Energy 52 (2013) 137–142

Contents lists available at SciVerse ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Organic silicon compounds in biogases produced from grass silage, grass and maize in laboratory batch assays

S. Rasi [a,*], M. Seppälä [a], J. Rintala [b]

[a] *Department of Biological and Environmental Science, P.O. Box 35, FI-40014 University of Jyväskylä, Finland*
[b] *Department of Chemistry and Bioengineering, P. O. Box 541, FI-33101 Tampere University of Technology, Finland*

ARTICLE INFO

Article history:
Received 25 June 2012
Received in revised form
20 December 2012
Accepted 8 January 2013
Available online 13 February 2013

Keywords:
Siloxanes
Biogas
Methane
Energy crops
Anaerobic digestion

ABSTRACT

In the present study the occurrence of volatile organic silicon compounds in biogas produced from grass silage, grass and maize in laboratory batch assays was analyzed and methane potentials were determined. Inoculum from a mesophilic farm digester was used, and its effects were subtracted. Methane yields from grass silage, grass and maize were 0.38, 0.42 and 0.34 m^3CH_4/kg – volatile solids added (VS_{add}), respectively. Trimethyl silanol, hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) were detected from all the biogases. Higher yields of volatile organic silicon compounds in the grass (from 21.8 to 37.6 $\mu g/kgVS_{add}$) were detected than in grass silage or maize assays (from 14.7 to 20.4 and from 7.4 to 12.1 $\mu g/kgVS_{add}$, respectively). Overall, it is important to consider silicon-containing compounds also in biogases in energy crop digestion as the number of biogas plants using energy crops as feeding material increases and some biogas applications are sensitive to organic silicon compounds.

1. Introduction

Biogas, produced through the anaerobic digestion of organic material, is a valuable source of renewable energy as it contains from 45 to 65% methane [e.g., [1]]. Biogas can be used in the production of electricity, heat or, after upgrading, vehicle fuel in order e.g., to decrease fossil fuel consumption and greenhouse gas emissions. Raw materials for anaerobic digestion include e.g., manure, biowaste, sewage sludge and energy crops. Recently energy crops have received a lot of attention as these could be an interesting option in seeking to increase domestic and sustainable biofuel production. In Germany there are over 6000 biogas plants in operation, most of them using energy crops as one of the feeding materials [2]. In several studies various crops have been screened for their methane potential [e.g., [3,4]]. In the Nordic countries, the use of perennial grasses in particular has been proposed for energy production on account of their good biomass production in boreal conditions [5].

Biogas often presents a good opportunity to increase the use of renewable energy. For heat and electricity, a wide range of technologies utilizing biogas already exists [6] and interest in the use of biogas e.g., as a vehicle fuel and in fuel cells has also increased [7–10].

Organic silicon compounds are commonly recognized as potentially affecting the use of biogas produced in landfills or sewage digesters [10–13]. The organic silicon compounds present in biogas are oxidized during biogas combustion into microcrystalline silicon dioxide which collects in deposits on valves, cylinder walls, and liners, causing abrasion and blockage of pistons, cylinder heads, and valves [11]. The use of spark ignition engines has increased the number of engine failures caused by siloxanes, as previous dual fuel engines were less vulnerable to silica deposits [12]. In addition, the use of biogas as vehicle fuel or in fuel cells maybe affected by siloxanes and other harmful compounds [13].

Siloxanes are subgroups of silicones containing Si–O bonds with organic radicals, which can include methyl, ethyl and other organic functional groups, bonded to the Si [14]. Volatile methylsiloxanes (VMS) and polydimethylsiloxanes (PDMS) are widely used in industry, for example in cleaners, personal care products, softeners and wetting agents in textile manufacturing. Dimethylsilanediol (DMSD) is the main degradation product of PDMS but VMSs and trimethyl silanol have also been detected [14–17]. In the case of trimethyl silanol it is also thought that other environmental pathways to its formation exist [16]. Because of the wide use of siloxanes in industry, they are commonly found in air, water, sediment, sludge and biota, with high variations in their concentrations [18].

---

[*] Corresponding author. Present address: MTT Agrifood Research Finland, FI-31600 Jokioinen, Finland. Tel.: +358 295317655.
E-mail addresses: saija.rasi@mtt.fi (S. Rasi), mari.p.seppala@jyu.fi (M. Seppälä), jukka.rintala@tut.fi (J. Rintala).

0360-5442/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2013.01.015

As organic silicon compounds are widely used in domestic and industrial products, e.g., in chemical products and in fuel additives [18], they easily end up in sewage plants and landfills, and further in biogas, but they are also released into the environment through direct evaporation into the air [19,20]. Organic silicon compounds are also reported to degrade and volatilize in different soil types [21]. Organic silicon compounds have also been detected in biogases produced from the co-digestion of manure and industrial confectionery by-products [1] and in biogas from a biogas plant in Germany processing grass and maize [22]. However, literature on siloxane concentrations from biogas produced from energy crops is scarce.

The objective of this study was to determine the occurrence of the organic silicon compounds in biogases produced from energy crops and determine possible differences in siloxane concentrations between biogases from some of the crops used in biogas plants.

2. Materials and methods

2.1. Substrates and inoculum

Grass silage, grass and maize used in assays were harvested at different times during years 2007–2008 from two farms in Central Finland (Table 1). Grass silage, grass and maize were chopped into particles of ca. 1 cm with scissors before used in assays. Inocula for assays (average values of total solids (TS) 4.7 ± 0.7%, volatile solids (VS) 3.6 ± 0.6%) were obtained from a mesophilic farm digester processing cow manure, industrial confectionery by-products and energy crops [23].

2.2. Batch assays and sampling

The batch assays were performed in duplicate or triplicate 2 l and 5 l glass bottles (liquid volume 1.6 l and 4.5 l) (Table 1) at 35 ± 1 °C. Inoculum and substrate in a $VS_{substrate}/VS_{inoculum}$ ratio of 1 were added into the bottles, tap water was added to produce a liquid volume of 1.6 l or 4.5 l, and sodium bicarbonate ($NaHCO_3$, 3 g/l) was added as buffer. The bottles were flushed with N_2 and then sealed with butyl rubber stoppers [4]. For the grass silage assays, 77, 650 and 873 g/bottle of crop, inoculum and water, respectively, were added, for the grass assays 80.9, 650 and 869.1 g/bottle, and for the maize assays 208.1, 600 and 753.1 g/bottle. Before the assays, after adding of buffer, pH in bottles with inoculum only was about 8.1 and in bottles with crops ranged from 7.6 to 8.0. After the assays, pH ranged from 7.4 to 7.6 in all the bottles. To determine the organic silicon compounds of the biogas produced from the inoculum, assays of inoculum only were carried out under the same conditions. The gas produced was collected in Napholan NA© bags. The methane production potentials were determined in similar batch assays in 1 l, 2 l and 5 l bottles, and the gas produced was collected in TECOBAG (PETP/AL/PE 12/12/75) aluminum gas bags (volume 10 l).

To obtain biogas samples for the volatile organic silicon compound measurements, the biogas was collected in gas bags until the required gas (minimum about 1 l) was produced. Thus the duration of the batch assays and number of gas samples taken were depended on the production of biogas in the actual assay. From each of the assays with crops two to three gas samples were taken, while from the assays with inoculum only one sample per bottle was taken, because of the low amount of gas produced. The yield of organic silicon compounds during the assays was calculated from all the biogas produced during the incubation period per bottle, minus the yields of organic silicon compounds from the biogas produced from inoculum only, which amount was divided with added VS of the crop ($\mu g/kgVS_{add}$). For the inocula assays, the yields are per added VS inocula. After the incubation period the samples were taken from the digestates with the crops and inoculum and inocula alone (the inoculum and crop material not degraded during the incubation period). Samples were also taken from the inoculum before it was used in the batch assays. The volatile organic silicon compounds were measured from these samples as $\mu g/kgVS_{add}$.

2.3. Analysis

TS and VS were determined according to the Standard Methods [24]. pH in the bottles was measured with a Metrohm 774 pH-meter before and after the batch assays.

Biogas volume in the aluminum gas bags was measured by water displacement. The methane content of the biogas samples was measured using a Perking Elmer Clarus 500 gas chromatograph with flame-ionization detector. The injector, detector and oven temperatures were 225 °C, 225 °C and 100 °C, respectively. Argon was used as carrier gas.

The biogas samples for the volatile organic silicon compound analyses were drawn from the Napholan NA© bags (volume about 7 l) into duplicate sampling tubes at a rate of about 90 ml/min/tube using a Gillian Personal Air Sampler (LFS-113DC) at room temperature (22 °C). The second sampling tubes were connected to first ones to ensure the complete capture of the compounds. The adsorption material in the sampling tubes was Tenax GR (200 mg). Before use, the sampling tubes were preconditioned by heating under a stream of nitrogen at 300 °C for 8 h. The tubes were capped and stored at −18 °C until analyzed. The samples were analyzed using thermal desorption gas chromatograph–mass spectrometry (Tekmar Purge & Trap Concentrator 3000/Agilent 6890+/5973 N MSD). The GC capillary column used for the analyses was Agilent Technologies HP5 (film 1 μm, diameter 0.25 mm, 30 m length). With the biogas samples desorption was performed at 250 °C for 10 min. During desorption, compounds are transferred in a cryogenic trap (−120 °C). After desorption the cryogenic trap was heated to 250 °C. The initial GC oven temperature for all samples was 40 °C for 2 min, then ramped at 5 °C/min up to 150 °C and 15 °C/min up to 250 and held at this temperature for 5 min. The flow rate of carrier helium was 1.1 ml/min. The MSD was operated

Table 1
Origin of energy crop materials used in this study.

Energy crops	Code for duplicate and triplicate sample bottles	Cultivation site and harvest time	Soil type	Fertilizer
Grass silage	S1&S2	Laukaa, Finland from 2007 harvest	Silt	Fermentation digestate
Grass	G1&G2	Jämsä, Finland from June 2008 harvest	Silt, containing 6–12% organic matter	Chemically produced fertilizers
Maize	M1, M2&M3	Laukaa, Finland, from August 2008 harvest	Silt	Fermentation digestate