästöjen vähentämisessä tilakohtaisissa järjestelmissä olivat pääasiassa fossiilisten polttoaineiden korvautuminen biokaasulla ja sitä seuraava päästöjen väheneminen lannan hallinnan (emakkosikalat) ja lannoitteiden käytön ja tuoton vuoksi (maitokarja- ja sikatilat). Tämän tutkielman tulokset osoittavat, että metaanintuottoa voidaan tehostaa, mikäli lannan ja energiakasvien tai teollisten orgaanisten jätteiden anaerobinen yhteiskäsittely sekä käsiteltyjen materiaalien jälkikypsytys otetaan osaksi tilakohtaisia biokaasun- tuotantojärjestelmiä.

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