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Bioizdelki - Pregled metod za določanje biodeleža v izdelkih

Bio-based products - Overview of methods to determine the bio-based content

Biobasierte Produkte - Überblick über verfügbare und mögliche Methoden und Techniken zur Bestimmung des gesamten biobasierten Gehaltes von Produkten

Produits biosourcés - Vue d'ensemble des méthodes pour déterminer la teneur biosourcée

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CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (CEN/TR 16721:2014) has been prepared by Technical Committee CEN/TC 411 “Bio-based products”, the secretariat of which is held by NEN.

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Introduction

Bio-based products from forestry and agriculture have a long history of application, such as paper, board and various chemicals and materials. The last decades have seen the emergence of new bio-based products in the market. Some of the reasons for the increased interest lie in the bio-based products' benefits in relation to the depletion of fossil resources and climate change. Bio-based products may also provide additional product functionalities. This has triggered a wave of innovation with the development of knowledge and technologies allowing new transformation processes and product development.

Acknowledging the need for common standards for bio-based products, the European Commission issued mandate M/492[1], resulting in a series of standards developed by CEN/TC 411, with a focus on bio-based products other than food, feed and biomass for energy applications.

The standards of CEN/TC 411 "Bio-based products" provide a common basis on the following aspects:

- Common terminology;
- Bio-based content determination;
- Life Cycle Assessment (LCA);
- Sustainability aspects;
- Declaration tools.

It is important to understand what the term bio-based product covers and how it is being used. The term "bio-based" means "derived from biomass". Bio-based products (bottles, insulation materials, wood and wood products, paper, solvents, chemical intermediates, composite materials, et cetera.) are products which are wholly or partly derived from biomass. It is essential to characterize the amount of biomass contained in the product by for instance its bio-based content or bio-based carbon content.

The bio-based content of a product does not provide information on its environmental impact or sustainability, which may be assessed through LCA and sustainability criteria. In addition, transparent and unambiguous communication within bio-based value chains is facilitated by a harmonized framework for certification and declaration.

The purpose of this Technical Report is provide an overview of methods for the determination of the bio-based content of solid, liquid and gaseous products.

The ability to determine the bio-based content of a product is an obvious prerequisite for developing the market for bio-based products. Currently, the bio-based content is usually derived from the determination of the bio-based carbon content by means of ^{14}C measurement (as described in ASTM D6866-12 [1]).This methodology is used because ^{14}C is measurable.

However, results based on the ^{14}C methodology are expressed as a fraction of bio-based carbon on the total (organic) carbon content of the sample. In some cases the bio-based content of a product can differ substantially from the bio-based carbon content. For example, for products in which a fraction of the raw materials has been replaced by bio-based materials/constituents containing other elements such as oxygen, nitrogen or hydrogen (e.g. carbohydrate-based products), the bio-based carbon content may be substantially lower than the fraction of the product that is derived from biomass. This Technical Report describes three different methodologies to determine the bio-based content in a product and proposes the development of standards.

It should be noted that the quantification of the bio-based content is not a measure of sustainability of a bio-based product.

[1] A Mandate is a standardization task embedded in European trade laws. M/492 Mandate is addressed to the European Standardization bodies, CEN, CENELEC and ETSI, for the development of horizontal European Standards for bio-based products.

1 Scope

This Technical Report gives an overview of methods which can be used for the determination of the bio-based content of solid, liquid and gaseous products. It describes more specifically:

a) a method using the radiocarbon analysis and elemental analysis: this method is based on a statement and a verification of the composition of the products;

b) methods based on measurement of stable isotopic ratio; and

c) a method based on the material balance.

This Technical Report gives guidance on the applicability of the different methods.

This Technical Report also gives recommendations for the further development of European Standards for the determination of the bio-based content.

2 Terms and definitions

For the purposes of this document, the terms and definitions given in FprEN 16575:2014 [2] and the following apply.

2.1
formulated product
product obtained by mixing of different constituents

2.2
material balance
comparison of physical quantities of inputs, outputs and inventory changes in a quantity centre over a specified time period

[SOURCE: ISO 14051:2011, 3.1]

3 Method using the radiocarbon analysis and elemental analysis

3.1 Background

Element carbon, C, has an isotope, ^{14}C, which allows for a clear distinction between carbon based substances derived from biomass and carbon based substances from fossil sources. The ^{14}C present in chemicals originates from recent atmospheric CO_2. Due to its radioactive decay, it is almost absent from fossil products older than 20 000 years to 30 000 years. The ^{14}C content may thus be considered as a tracer of chemicals recently synthesized from atmospheric CO_2 and particularly of recently produced products.

The approach based on isotopic measurements to determine the bio-based content of a sample can be used for carbon but not for other elements, such as oxygen, nitrogen or hydrogen.

However the content of each element can be determined by an elemental analysis which leads to the total content of each element, but does not differentiate the elements according to their origin from bio-based resources or fossil resources. Therefore, the combination of the ^{14}C content determination and an elemental analysis does not give the bio-based content of a sample. To circumvent this difficulty, the method as given in 3.2 is proposed.

NOTE The bio-based content of a product can be derived from the bio-based carbon content if the composition of the biomass used is unchanged. Even for derivatives the bio-based carbon content can be used if the chemistry behind the conversion is well known and constant.

3.2 Principle

NOTE 1 This method is under development and at the end of experiment phase the results will be taken into account when drafting the European Standard dealing with this method.

This method, supported by rules described in 3.3, consists of the statement of the bio-based content and of the elemental content of the sample obtained by calculation. This statement is validated by means of a comparison with the same kind of data resulting from the ^{14}C analysis and the elemental analysis of the sample.

NOTE 2 The "statement" in the sense of this document is not to be confused with the "declaration" of the bio-based content, based on the results of this method.

Products can be classified into two groups, chemicals and formulated products depending on the type of analyses to be carried out:

a) Group 1: products obtained by chemical synthesis. A representative sample is analysed on the following criteria: ^{14}C content determination and elemental analysis of carbon, hydrogen, oxygen and/or nitrogen. If other elements are present, they may also be analysed. The validation process uses common rules of stoichiometry for these products. See 3.5;

b) Group 2: formulated products. A representative sample is analysed with the ^{14}C method only, if the bio-based content of the constituents (Group 1) of the product are analysed according to this method. The validation process uses a calculation by mass for these products. See 3.6.

NOTE 3 Since Group 2 formulated products can be made from several constituents, even in a large number, the complete method described for Group 1 may be difficult to implement. This is the reason why a simplified method was developed for the formulated products of Group 2.

3.3 Basic rules

3.3.1 Oxygen, hydrogen and nitrogen elements

As it is not possible to make a distinction between bio-based and non-bio-based elements such as oxygen, hydrogen or nitrogen, for the application of this method in this Technical Report, the following convention applies:

If oxygen (O) and/or hydrogen (H) and/or nitrogen (N) element(s) is(are) bound to a biomass carbon structure, it(they) is(are) considered to be part(s) of the bio-based content.

3.3.2 Chemical reactions

For products/constituents of products obtained by chemical synthesis, the following guidance is proposed:

a) in case that the chemical reaction occurs without release of by-products:

   1) if the reactants are exclusively derived from biomass, the bio-based content of the product/constituent of the product is 100 %; if none of the reactants is derived from biomass, the bio-based content of the product/constituent of the product is 0 %;

   2) if the reactants are derived from both biomass and fossil resource, the final product has a bio-based content proportional to the bio-based content of each reactant;

b) in case that the chemical reaction leads to the release of a molecule which is not part of the main product, the allocation of the main elements of the reactants follows the basic chemical rules.

EXAMPLE Esterification leads to the release of a water molecule, in which the oxygen will be considered as coming from the acid according to the usual chemical rules.

3.3.3 Natural products

The bio-based carbon content and the bio-based content of natural products [e.g. wood (including pulp), flax, hemp, bamboo] are each equal to 100 %. Therefore, it is not necessary to determine these contents by analytical methods.

3.4 Test methods

The bio-based carbon content of a sample can be determined according to FprCEN/TS 16640 [3], Method C (AMS). Alternatively, the bio-based carbon content can be determined according to EN 15440 [4] or CEN/TS 16137 [5], Method C, and declared according to CEN/TS 16295 [6] or ASTM D6866-12 [1] and the results can be reported according to ASTM D7026-04 [7].

NOTE CEN/TS 16137 is applicable to plastic material and products, but the test methods can be in principle applied to any other product.

For the elemental analysis, standard analytical methods should be used.

3.5 Products obtained by chemical synthesis (Group 1)

3.5.1 General

The statement (see 3.2) should include a detailed elemental composition of the bio-based part and the fossil part of the product, as well as the bio-based content.

EXAMPLE 1 Bio-ethyl acetate obtained by esterification between bio-ethanol from fermentation of sugar and acetic acid from fossil resources:

Fraction	C %	H %	O %	Total %
Fossil fraction (from acetic acid)	27,3	3,4	18,2	48,9
Bio-based fraction (from ethanol)	27,2	5,7	18,2	51,1
Total	54,5	9,1	36,4	100,0

Then, the data of the statement are compared with the results of the analysis.

If the data of the statement and the analytical results range within a defined error margin, as shown in Table 1, the bio-based content should be validated as stated or should be rounded down according to the rules given in 3.5.2.

The analytical results can differ from the stated values for the following reasons:

a) the composition of the product may show some variability due to its natural origin;

EXAMPLE 2 Natural fatty acids used in the production of fatty acid esters.

b) the production process may also to some extent be a cause of variability of the composition of the final product;

c) the analytical methods are also a source of uncertainty, as follows (values pertaining to the methods):

   1) ± 3 % of the measured value for the bio-based carbon content;

   2) ± 0,4 % of the measured value for the total carbon, total oxygen or total nitrogen content;

3) ± 0,2 % of the measured value for the total hydrogen content.

3.5.2 Validation criteria

The stated bio-based content of a sample can be validated by considering the bio-based carbon content obtained from the ^{14}C content determination and the analytical results of at least two more elements chosen among total carbon, total oxygen, total hydrogen or total nitrogen.

If nitrogen and/or oxygen element(s) is(are) not present in the molecule, it(they) is(are) not taken into account.

In case of bio-ethyl acetate in 3.5.1, EXAMPLE 1, nitrogen element is not present in the molecule; therefore nitrogen element cannot be taken into account. The validation is done by comparing the values of the bio-based carbon content as well as the total carbon content and the hydrogen content. The total oxygen content may also be considered instead of the total carbon content or total hydrogen content.

Three confidence levels are defined depending on the closeness between the stated values and the values obtained by analysis. The stated bio-based content of a sample is validated if the differences between the stated values and the values obtained by analysis comply with Table 1.

Table 1 — Decision process

Confidence level	Deviation between calculation and results of analysis				
	Bio-based carbon content %	Total carbon content %	Total hydrogen content %	Total oxygen content %	Total nitrogen content %
1 (High)	± 3,0	± 0,4	± 0,2	± 0,4	± 0,4
2 (Medium)	± 4,5	± 1,0	± 0.5	± 1,0	± 1,0
3 (Low)	± 6,0	± 2,0	± 1,0	± 2,0	± 2,0

If at least three of the values of the differences between the stated values and the values obtained by analysis are comprised within the uncertainties given in Table 1, then:

a) for confidence level 1, the stated value for the bio-based content is validated;

b) for confidence level 2, the stated value for the bio-based content is rounded down to the nearest "multiple of five" percentage (e.g. 52 % is rounded down to 50 %, 57 % is rounded down to 55 %);

c) for confidence level 3, the stated value for the bio-based content is rounded down to the second nearest "multiple of five" percentage in such a way that the difference between the stated value and the rounded value is > 5 % (e.g. 48 % is rounded down to 40 %, 45,2 % is rounded down to 40 %).

In addition, none of the values of the differences between the stated values and the values obtained by analysis should be higher than the values given in Table 1 for confidence level 3.

All calculations are based on results reported on a dry matter basis.

EXAMPLE 1:

	Bio-based carbon content %	Total carbon %	Total hydrogen %	Total oxygen %	Bio-based content %
Stated values	25,00	50,00	5,56	44,44	56
Measured values	25,86 ± 3	49,80 ± 0,4	5,68 ± 0,2	44,60 ± 0,4	-
Three values are within the maximum difference between stated value and the result of analysis defined for confidence level 1. "56 %" is validated.					

EXAMPLE 2:

	Bio-based carbon content %	Total carbon %	Total hydrogen %	Total oxygen %	Bio-based content %
Stated values	40,8	53,0	9,0	24,2	52
Measured values	40,1 ± 4,5	52,1 ± 1,0	8,82 ± 0,5	22,46 ± 1,0	-
Three values are within the maximum difference between stated value and the result of analysis defined for confidence level 2. "50 %" is validated.					

EXAMPLE 3:

	Bio-based carbon content %	Total carbon %	Total hydrogen %	Total oxygen %	Bio-based content %
Stated values	47,25	50,15	7,23	42,62	67
Measured values	42,2 ± 6	47,5 ± 2	7,86 ± 1	40,79 ± 2	-
Three values are within the maximum difference between stated value and the result of analysis defined for confidence level 3. "60 %" is validated.					

3.6 Formulated products (Group 2)

3.6.1 General

On the one hand, the bio-based carbon content (based on ^{14}C content) of the sample should be determined by analysis. On the other hand, the bio-based carbon content and bio-based content of the sample are calculated from data related to the constituents and stated. It implies that the constituents of the sample have been analysed and the statement of the bio-based content of each constituent has been validated according to 3.5.2.

3.6.2 Calculation of the bio-based content of a sample

The bio-based content of a sample is calculated using Formula (1):

$$B_s = 100 \frac{\sum_{i=1}^{n} B_i \cdot m_i}{m_s} \quad (1)$$

Where