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THE ROLE OF MINERAL PHASES IN THE BIOGAS PRODUCTION TECHNOLOGY

ROLA FAZ MINERALNYCH W TECHNOLOGII PRODUKCJI BIOGAZU

Abstract: In the field of electric power industry, renewable energy sources, fertilisers, reclamation, and waste management, biomass is widely studied and used. Minerals are present in every step of biogas transformation, but their forms, occurrence, and composition have not been studied yet. However, there is no comprehensive study research that would address the presence of mineral phases in the process of biogas production. This aim of the study is determination of the amount and composition of the mineral phases present in fermentation residues resulting from different production technologies. Digestate mineral composition was analysed using 46 samples from agricultural biogas plants and university testing biogas reactor. The majority of samples contained the amorphous phase. Minority phases consisted of quartz, albite, orthoclase, muscovite, and amphibole. Opal-CT was found in eleven samples (1.26 to 12.1% wt.). The elements present in gas-liquid fluids or in liquids, gases and aerosols within the biogas technology system may create mineral phases, namely the amorphous phase or the crystalline phase under certain conditions. Opal-CT may enter the fermenter as part of plant tissues referred to as phytoliths, or as an unwanted admixture of different origin. It may also originate from the present amorphous SiO₂.

Keywords: biogas production, digestate, X-ray diffraction analysis, Rietveld method, opal-CT

Introduction

Biogas is a type of universal renewable fuel which can be used for electric power and heat generation or as fuel in vehicle engines. It has been suggested that major part of the EU 27's 2020 renewable energy target would come from bioenergy and at least 25% of bioenergy could originate biogas produced from wet organic materials including manure, whole crop silage, wet food and feed wastes [1]. Several studies were performed to reduce Greenhouse Gasses (GHG) emissions from anthropogenic activities [2] and define environmental effects of biogas deployment on carbon balance [3-5].

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The process of anaerobic decomposition of biodegradable materials primarily produces biogas. Raw biogas generally consists of methane (40-75%) and carbon dioxide (15-60%); the water content is about 5-10%. It includes trace amounts of such components as hydrogen sulphide (0.005-2%), ammonia (< 1%), halogenated hydrocarbons (< 0.6%), siloxanes (0-0.02%), nitrogen (max. 2%), and oxygen (max. 1%); carbon monoxide (< 0.6%) can be present and might be inconvenient when not removed [6, 7].

Detailed composition of biogas and fermentation residues is significantly influenced by the type of input material, especially from the perspective of minor components that can be considered harmful. The total of 12 to 53% organic material is decomposed during anaerobic fermentation [8, 9].

The high content of heavy metals in digestate inhibited the use as a fertiliser. Heavy metals enter digestate as part of the feed material and as supporting substances to increase microbial activity of the processes underway in the biogas plant [10]. The elements present in gas-liquid fluids or in liquids, gases and aerosols within the biogas technology system may create mineral phases, namely the amorphous phase or the crystalline phase under certain conditions.

The main sources of organosilicon compounds in substrates include many types of cosmetic products that in the aqueous phase of the wastewater treatment process cause siloxanes to bind to the solid components of sewage sludge. For biogas, which originated from the decomposed sewage sludge, the measured siloxane concentrations increase in the long term; this is caused by the ever-increasing consumption of products containing silicon compounds. The biogas plants used for processing materials coming from agriculture have usually low concentration of halogenated and organic silicon compounds. However, low amounts of organic silicon compounds have been detected in biogas from plants that process only manure and energy crops even though the origin of these was not clear [11]. Problems occur if the amount of siloxanes in the biogas surpasses a critical value that jeopardizes the valves and pistons of the engine of the power generator through the formation of SiO₂. Siloxane compounds decompose in engines under high temperatures. The composition of the released fuel gas needs to be analysed to avoid severe damage of the engine that is caused even by small amounts of siloxanes present when deposited over a longer period [12-14]. EU has no standards on maximum permissible siloxane content in biogas. Austria and the Netherlands where the siloxane specifications are 10 mg Si/m³ and 5 ppm, respectively, are the only exceptions [15].

Exceeding siloxane concentrations leads to a considerable reduction in technology service and maintenance period and disproportionate increase the costs of maintenance [16, 17]. A fermentation residue is formed as a biogas production co-product. Referred to as "digestate" [18], the material is used as a fertiliser, raw material for composting or solid fuel. The combustion of the matter does not increase the carbon content in its natural cycle [2]. Digestate contains a high amount of phosphorus, potassium, and total nitrogen, the latter found in the form of ammoniacal nitrogen; all of the substances are beneficial for agricultural soils [19, 20]. pH of the fermentation residue is usually 7.5 to 8.3 [21]. The chemical and mineral composition of fermentation residues is influenced by the type of the raw material being processed, the manner of pre-treatment, the operating temperature in the digester, the residence time, the content of solids etc., plus the storing method and period are factors. The usual content of total solids is 4 to 15% for liquid fermentation residues and 30 to 45% for non-liquid fermentation residues.

However, there is no comprehensive study that would address the presence of mineral phases in the process of biogas production. The aim of this study is to determine the amount and composition of the various mineral phases present in fermentation residues resulting from different biogas production technologies.

Experiment and sample collection

The mineral composition of the fermentation residues was evaluated during 2013-2014 using 30 samples from nine agricultural biogas plants, with at least three samples per biogas plant taken in each of the two seasons (summer and winter) (Table 1). At the same time, 12 samples were investigated from six university laboratory fermenters. The fermentation residue from the all sampling points was sourced from liquid manure, maize silage and sorghum silage, hay silage and waste from gastronomy. Processes in the biogas plants were not altered by chemicals.

A biogas plant with an infeed dry matter (Table 1) content of less than 15% (typically about 4%) is referred to as a liquid fermentation biogas plant. Liquid fermentation biogas plants operate on a continuous basis; samples were taken from the terminal digestate storage. A biogas plant with dry matter content higher than 15% (typically 30-45%) is termed a non-liquid fermentation biogas plant. Mendel University's laboratory fermenters had the capacity of 130 dm³ with a dry matter content of about 4%. They operate on a discontinuous basis and digestate samples were taken after 28 days of reaction.

Samples of mineral coatings (Table 1) were taken from cogeneration unit's engine cylinders and pistons. The unit is equipped with a petrol engine and operated as part of a liquid fermentation biogas plant. Four silage samples were taken from silage pits. This involved standard silage made of maize hybrids intended for biogas production.

Table 1

Substrates and materials specifications of evaluated samples

Type of biogas plant	Fermentation type	Raw substrate	Number of samples
Agricultural A	Liquid	Mixture: maize silage, sorghum silage, manure	12
Agricultural B	Liquid	Mixture: maize silage, hay silage, manure	6
Agricultural C	Liquid	Mixture: maize silage, hay silage, animal faeces, slurry	6
Agricultural	Non-liquid	Mixture: maize silage, manure, gastronomy waste	6
Laboratory 130 l fermenters	Liquid	Mixture: maize silage, sorghum silage, slurry, or gastronomy waste	12
Raw maize silage	Silage	Maize tissue (leaves)	4
Samples of mineral coatings	cogeneration unit's	Cylinders and pistons	12

Analytical methods

Bulk parameters

The collected samples were dried at 105°C, subsequently milled by a cutting mill to make a fraction below 0.100 mm, and homogenised. Solids, total organic carbon (TOC), total inorganic carbon (TIC), combustibles at 550°C and the heat of combustion were determined in all the samples.

X-ray diffraction

Quantitative phase analyses were carried out by the X-ray powder diffraction method (XRD) using the Bruker D8 Advance diffractometer, radiation $\text{CoK}\alpha/\text{Fe}$, 40 kV/40 mA, the angular interval 2-80° 2 θ , step 0.014° 2 θ , 0.75 sec., with the Lynxeye position sensitive detector. The homogenised powder compositions of samples with the addition of internal standard (ZnO) were used for the analysis, with 6% wt. added to the sample e.g. [22]. The quantitative phase analysis was carried out by the Rietveld method [23-26] using the Topas program, version 4.2.

Electron microscopy

Microscopic images were taken using the electron microscope, FEI Quanta 650 FEG (VŠB-TUO ICT Ostrava), fitted with wavelength-dispersive and energy dispersive detectors, as well as with EBSD and CL detectors. The microscopic images were taken by a backscattered electron detector (BSED). Neither silage nor digestate samples were adjusted using classic mineralogy methods. The specimens were scanned at an acceleration voltage of 15 kV, using the electron beam of the diameter of 6 μm , and under pressure in a 50 Pa chamber.

Results

Fermentation residues and raw maize silage

The total organic carbon content (TOC) and the higher heating value provided parameters for evaluation of the methods that serve for determining the ratios of organic and inorganic components within the tested fermentation residues. TOC in the evaluated samples ranged 32.0-52.0% wt. (median = 41.2% wt., variance = 38.6% wt.). The digestate higher heating value was 12.67-18.07 $\text{MJ}\cdot\text{kg}^{-1}$. All the studied samples contained an amorphous phase of 77.5 to 98.7% wt. (median = 91.8% wt., variance = 43.5% wt.) based on the x-ray diffraction method (Table 2).

All the samples contain calcite (1.0 to 5.6% wt.); it possibly comes from the allochthonous environment or from autochthonous reactions. Their presence stabilises fermenter pH as well as pH of the fermentation residue.

Mineral phases of the autochthonous origin are represented by sylvite, its detection interval ranging from to 4.1% wt., with cell parameters $a_0 = 6.29459(28)$. This is a new type of mineral that typically forms from elements present in biomass, which is possible only after the completion of the technological process in fermenters. The growth potential of the mineral is determined by physico-chemical conditions occurring at the temporary storage facility for fermentation residues.

Table 2

Identified mineral phases in the digestion residues and raw maize silage

Mineral phase	Liquid fermentation A	Liquid fermentation B	Liquid fermentation C	Non-liquid fermentation	Laboratory fermenters (Liquid f.)	Raw maize silage
	<i>n</i> = 12	<i>n</i> = 6	<i>n</i> = 6	<i>n</i> = 6	<i>n</i> = 12	<i>n</i> = 4
	Maize silage, sorghum silage, manure	Maize silage, hay silage, manure	Maize silage, hay silage, animal faeces, slurry	Maize silage, manure, food waste	Maize silage, sorghum silage, slurry, food waste	Maize silage substrate
Amorphous content [% wt.]	87.6-98.7	88.2-96.1	90.3-92.4	77.5-90.4	82.5-92.3	99.2-99.9
Quartz [% wt.]	0.3-1.9	1.6-5.6	bellow LOD	7.3-11.8	LOD-0.6	LOD-0.8
Illit-muscovite [% wt.]				LOD-3.6		
Albite [% wt.]	LOD-2.5	LOD-2.5		2.1-2.9		
Orthoclase [% wt.]	LOD-0.9	LOD-0.9		LOD-2.3		
Calcite [% wt.]	LOD-2.5	1.85-2.3	LOD-5.6	LOD-1.8		
Hornblende [% wt.]					LOD-0.1	
Opal-CT [% wt.]	LOD-12.1				LOD-15.2	
Sylvite [% wt.]	LOD-2.56				LOD-4.1	LOD-0.07
Total organic carbon (TOC) [% wt.]	44.7-52.0	41.5-48.6	42.4-44.6	32.0-42.0	34.7-37.4	
The higher heating value [MJ · kg ⁻¹]	17.06-18.07	16.82-17.57	15.66-16.56	12.67-15.49	11.48-17.74	

n - number of samples; LOD - limit of detection

Electron microscopy and maize leaf micro analysis

The raw maize silage was prepared from leaves of maize intended for preparing silage to be used at a biogas plant was found to contain phytoliths shaped as two connected ovals and corresponding to SiO₂ in terms of composition. An electron microprobe tested the phytolith point composition of elements (Table 3). In addition to the elements shown below Al, Ca, Cl, Fe, K, Mg, Na, P, and S were also detected in the leaves.

Table 3

Elemental composition of phytoliths obtained from maize leaves

	Wt [%]	At [%]
C	12.26-28.58	19.49-40.45
O	36.81-40.93	39.12-50.27
Si	27.28-45.59	16.49-30.99
Al, Ca, Cl, Fe, K, Mg, Na, P, S	bellow LOD	bellow LOD

Points analysis number *n* = 12; LOD - limit of detection

Results of XRD analysis of the engine layer

Chalcanthite and chalcocyanite are the predominant minerals found in the engine cylinder and piston coatings; quartz containing 7.44% is found in place 4 (Table 4).

Table 4

Mineral phase in the coatings of the cogeneration unit's engine

Phase	Mineral	Content [% wt.]
Phase 1	Chalcanthite	67.58
Phase 2	Chalcocyanite	11.65
Phase 3	Bonattite	8.89
Phase 4	Quartz	7.44
Phase 5	Tenorite	1.89
Phase 6	Ramsbeckite	1.75
Phase 7	Antlerite	0.79

Discussion - The effect of minerals found in the digestion residues

Quartz represents a mineral phase of allochthonous origin in all the studied samples. Minerals such as illite-muscovite, albite, orthoclase and hornblende come from agricultural soil. They enter the technological process as part of contamination of the substrate for silage production. The proportion of the detected mineral phases in the fermentation residues varies as per the local soil situation. The highest amount of mineral admixtures was found in biogas plants with dry fermentation.

The amorphous phase content as determined by the XRD method and TOC reached the correlation coefficient of 0.87 in the data set. The results are supported by the higher heating value analyses. This procedure is used for validating the results of the mineral phase analysis.

The quantity of the admixture can however be assumed to be very similar in all the technologies studied. For liquid fermentation technology, the minerals supplied are gravity-separated in the fermentor, sediment on the bottom and are not present in the exiting digestate, unlike the non-liquid technology, where digestate is always quantitatively removed from the fermenter. These minerals occur naturally in this process and are returned to the soil when the fermentation residue is applied as a fertiliser.

Opal-CT was found in eleven cases (1.26-12.1% wt., median = 4.1% wt.), the cell parameters being $a_0 = 4.9996(11)$, and $c_0 = 7.0068(31)$. It may enter fermenters as part of plant tissues - phytoliths, or as admixture of a different origin; it may also come from the present amorphous SiO_2 .

Analysis of coatings collected from Otto engine cylinder heads was the subject of studies carried out by [27] who concluded that the theoretical O/Si mass rate in the silicate unit $(\text{SiO}_4)_4$ - is 2.278; analysing the O/Si ratios indicated 1.67-2.46. It can be concluded that the silica layer on the cylinder head surface is one of the orthosilicate form. The authors also analysed soft deposit samples extracted from the piston ring groove zone for SEM-EDX analysis. Because the theoretical mass rate in the silicon dioxide, SiO_2 , is 1.14, this soft paste deposit can be assumed to be silicon dioxide.

When burning biogas, siloxanes become oxidised to form a very fine powder composed mainly of SiO_2 which is formed on the inner metal surfaces in the combustion chambers of cogeneration unit engines, e.g. piston walls, cylinder heads, spark plugs and valves. In the gas engine combustion process, organic silicon compounds form a solid insoluble coat on the inner piston surface that cause engine damage [27].

Using the XRD method, SiO_2 was found in the form of quartz in the treated samples of maize silage, the amount being max. of 0.8% wt. As no other minerals were found which would come from soil, the presence cannot be explained through remnants of soils on plants

fed in to the system. Since SiO_2 was found in samples of maize leaves in the form of phytoliths using the method of electron microscopy with an electron microprobe, it can be assumed that SiO_2 found in the silage comes from maize tissue phytoliths.

Cryptocrystalline quartz (opal-CT) was also found in a total of 12 samples of fermentation residues of liquid fermentation technology. Since the mineral is present in the microcrystalline form of opal, it is not capable of sedimentation and is entrained along with biogas into the combustion chamber of the cogeneration unit via the pipeline, where it converts into stable quartz at high temperature and under high pressure.

Conclusions

Mineral phase composition was identified in samples of fermentation residues from different technological processes of biogas production: (1) liquid fermentation; (2) non-liquid fermentation; and (3) liquid fermentation in university's laboratory fermenters. The total organic carbon (TOC) content ranged from 32.0 to 52.0% wt. (median = 41.2% wt.) in all samples. The majority of samples consisted of the amorphous phase (77.5 to 98.7% wt., median = 91.8% wt.), while the minority phases consisted of quartz, albite, orthoclase, muscovite and amphibole (LOD up to 1.92% wt.). Variable proportions of the mineral substances were detected in the fermentation residues reflecting the local pedological situation. The largest amount of these admixtures was found in biogas plants with dry fermentation. These minerals occur naturally in this process and are returned to the soil when the fermentation residue is applied as a fertiliser. If, however, the fermentation residue is used as fuel, they can cause increased wear of machine parts, reduce the pumping potential and cause further complications. All the samples were found to contain calcite and/or magnesium calcite (1.0-5.7% wt.). These minerals possibly originate from the allochthonous environment or autochthonous reactions. Their presence stabilises pH in the fermenter and that of the fermentation residue.

Opal-CT was found in eleven cases (1.26 to 12.1% wt., median = 4.1% wt.). Unwanted Opal-CT is entering fermenters either as phytoliths - plant tissues, or as an admixture of unknown origin. Opal-CT may also develop as autochthonous amorphous SiO_2 . Any link between the occurrence of opal-CT and the production technology/the composition of input raw materials was not identified.

The presence of SiO_2 detected on the surface of the cogeneration unit's cylinders and pistons proved that SiO_2 coating can developed during the agricultural processes with none siloxanes present. If mobilised as an aerosol, it can be carried along with biogas into the cogeneration unit. The SiO_2 aerosol then forms the base for quartz, a stable mineral, to generate. Simultaneously, other stable minerals generate from present sulphur and copper released from sliding bearings of crankshafts (Table 4) to form a coat on the inner surfaces of engines.

The positive symptoms here include the binding of elements suitable for plant nutrition to mineral phases, which leads to the stabilisation and gradual release when the fermentation residue is applied to the soil.

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