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Solid recovered fuels — Methods for the determination of biomass content

Combustibles solides de récupération — Méthode de détermination de la teneur en biomasse

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 300, *Solid recovered fuels*.

This corrected version of ISO 21644:2021 incorporates the following corrections:

— Correction of "$4\ \mathrm{ml}\ \mathrm{l}^{-1}$" to "$4\ \mathrm{mol{\cdot}l}^{-1}$" in Annex A.

— Editorial corrections made to several symbols.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The biomass content of solid recovered fuels is relevant for the evaluation of the impact of energy production on greenhouse gas emission. Instrumental methods, wet chemical and manual procedures are available for the calculation of the renewable energy fraction. Instrumental methods are based on the determination of ^{14}C content while manual procedures are based on separation of different fractions by visual inspection. The wet chemical procedure differentiate biomass from non-biomass materials as function of the acid dissolution behaviour.

The fraction of biomass is expressed:

- by mass;
- by energy content (gross or net calorific value);
- by carbon content.

This document is primarily intended for laboratories, producers, suppliers and purchasers of solid recovered fuels, but is also useful for the authorities and inspection organizations.

Solid recovered fuels — Methods for the determination of biomass content

1 Scope

This document specifies three methods for the determination of the biomass content in solid recovered fuels: the ^{14}C content method, the selective dissolution and the manual sorting methods.

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.

ISO 21637:2020, *Solid recovered fuels — Terminology, definitions and descriptions*

ISO 21645[1)], *Solid recovered fuels — Methods for sampling*

ISO 21646[2)], *Combustibles solides de récupération — Préparation des échantillons*

ISO 21654[3)], *Solid recovered fuels — Determination of calorific value*

ISO 21656[4)], *Solid recovered fuels — Determination of ash content*

ISO 21663, *Solid recovered fuels — Methods for the determination of total carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) by the instrumental method*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 21637:2020 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1

ash content on dry basis
mass of inorganic residue remaining after ignition of a fuel under specified conditions, expressed as mass fraction in percent of the dry matter in the fuel, also includes removed ash contributors

Note 1 to entry: This is typically expressed as a percentage of the mass of dry matter in the fuel source.

Note 2 to entry: Depending on the combustion efficiency the ash may contain combustibles.

Note 3 to entry: If a complete combustion is realized, ash contains only inorganic, non-combustible components.

[SOURCE: ISO 21637:2020, 3.3]

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1) Under preparation. Stage at the time of publication ISO/FDIS 21645.

2) Under preparation. Stage at the time of publication ISO/DIS 21646.

3) Under preparation. Stage at the time of publication ISO/FDIS 21654.

4) Under preparation. Stage at the time of publication ISO/FDIS 21656.

3.2
biogenic
produced in natural processes by living organisms but not fossilized or derived from fossil resources

3.3
biomass
material of biological origin excluding material embedded in geological formations and/or fossilized

[SOURCE: ISO 16559:2014, 4.32, modified — Notes 1 and 2 to entry have been removed.]

3.4
calorific value
quantity of heat produced by the complete combustion, at a constant pressure equal to 1 013,25 mbar, of a unit volume or mass of gas, the constituents of the combustible mixture being taken at reference conditions and the products of combustion being brought back to the same conditions

[SOURCE: EN 437: 2018, modified — Second paragraph (the list) has been removed.]

3.5
gross calorific value
calorific value where the water produced by combustion is assumed to be condensed

[SOURCE: ISO 21637:2020, 3.34]

3.6
isotope abundance
fraction of atoms of a particular isotope of an element

3.7
laboratory sample
part of the *sample* (3.13) sent to or received by the laboratory

Note 1 to entry: When the laboratory sample is further prepared (reduced) by subdividing, mixing, grinding, or by combinations of these operations, the result is the test sample. When no preparation of the laboratory sample is required, the laboratory sample is the test sample. A test portion is removed from the test sample for the performance of the test or for analysis.

Note 2 to entry: The laboratory sample is the final sample from the point of view of sample collection, but it is the initial sample from the point of view of the laboratory.

Note 3 to entry: Several laboratory samples may be prepared and sent to different laboratories or to the same laboratory for different purposes. When sent to the same laboratory, the set is generally considered as a single laboratory sample and is documented as a single sample.

3.8
moisture
water removable under specific conditions

[SOURCE: ISO 21637:2020, 3.46]

3.9
net calorific value at constant volume
calorific value where the water produced by combustion is assumed to be in the vapour state

[SOURCE: ISO 21637:2020, 3.47]

3.10
nominal minimum particle size
aperture size of the sieve used for determining the particle size distribution of solid recovered fuels through which no more than 5 % by mass of the material passes

3.11

nominal top size

smallest aperture size of the sieve used for determining the particle size distribution of solid recovered fuels through which at least 95 % by mass of the total material passes through the sieve

[SOURCE: ISO 21637:2020, 3.48]

3.12

percentage modern Carbon

pmC

carbon mass fraction from biogenic origin

Note 1 to entry: The internationally accepted radiocarbon dating reference value is 95 percent of the activity, in AD 1950, of this NBS oxalic acid SRM4990B.

Note 2 to entry: In 2015, the value of 100 % biogenic carbon was set at 102 pmC.

Note 3 to entry: The biogenic origin is expressed in percentage.

3.13

sample

quantity of material, from a larger amount for which the quality is to be determined

[SOURCE: ISO 21637:2020, 3.63, modified — Notes 1–3 to entry have been removed.]

3.14

sample preparation

actions taken to obtain representative *laboratory samples* (3.7) or test portions from the original *sample* (3.13) as received

[SOURCE: ISO 21637:2020, 3.66]

4 Symbols and abbreviations

For the purposes of this document, the following symbols and abbreviations apply.

C	symbol for element carbon
D	diameter (mm)
^{14}C	carbon isotope with an atomic mass of 14 u
LSC	Liquid Scintillation Counter or Liquid Scintillation Counting
M_{sort}	manual sorting method
RSD	relative standard deviation
SDM	selective dissolution method
SRF	solid recovered fuel
TC	total carbon content
u	atomic mass unit
w	mass fraction expressed as a percentage by mass
w_{cal}	content expressed as a percentage of the energy content
w_{TC}	content expressed as a percentage of the total carbon content

The different references used in this document are indicated by the following indices:

- $_{(ad)}$ for air dried (dried at room temperature 20°C to 25 °C for 24 h)
- $_{(ar)}$ for as received
- $_{(d)}$ for dry
- $_{(daf)}$ for dry and ash free, where appropriate.

EXAMPLE $w_{\text{cal,NB}(d)}$ means the fraction of energy content in the non-biomass fraction by calorific value, on dry basis.

5 Principle

The determination of the biomass content is based on selective dissolution, manual sorting or ^{14}C measurement of biomass in solid recovered fuel. The choice for the method to be used is described in Clause 6. The biomass content gives an estimation of the content of the biogenic fraction in solid recovered fuel.

6 Determination of biomass content

6.1 Sampling

Sampling, transport, storage of the solid recovered fuel and sample preparation in the field shall be conducted according to ISO 21645 and ISO 21646.

6.2 Sample preparation

Preparation of the test sample for the ^{14}C or SDM shall be conducted according to ISO 21646. For the M_{sort}, no sample preparation is performed.

Since SRF is considered as a heterogeneous material, the minimum sample amount to be used for each test shall be:

- ^{14}C method: a quantity between 0,4 g and 2 g of the material with a nominal top size of 1 mm or less, depending on the device used for combustion (bomb, combustion tube furnace or elemental analyser) or the quantity indicated by the constructor in the case of the use of a laboratory scale combustion apparatus;
- selective dissolution method (SDM): at least 5 g of the material with a nominal top size of 1 mm or less;
- manual sorting method (M_{sort}): at least as big as the minimum sample size according to ISO 21645 (as received), as calculated in ISO 21646.

6.3 Applicable methods

For the determination of biomass content three methods are available:

1) the instrumental ^{14}C method shall be according to Annex A. This method is based on the determination of the ratio of ^{14}C to the total carbon content; the ^{14}C is proportional to the biomass content of the SRF. This method is suitable for samples of all types of fuel and shall be according to Annex A. A value of 10 % biogenic carbon can be considered as the lower range of application of ^{14}C method by liquid scintillation counter (LSC);

2) the selective dissolution method (SDM) shall be according to Annex B. The determination of the biomass content by the SDM is based on the property of biomass that it can be dissolved in a sulphuric acid / hydrogen peroxide mixture. This method has limitations that makes it less suitable

if the content of natural and/or synthetic rubber in the SRF is more than 10 %, or if the sum of the content of hard coal, coke, brown coal, lignite, degradable plastics of fossil origin, non-degradable plastic of biogenic origin, oil or fat present as a constituent of biomass, wool, viscose, nylon, polyurethane or other polymers containing molecular amino groups and silicon rubber exceeds 5 %. Additional information about these limitations is found in Annex D. The selective dissolution method (SDM) is applicable for the biomass percentage content between 10 % and 90 %;

3) the manual sorting method (M_{sort}) shall be according to Annex C. The determination of the biomass content by the manual sorting method is based on the visual examination of fractions and their separation on the basis of their nature and origin. The method is suitable for samples with a particle size >10 mm.

For the limitations of the three methods see Annex D.

7 Expression of results

Depending on the use of the results, three different dimensions are used to express the biomass content:

a) biomass in percent by mass w_B;

b) biomass in percent by calorific value $w_{B,cal}$;

c) biomass in percent by carbon content $w_{B,TC}$.

The expression of results by ^{14}C method shall be according to Annex A.

The expression of results by SDS method shall be according to Annex B.

The expression of results by M_{sort} method shall be according to Annex C.

8 Performance characteristics

External data for the calculation of the expanded uncertainty of measurements are presented in Annex E where results of round robin and validation studies are summarized. These values should be used in combination with individual laboratory performance characteristics and a desired coverage factor to get the overall uncertainty.

Practical examples of use of the data from Annex E:

EXAMPLE 1

A laboratory wants to determine the expanded uncertainty of measurement of SDM method (% by mass).

The intra-laboratory reproducibility for the laboratory calculated from internal validations studies and control charts was determined to be 2,5 % (RSD).

The round robin results from the QUOVADIS[3] study (Table E.2) give a RSD value of 3,43 % (at 67,79 % level).

$$u_{c,rel} = \sqrt{(2{,}5^2+3{,}43^2)} = 4{,}24\ \%$$

$$U_{rel} = 2 \times u_{c,rel} = 8{,}48\ \%$$

where $u_{c,rel}$ is the combined uncertainty of measurement and U_{rel} is the expanded uncertainty of measurement using a coverage factor of 2 (~95 % confidence interval).

EXAMPLE 2

A laboratory measures the biomass content by ^{14}C method – LSC B (% by TC).

The intra-laboratory reproducibility for the laboratory calculated from internal validations studies and control charts was determined to be 2,4 % (RSD).

The round robin results from the QUOVADIS[3] study (Table E.6) give a RSD value of 2,5 % (at 55,5 % level).

$$u_{c,rel} = \sqrt{(2{,}4^2+2{,}5^2)} = 3{,}5\ \%$$

$$U_{rel} = 2 \times u_{c,rel} = 7{,}0\ \%$$

where u c,rel is the combined uncertainty of measurement and U_{rel} is the expanded uncertainty of measurement using a coverage factor of 2 (~ 95 % confidence interval).

9 Test report

The test report shall contain at least the following information:

a) identification of the laboratory performing the test;

b) date of the test;

c) identification of product (sample) tested;

d) sample preparation (e.g. method of size reduction, drying, subdivision);

e) storage conditions;

f) date of receipt of laboratory sample and dates of the test (beginning and end);

g) a reference to this document (ISO 21644:2021) and the method used;

h) in case of ^{14}C-method, the results of the test including the basis on which they are expressed and application of the isotope correction;

i) the biomass content expressed as a percentage by mass, calorific value and/or carbon content, rounded to the nearest 0,1 %;

j) any operation not included in this document, or regarded as optional;

k) any unusual features noted during the test procedure.

Annex A
(normative)

Determination of the biomass content based on the ^{14}C method

A.1 General

The two proposed methods for ^{14}C measurement, Proportional Scintillation Method (PSM) or Accelerated Mass Spectrometry (AMS), require specialised personnel and instrumentation. However, the preparation step for instrumental analysis can be completed as normal routine laboratory activity. For the collection from the sample of the ^{14}C fraction, generally accepted methods for the conversion of the carbon present in the sample to CO_2 are described.

A.2 Principle

The methods for the determination of the biomass content specified in this annex are based on the determination of the ^{14}C content. The amount of biomass carbon in solid recovered fuel is proportional to this ^{14}C content.

The carbon present in the sample is converted to CO_2 by combustion. The combustion is carried out in a way to comply with the requirements of the subsequent measurement of the ^{14}C content. This measurement is carried out according to one of the two following methods, Proportional Scintillation Method (PSM) or Accelerated Mass Spectrometry (AMS). These methods are considered equivalent, giving the same results within the scope of this document. The results are expressed as the percentage biomass carbon of the total carbon content. The fraction of biomass content by mass and the fraction of biomass by energy content are calculated from the carbon content of biomass, using the carbon content of biomass and the energy content of the biomass fraction that is present in the sample.

A.3 Limitations

For the limitation of this method see Annex D.

A.4 Symbols

For the purposes of this annex, the following symbols apply.

C	symbol for element carbon
^{14}C	carbon isotope with an atomic mass of 14
AMS	Accelerator Mass Spectrometry
β	beta particle, electron emitted during radioactive decay
Bq	Bequerel, disintegrations per second
d	on dry base
DPM	disintegrations per minute
CPM	counts per minute

C_V	coefficient of variation
GM	Geiger Müller
LCV	Low calorific value
LLD	Lower Limit of Detection
m	mass expressed as a percentage by mass
M	moisture expressed as a percentage by mass
MOP	3-Methoxy 1-propyl amine
NCV	Net Calorific Value
LSC	Liquid Scintillation Counter or Liquid Scintillation Counting
REF	reference value of 100 % biogenic carbon
pmC	percentage modern Carbon
PSM	Proportional Scintillation-counter Method
X	fraction expressed as a percentage by mass
RSD	Relative Standard Deviation
SRF	Solid recovered fuel
TC	Total carbon content

A.5 Reagents and materials

CO_2 absorber for LSC (methoxypropylamine or equivalent).

Universal LSC cocktail for aqueous and non-aqueous sample.

2 mol·l^{-1} to 4 mol·l^{-1} KOH or NaOH absorption liquid (standard glass bottles with plastic screw caps that are resistant to alkaline solutions shall be used).

For the preparation of a carbonate free adsorption liquid, preparation using freshly opened KOH or NaOH pellet containers is sufficient. Dissolve the KOH (NaOH) pellets in a small amount of water (the heat produced during the dissolution process will enhance the dissolution process). When NaOH is used, small amounts of precipitation are an indication of the presence of Na_2CO_3. By decanting the clear phase, the almost carbonate free solution shall be diluted to the desired volume. As the dissolution of KOH or NaOH is an exothermic process, extra care should be taken as boiling of the concentrated solution during dilution can occur.

For high precision measurements the following procedure shall be used to produce a 0,7 l carbonate free KOH (NaOH) 4 mol·l^{-1} solution.

- 670 ml demineralised water (water from a system producing ultrapure water for laboratory use);
- 156,8 g KOH pellets (112 g NaOH);
- 30 ml saturated $Ba(OH)_2$ solution. [2,4 g $Ba(OH)_2$ ÷ 2,6 g $Ba(OH)_2$ in 30 ml demineralised water];
- dissolve the KOH (NaOH) pellets in the demineralised water (use magnetic stirrer);