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Solid biofuels — Determination of self-heating of pelletized biofuels —

Part 1: Isothermal calorimetry

Biocombustibles solides — Détermination de l'auto-échauffement des granulés de biocombustibles —

Partie 1: Détermination calorimétrique isotherme

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Foreword

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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).

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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 238, *Solid biofuels*.

A list of all parts in the ISO 20049 series can be found on the ISO website.

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.

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Introduction

There is a continuous global growth in production, storage, handling, bulk transport and use of solid biofuels especially in the form of pelletized biofuels.

The specific physical and chemical characteristics of solid biofuels, their handling and storage can lead to a risk of fire and/or explosion, as well as health risks such as intoxication due to exposure to carbon-monoxide, asphyxiation due to oxygen depletion or allergic reactions.

Heat can be generated in solid biofuel by exothermic biological, chemical and physical processes. Biological processes include the metabolism of fungus and bacteria and occur at lower temperatures; the oxidation of wood constituents increases with temperature and dominates at higher temperatures; the heat production from biological and chemical processes leads to transport of moisture in the bulk material, with associated sorption and condensation of water, which both are exothermic processes. In, for example, a heap of stored forest fuel or a heap of moist wood chips, all of these processes can be present and contribute to heat production.

Solid biofuels such as wood pellets, however, are intrinsically sterile[1] due to the conditions during manufacturing (exposure to severe heat during drying, fragmentation during hammermilling and pressure during extrusion) but can attract microbes if becoming wet during handling and storage resulting in metabolism and generation of heat. Leakage of water into a storage of wood pellets can also lead to the physical processes mentioned above. Non-compressed wood like feedstock and chips typically have a fauna of microbes which under certain circumstances will result in heating. All the processes mentioned above contribute to what is called self-heating although oxidation is likely to be one of the main contributing factors in the temperature range under which most biofuels are stored. The heat build-up can be significant in large bulk stores as the heat conduction in the material is low. Under certain conditions the heat generation can lead to thermal runaway and spontaneous ignition.

The potential for self-heating seems to vary considerably for different types of solid biofuel pellets. The raw material used, and the properties of these raw materials have proven to influence the propensity for self-heating of the produced wood pellets. However, the production process (e.g. the drying process) also influences the potential for self-heating. It is therefore important to be able to identify solid biofuel pellets with high heat generation potential to avoid fires in stored materials.

Two intrinsically different types of tests methods can be used to estimate the potential of self-heating;

a) In the isothermal calorimetry method described in this document, the heat flow generated from the test portion is measured directly.

b) In basket heating tests, the temperature of the test portion is being monitored and the critical ambient temperature (CAT), where the temperature of the test portion just does not increase significantly due to self-heating, is used for indirect assessment of self-heating.

These two methods are applied at different analysis temperature regimes. The operating temperature for an isothermal calorimeter is normally in the range 5 °C to 90 °C whereas basket heating tests are conducted at higher analysis (oven) temperatures. For basket heating tests with wood pellets, CATs are found for a 1 l sample portion in the range 150 °C to 200 °C.

The application of the test data should thus be identified before selecting the appropriate analytical method.

NOTE 1 The two types of test methods referred to above do not measure heat production from physical processes such as transport of moisture.

NOTE 2 It is likely that oxidation reactions taking place in the low respective high temperature regimes for solid biofuel pellets are of different character and thus have different reaction rates and heat production rates. In such a case, extrapolation of the data from a high temperature test series can lead to non-conservative results and might not be applicable without taking the low temperature reactions into account. In the general case of two reactions with different activation energies, the high activation energy is “frozen out” at low temperatures and the low activation energy reaction is “swamped” at higher temperatures[2].

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NOTE 3 It has been shown for a limited number of different types of wood pellets that the reaction rates in the lower temperature regime measured by isothermal calorimetry were higher compared to the reaction rate data determined from basket heating tests in the higher temperature regime[3].

Isothermal calorimetry is used for determination of the thermal activity or heat flow of chemical, physical and biological processes. The method described in this document is developed for the measurement of heat flow from the self-heating of solid biofuel pellets, but the technique is most commonly used in the fields of pharmaceuticals, energetic materials, and cement[3] to [7].

Data from the isothermal calorimetry screening test procedure included in this document is intended for comparison of the spontaneous heat generation (self-heating) of solid biofuel pellets (Annex B).

Guidance is additionally given on the use of isothermal calorimetry test data for the calculation of the overall reaction rate of the heat producing reactions (Annex C).

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Solid biofuels — Determination of self-heating of pelletized biofuels —

Part 1: Isothermal calorimetry

1 Scope

This document:

a) specifies a general test procedure for quantification of the spontaneous heat generation from solid biofuel pellets using isothermal calorimetry;

b) specifies a screening test procedure for wood pellets using an instrument temperature of 60 °C;

c) establishes procedures for sampling and sample handling of solid biofuel pellets prior to the analysis of spontaneous heat generation; and

d) gives guidance on the applicability and use of isothermal calorimetry for calculation of the net reaction rate of the heat producing reactions of solid biofuel pellets.

The test procedure given in this document quantifies the thermal power (heat flow) of the sample during the test, it does not identify the source of self-heating in the test portion analysed.

Data on spontaneous heat generation determined using this document is only associated with the specific quality and age of the sample material. The results are product specific.

This document is applicable to solid biofuel pellets only.

The information derived using this document is for use in quality control and in hazard and risk assessments related to the procedures given in ISO 20024:2020.

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 14780, *Solid biofuels — Sample preparation*

ISO 16559, *Solid biofuels — Terminology, definitions and descriptions*

ISO 18135, *Solid Biofuels — Sampling*

ISO 18846, *Solid biofuels — Determination of fines content in quantities of pellets*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 16559 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

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— IEC Electropedia: available at http://www.electropedia.org/

3.1
analysis temperature
temperature of the analysis environment, i.e. the calorimeter temperature

3.2
self-heating
rise in temperature in a material resulting from an exothermic reaction within the material

[SOURCE: ISO 13943:2017, 3.341, modified — "<chemical>" omitted at the beginning of the definition.]

3.3
spontaneous ignition
ignition caused by an internal exothermic reaction

[SOURCE: ISO 13943:2017, 3.24]

Note 1 to entry: See definitions of ignition in ISO 13943.

3.4
test portion
sub-sample either of a *laboratory sample* (3.6) or a *test sample* (3.5)

[SOURCE: ISO 16559:2014, 4.202]

3.5
test sample
laboratory sample (3.6) after an appropriate preparation made by the laboratory

[SOURCE: ISO 16559:2014, 4.203]

3.6
laboratory sample
combined sample or a sub-sample of a combined sample for use in a laboratory

[SOURCE: ISO 16559:2014, 4.124]

3.7
thermal power
heat rate produced by the sample during the test and commonly expressed, with reference to the unit mass of pelletized biofuel, in W/g or J/(s · g)

[SOURCE: CEN/TR 16632:2014, 8.3, modified — substitution of "cement" with " pelletized biofuel".]

4 Principle

Isothermal calorimetry is a sensitive technique for studying heat production or heat consumption from samples of different kinds. It is non-destructive and non-invasive to the sample. When heat is produced in a sample, an isothermal heat conduction calorimeter (here isothermal calorimeter) measures the thermal power (heat flow). The sample is placed in an ampoule that is in contact with a heat flow sensor that is also in contact with a heat sink. When heat is produced or consumed by any process, a temperature gradient is developed across the sensor. This will generate a voltage, which is measured. The voltage is proportional to the heat flow across the sensor and to the rate of the process taking place in the sample ampoule. This signal is recorded continuously and in real time.

NOTE 1 A commercial instrument for isothermal calorimetry normally has multiple channels and can thus be used for measurements of several samples simultaneously.

For each sample (channel) there is an inert reference that is on a parallel heat flow sensor. During the time that the heat flow is monitored, any temperature fluctuations entering the instrument will

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