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Document type	Related content	Document date	Expected action
Project / Draft		2022-04-21	**INFO**

Description

Enclosed, please find the 1st working draft of WI 00223120.

As agreed during the last meeting of CEN/TC 223/WG 4 on 2022-03-09, the draft was circulated to WG 4 for comments. No comments were received and the draft is therefore accepted by WG 4 as 1st working draft (see conclusion 01/2022).

As agreed during the same meeting, the 1st working draft and the forms for the activation of the work item will be sent to CEN/TC 223 as soon as the call for tender for the project leaders is completed and the project leaders are known.

CEN/TC 223

Date: 2022-04

WI 00223120:2022

Secretariat: NEN

Digestate – Determination of the residual biogas potential

Einführendes Element — Haupt-Element — Ergänzendes Element

Élément introductif — Élément central — Élément complémentaire

ICS:

CCMC will prepare and attach the official title page.

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European foreword

This document (prEN 00223120:XXXX) has been prepared by Technical Committee CEN/TC 223 “Soil improvers and growing media”, the secretariat of which is held by NEN.

This document is a working document.

This document has been prepared under a standardization request given to CEN by the European Commission and the European Free Trade Association.

Introduction

The anaerobic digestion is a biological process leading, in absence of oxygen, to the degradation of organic carbon and to the production of biogas, a gas mixture composed mainly by methane (CH_4) and carbon dioxide (CO_2). The degradation process is carried out by a wide range of mesophilic or thermophilic microorganisms and applied on an industrial scale as an exploitation strategy to produce added-value products from crops, livestock manure, agro-industrial by-products, biowaste and sludges. The digestate obtained is a stabilized, nutrient-rich material, and a suitable component for soil improvers, growing media and other organic fertilizers.

When the organic material is not efficiently converted into biogas, the digestate coming out from the plant is unstable and continues to produce biogas in the final storage tank.
The assessment of the digestate's stability can be carried out through the residual biogas potential (RBP) test which represents the amount of biogas that could still be produced from the organic material present at the end of the anaerobic digestion process.

1 Scope

This European Standard specifies a method for the determination of the residual biogas potential in digestate in an anaerobic environment.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13039:—[1], *Soil improvers and growing media — Determination of organic matter content and ash*

EN 13040-1:—[2], *Soil improvers and growing media — Sample preparation – Part 1: Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory bulk density*

EN 45501, *Metrological aspects of non-automatic weighing instrument*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in CEN/TS 00223137:—[3] and the following apply.

3.1

Biogas

mixture of gases mainly composed of CH_4 (methane) and CO_2 (carbon dioxide) and produced by the anaerobic degradation of organic material

3.2

Inoculum

biological material with active anaerobic microorganisms able to initiate and enhance the degradation process

3.3

Working volume

usable volume within a reaction vessel taken up by inoculum, sample, nutrients solution and water

3.4

Headspace

remaining volume within the reaction vessel obtained by subtraction of the working volume, occupied by the biogas

[1] Under preparation. Stage at the time of publication: EN 13039:20**.

[2] Under preparation. Stage at the time of publication: EN 13040-1:20**.

[3] Under preparation. Stage at the time of publication: CEN/TS 00223137:20**

4 Principle

The test is carried out under anaerobic conditions and in a temperature-controlled environment. Closed reaction vessels are filled with adjusted quantities of inoculum, sample and a nutrient solution. The biogas is cumulated within the headspace of the reaction vessel and its amount and composition are measured by manometric or volumetric methods. The residual biogas potential (RBP) is referred to the normal conditions of pressure and temperature and to the amount of organic matter (volatile solids) added to the reaction vessel.

5 Apparatus

5.1 Test facility

Temperature controlled room, climate cabinet or water bath, mesophilic temperature adjustable to (38 ± 2) °C.

The laboratory may carry out the analysis in thermophilic temperature (52 ± 1) °C.

5.2 Reaction vessels

Glass or steel gastight vessels (with a volume of 0,5 l to 2,5 l).

5.3 Pressure transducer

Operating range of 0 kPa to 50 kPA and a maximum uncertainty set lower than 1,5 % of the full scale.

5.4 Volume displacement devices

Liquid displacement gasometers, lubricated gas syringes and gas counters.

5.5 Barometer

To measure atmospheric pressure.

5.6 Mixing device

Shaking table (120 ± 20) rpm or magnetic stirring unit.

5.7 Balance

Meeting EN 45501 class II tolerances with a scale interval of 0,01 g.

5.8 pH meter

With slope adjustment and temperature control.

5.9 Sieves

5 mm square aperture size or smaller.

6 Reagents

6.1 Water with a specific conductivity not higher than 0,2 mS/m at 25 °C, free from the elements to be determined.

6.2 NaOH (0,5 mol/l)

6.3 HCl (0,5 mol/l)

6.4 Trace elements stock solution

Dissolve the following masses of chemical compounds in 1000 ml water (see 6.1):

- 0,05 g of $MnCl_2 \cdot 4H_2O$;
- 0,005 g of H_3BO_3;
- 0,005 g of $ZnCl_2$;
- 0,003 g of $CuCl_2$;
- 0,001 g of $Na_2MoO_4 \cdot 2H_2O$;
- 0,1 g of $CoCl_2 \cdot 6H_2O$;
- 0,01 g of $NiCl_2 \cdot 6H_2O$;
- 0,005 g of Na_2SeO_3.

6.5 Complete nutrient solution

Dissolve the following masses of chemical compounds in 1000 ml water (see 6.1):

- 0,27 g of KH2PO4;
- 1,12 g of Na2HPO4·12H2O;
- 0,53 g of NH4Cl;
- 0,075 g of CaCl2·2H2O;
- 0,10 g of MgCl2·6H2O;
- 0,02 g of FeCl2·4H2O;
- 10 ml of trace elements stock solution (see 6.4).

Adjust the pH of the medium, if necessary, with dilute mineral acid or alkali to 7 ± 0.2 (see 6.2 and 6.3).

6.7 N_2 gas

6.8 Microcrystalline cellulose (CAS 9004-34-6)

7 Procedure

7.1 Storage and preparation of sample

Transportation, reception and storage of samples shall be determined according to EN 13040-1:—, clauses 6 and 7; samples preparation shall follow clauses 9.2.1, 9.3 and 9.4. The sample shall be

characterized by the following parameters: total solids (TS) (according to EN 13040-1) and volatile solids (VS) (according to EN 13039). Volatile solids shall be submitted to the preparation procedure within 24 hours after sampling. Otherwise, the sample shall be stored (max 1 month) at (3 ± 2) °C under anaerobic/anoxic condition.

NOTE For further characterisation of the sample, the determination of pH, ammonium content ($N\text{-}NH_4^+$), volatile fatty acid profile (VFA) and the chemical oxygen demand (COD) is applicable.

7.2 Sampling, storage and preparation of inoculum

The inoculum (3.2) shall be sieved with a maximum square aperture size of 5 mm to remove the particles retained and then pre-digested without the addition of any nutrients and carbon sources at test temperature at least for 5 days, in order to reduce background gas production and to decrease the influence of the blank controls. The inoculum shall be characterized, after pre-digestion period, by TS and VS.

To check the suitability of inoculum, it is required a pH range between 7.0 to 8.5, a VFA concentration <1 g HAc eq/l , an $N\text{-}NH_4^+$ concentration < 5 g/l and alkalinity >3 g $CaCO_3$eq/l, according to process monitoring in biogas plants [3].

NOTE Inoculum should come from a digester working at mesophilic (or thermophilic) condition; a pre-digestion step for about 5 days at test temperature gives an optimal reduction in gas production of the blank without increases of the lag phase period.

7.3 Starting the procedure

For the preparation of each reaction vessel (5.2) it is necessary to calculate masses of the sample (7.1) and the inoculum (7.2) as well as the volumes of the complete nutrient solution (6.5) and the dilution water (6.1).

NOTE The addition of nutrients can be optional when their concentration in the digester is already known and suitable.

Calculate the masses according to an inoculum – sample ratio equal to 2 on volatile solids basis and considering that the final concentration of total solids in the reaction vessel shall be 10 g/l to 50 g/l.

The amount of inoculum (fresh matter) to be added to 1 g of digestate (fresh matter) is given by the following equation:

$$FM_I = \frac{VS_D \times TS_D}{VS_I \times TS_I} \times 2 \tag{1}$$

FM_I is the inoculum in g per 1 g of digestate;

VS_I is the volatile solid of the inoculum, in % TS mass;

VS_D is the volatile solid of the digestate, in % TS mass;

TS_I is the total solid of the inoculum, in % mass;

TS_D is the total solid of the digestate, in % mass;

Prepare the reaction vessel filled with the test sample and the inoculum and add an amount of nutrient solution corresponding to 5 % of the working volume (3.3) and an amount of water leaving enough headspace (usually 30 % to 40 % of the total vessel volume, see Annex B). In order to measure the

background biogas produced by inoculum, a blank vessel shall be prepared using the same mass of inoculum added to the test vessel, except for the sample, which is replaced with an equal mass of dilution water.

Measure the pH in the reaction vessel. The value shall be between 7 and 8.5. If this is not the case, base or acid shall be added (6.2 and 6.3).

Place the reaction vessels in the conditioned room (5.1). Flush the headspace (3.4) with inert gas, O_2-free, preferably N_2. The flushing shall guarantee a turnover equal to 5 times the volume of the headspace. Close the reactors in order to avoid air inlet. Start the stirring system (5.4 or daily manual stirring). Record the measurements (gas pressure or gas volume) at least once a day and release the overpressure gas (venting) in system where this is required.

7.4 Measurement methods

The measurement of the biogas produced can take place with:

- manometric method: based on the principle of measuring the pressure variation inside the headspace of the reaction vessel and conducted in constant volume;
- volumetric method: based on the principle of measuring the volume of gas produced in the reaction vessels maintained at constant pressure.

NOTE Gas chromatography, non-dispersive infrared technique (NDIR) or carbon dioxide absorption unit can be used for gas quality analysis (percentage of CH_4 and CO_2 in biogas).

The reading and recording of the measurement intervals can be manual or carried out through a continuous detection system, until the end of the test. The test duration shall be 28 days.

The pH at the end of the test shall be between 7 and 8.5. If not, the test shall be repeated.

For vessel volume smaller than 1 l, the test shall be performed at least in duplicates.

In order to guarantee that the test provides reliable and repeatable results, check on the equipment and instrumentation used (e.g. calibration, checks on the absence of biogas leaks, etc.) should be carried out periodically.

Microcrystalline cellulose shall be used as reference substance; the stoichiometric biogas potential for cellulose ($C_6H_{10}O_5$) is of 829 L_{biogas} /kg VS [6]. The calibration is valid for test values > 85% of the stoichiometric biogas potential. Validation criteria will result from interlaboratory test (see Annex A).

8 Calculation

Biogas produced accumulates within the headspace of a sealed reaction vessel over measurement intervals, *i*.

For volumetric method, to standardize biogas produced (at 273,15 K (0 °C) and 1013,25 hPa), the following equation is used:

$$V_{i,std} = V_{gas}\left(\frac{P_{atm}}{P_0} \times \frac{273{,}15}{R(T + 273{,}15)}\right) \tag{2}$$

where

$V_{i,\,std}$ is the standardized biogas volume in each interval *i* (venting), in litre;

V_{gas} is the measured biogas volume, in litre;

P_{atm} is the measured atmospheric pressure, in hPa;

P_0 is the pressure in standard condition (1013,25 hPa);

T is the temperature performed in °C;

R is the gas constant (8,314 l · kPa ·K^{-1} · mol^{-1}).

For manometric method, to standardize biogas produced (at 273,15 K (0 °C) and 1013,25 hPa), the following equation is used:

$$V_{i,std} = V_{gasHS}\left(\frac{\Delta P}{P_0} \times \frac{273{,}15}{R(T + 273{,}15)}\right) \tag{3}$$

where

$V_{i,\,std}$ is the standardized biogas volume in each interval *i* (venting), in litre;

V_{gasHS} is the measured biogas volume in the headspace, in litre;

ΔP is the difference between the pressure measured pre and post gas venting in the headspace, in hPa;

P_0 is the pressure in standard condition (1013,25 hPa);

T is the temperature performed in °C;

R is the gas constant (8,314 l · kPa · K^{-1} · mol^{-1}).

NOTE: The equations are based on the assumption that all gas production is biogas (CH_4 and CO_2).

Cumulative biogas production (V_{std}) is calculated by adding the sum of biogas volume ($V_{i,\,std}$) in each interval *i* (venting) to the residual biogas volume ($V_{r,\,std}$) in the headspace at the end of the last venting:

$$V_{std} = \sum_{i=1}^{n} V_{i\,std} + V_{r,std} \tag{4}$$

where

V_{std} is cumulative biogas production, in litre;

n is the number of vents;

$V_{i,\,std}$ is the standardized biogas volume in each interval *i* (venting), in litre;

$V_{r,\,std}$ is the standardized residual biogas volume after the last venting, in litre (calculated using Eq. 2).

According to the same formulas described for the reaction vessel, the biogas volume of the blank vessel (V_b) is calculated.

NOTE: If measurements are cumulative instead of interval, the summation operation is omitted and a single value from interval *i* is added instead.

The residual biogas potential (RBP in l per g VS) is calculated according to the formula:

$$RBP = \left(\frac{V_{std} - V_b \times f}{W \cdot TS \cdot VS}\right) \tag{5}$$

where

RBP is the residual biogas potential (RBP in l per g VS)

W is the initial mass of the sample, in g;

TS is the total solid content of the sample, in % mass;

VS is the volatile solids content of the sample, in % TS mass;

V_b is the standardized biogas volume of the blank vessel, in litre;

f is the correction factor (see below).

In the case where the inoculum mass in the reaction vessel and in the blank vessel is not the same, the correction factor shall be used:

$$f = \frac{W_i}{W_{ib}} \tag{6}$$

where

W_i is the mass of the inoculum in reaction vessel, in g;

W_{ib} is the mass of the inoculum in blank vessel, in g.

9 Test report

The test report shall contain at least the following:

a) a reference to this document;

b) identification of the sample;

c) information about the inoculum (total solids, volatile solids and origin/source);

d) the number of replicates;

e) the mean *RBP*, rounded to one decimal place;

f) the testing temperature;

f) test duration;

g) measurement gas method (manometric or volumetric);

h) net daily production of biogas at the end of the test: percentage of cumulative production;

i) details of all work cycles not contained in this standard or that were considered optional, as well as all factors that may have influenced the results.

Annex A
(informative)

Validation

Sample:

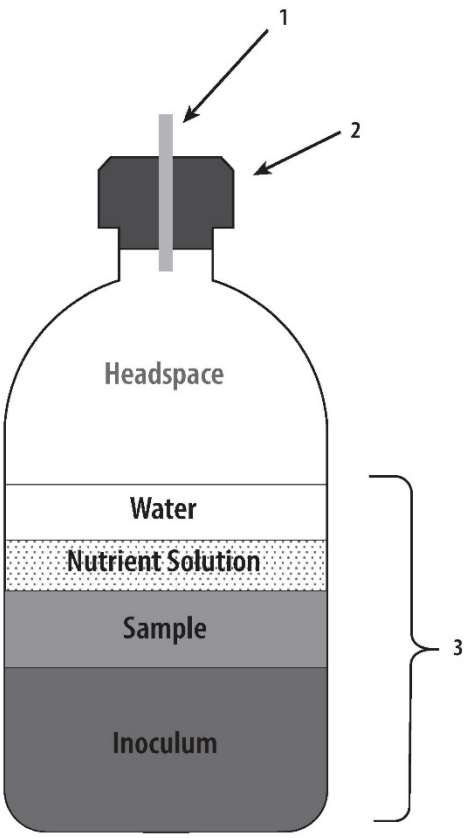
- Fresh crop digestate (CMC 4): 2 x (digestate and solid fraction of digestate)
- Digestate other than fresh crop digestate (CMC 5): 2 x (digestate and solid fraction digestate)
- Microcrystalline cellulose (CAS 9004-34-6)

In the interlaboratory trial the percentage distance between two replicates or the standard deviation between multiple replicates shall not exceed 5 %.

Annex B
(informative)

Specific information on RBP - test

Figure B.1 shows an example of the experimental setup of a reaction vessel.



Key

1 gas outlet

2 gas-tight cap

3 working volume

Figure B.1 – Reaction vessel (RBP)

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