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Solid recovered fuels — Determination of self-heating —

Part 2:
Basket heating tests

Combustibles solides de récupération — Détermination de l'auto-échauffement —

Partie 2: Essais utilisant la méthode du point de croisement

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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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This document was prepared by Technical Committee ISO/TC 300, *Solid recovered materials, including solid recovered fuels*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 343, *Solid recovered materials, including solid recovered fuels*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

A list of all parts in the ISO 21911 series can be found on the ISO website.

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Introduction

There is continuous global growth in trading and use of solid recovered fuels (SRFs). Therefore, intensive investigations about the risk of fires within SRF production, handling and storing have been conducted, see ÖNORM S 2098. Recommendations are given in ISO 21912.

Depending on the kind of input wastes, the treatment technology applied, the quality of the SRF produced and the realized storage versions, SRFs can generate heat spontaneously by exothermic biological, chemical and physical processes. The heat build-up can be significant in large storage volumes if the heat conduction in the material is low. During some conditions the heat generation can lead to pyrolysis and spontaneous ignition. The potential for self-heating varies considerably for different types and qualities of SRF and it is important to be able to identify SRF fractions with high heat generation potential to avoid fires in stored materials.

Avoiding fires throughout the production and supply chain will have positive consequences on the acceptance of SRFs and the costs for insurance coverage,

Application of SRF standards and the use of dedicated standards for the determination of self-heating will help to reduce the risk of fires and to develop tailor-made recommendations for SRF producers, logistics providers, SRF users, equipment suppliers or manufacturers, consultants, authorities and insurance providers.

As part of the determination and the assessment of risks for SRF, defined test methods and standards are established or need to be developed. However, ageing and degradation due to handling and storage of SRF in actual environments affects their characteristics, so safety margins should be established in relation to actual analysis results.

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

a) In the isothermal calorimetry method described in ISO 21911-1[1)], the heat flow generated from the test portion is measured directly.

b) In the basket heating tests described in this document, the temperature of the test portion is being monitored and the critical ambient temperature (CAT), where the temperature of the test portion 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.

NOTE 1 These two types of test methods 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 SRFs are of different character and thus have different reaction rates and heat production rates. In such cases, extrapolation of the data from a high-temperature test series can lead to non-conservative results and will possibly 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[7].

Basket heating tests have been used traditionally for characterization of the tendency for spontaneous ignition of predominantly coals, but also for other reactive organic materials, such as cottonseed meal, bagasse and milk powder[9]. The principle used in these types of test is to find the CAT for a self-heating sample material of specific size and geometry.

There are several different methods described in the literature with different degrees of sophistication. The variations span from simple pass and fail tests to more advanced tests from which data on reaction rates can be extracted[10].

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1) In preparation. Stage at the time of publication: ISO/FDIS 21911-1:2022.

Basket heating tests are useful for assessment of self-heating of SRFs. The test method selected can be evaluated for its applicability based on the information given in this document.

A compilation of available basket heating test methods is given in this document. Guidance on the suitability for application of these methods for tests with SRFs is provided.

Basic theory of the use of basket heating test data for calculations of critical conditions in storage is provided in Annex C.

The test methods presented require representative samples for the conditions prevailing in the process (e.g. of SRF storage). Sample preparation is necessary for this purpose. The methods presented are not suitable for assessing the fire hazard caused by impurities (disturbing materials) as they occur mainly in the input area and the first steps of SRF production.

Solid recovered fuels — Determination of self-heating —

Part 2:
Basket heating tests

1 Scope

This document gives guidance on basket heating tests for characterization of self-heating properties of solid recovered fuels (SRFs).

This document includes:

a) a compilation of basket heating test methods;

b) guidance on the applicability and use of basket heating tests for SRF;

c) information on the application of basket heating test data for calculations of critical conditions in storage.

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

The information derived using this document is intended for use in quality control and in hazard and risk assessments related to the procedures given in ISO 21912.

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 21646, *Solid recovered fuels — Sample preparation*

ISO 21637:2020, *Solid recovered fuels — Vocabulary*

ISO 21645, *Solid recovered fuels — Methods for sampling*

3 Terms and definitions

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

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

— ISO Online browsing platform: available at https://www.iso.org/obp

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

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

3.2
Biot number
quotient of the convective heat transfer coefficient (between the sample boundary and the surrounding air) and the conduction in the sample material normalized by the characteristic dimension of the test basket

3.3
critical ambient temperature
CAT
ambient temperature (the *analysis temperature* (3.1) or the storage temperature) where the internal temperature of the test portion or the stored material increases significantly (due to *self-heating* (3.4))

Note 1 to entry: In EN 15188 the critical ambient temperature is defined as self-ignition temperature, T_{SI}.

3.4
self-heating
rise in temperature in a material resulting from an exothermic reaction within the material

[SOURCE: ISO 13943:2017, 3.341, modified — "<chemical>" domain omitted from definition.]

3.5
spontaneous ignition
ignition caused by an internal exothermic reaction

[SOURCE: ISO 13943:2017, 3.24, modified — Notes to entry removed.]

3.6
test sample
laboratory sample (3.7) after an appropriate preparation made by the laboratory

Note 1 to entry: The test sample is here typically a representative sample from a batch of solid recovered fuel.

[SOURCE: ISO 21637:2020, 3.84, modified — Note 1 to entry added.]

3.7
laboratory sample
sample delivered to a laboratory

[SOURCE: ISO 16559:2022, 3.120, modified — Note 1 to entry removed.]

4 Symbols

Symbol	Quantity	Typical unit
A	pre-exponential factor in Arrhenius expression	s^{-1}
B	dimensionless adiabatic temperature rise	dimensionless
Bi	Biot number, ($\mathrm{Bi} = \frac{h \cdot L}{\lambda}$)	dimensionless
c_0	ambient oxygen concentration by volume fraction	dimensionless
C	specific heat capacity of the reaction products	$J\ kg^{-1}\ K^{-1}$
C_p	specific heat capacity of the bulk material	$J\ kg^{-1}\ K^{-1}$
d	diameter of body	m
D	diffusion coefficient	$m^2\ s^{-1}$
E_a	activation energy	$J\ mol^{-1}$
H_0	gross calorific value	$J\ kg^{-1}$
h	heat transfer coefficient	$W\ m^{-2}\ K^{-1}$
h_r	radiative amount on heat transfer coefficient	$W\ m^{-2}\ K^{-1}$

Symbol	Quantity	Typical unit
h_c	convective amount on heat transfer coefficient	$W\ m^{-2}\ K^{-1}$
L	characteristic length	m
n	order of reaction	dimensionless
P	constant	dimensionless
$\dot{q}'$	heat generation term	$W\ m^{-3}$
Q	heat of reaction	$J\ kg^{-1}$
Q_0	heat of reaction by volume of oxygen	$J\ m^{-3}$
R	universal gas constant	$J\ mol^{-1}\ K^{-1}$
Ra	Rayleight number	dimensionless
S	surface	m^2
t	time	s
T	temperature	K
T_0	ambient temperature	K
T_p	crossing point temperature	K
T_{SI}	self-ignition temperature	K
V	volume	m^3
x	length coordinate	m
δ	Frank-Kamenetskii parameter	dimensionless
δ_c	critical value of δ	dimensionless
ε	activation energy parameter, $\left(\varepsilon = \frac{RT_0}{E_a}\right)$	dimensionless
Φ	oxygen diffusion parameter	dimensionless
λ	thermal conductivity of sample	$W\ m^{-1}\ K^{-1}$
λ_{air}	thermal conductivity of air	$W\ m^{-1}\ K^{-1}$
ρ	bulk density	$kg\ m^{-3}$
σ	Stefan-Boltzmann coefficient	$W\ m^{-2}\ K^{-4}$

5 Basket heating tests

The detailed test procedure varies between different isoperibolic and adiabatic methods. Isoperibolic methods include that the test portion is put in a wire-mesh basket which is placed in an oven heated to a fixed elevated temperature. The oven is equipped with a fan to keep the temperature uniform and to give a relatively large convective heat transfer coefficient to the test specimen[9] [10]. For adiabatic tests, the oven temperature is adjusted to the temperature at the centre of the sample, see EN 15188.

Basket heating tests are based on the Frank-Kamenetskii theory of criticality of a self-heating isotropic slab (see Annex C) and have been developed to determine the reaction kinetics of the global reaction responsible for heat production in a self-heating material. The large gap volume of pelletized material can lead to convective heat transport in the bulk if the furnace is equipped with a fan. In this case air flow in the vicinity of the sample should be kept at a low level and the critical Frank-Kamenetskii parameter should be corrected (see C.1.3) or the convective transport within the sample should be prevented by further measures (e.g. finer mesh wire of the basket).

NOTE The CAT for the test portion in a basket heating test is not equal to the CAT for spontaneous ignition in, for example, large-scale storage. The critical size for spontaneous ignition (if only heat transfer is considered) is directly related to the surface area-volume ratio of the self-heating specimen where heat is produced distributed in the volume and heat is dissipated from the surface area only. The test sample in a laboratory-size basket heating test has a very high surface area-volume ratio and, consequently, a high CAT compared to a larger specimen.

6 Tests for product classification

6.1 UN classification

6.1.1 General

The United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS)[11] is the international convention for hazard communication and labelling of gases and vapours, solid and liquid substances and mixtures. GHS defines limit values, classes and categories and related measures in relation to the level of hazards during transportation, handling and storage.

The United Nations Manual of Test and Criteria (MTC)[12] prescribes specific test procedures in support of GHS.

6.1.2 Test method for self-heating substances – MTC Test N.4

Test N.4 is described in the MTC, Part III, 33.3.1.6,[12] sometimes called the basket test.

This basket heating test determines the ability of a substance to undergo oxidative self-heating with exposure to air at temperatures of 100 °C, 120 °C or 140 °C in a 25 mm or 100 mm wire mesh cube.

The N.4 test basket heating test is not intended for determination of self-heating kinetics but rather prescribed to classify a material (e.g. SRFs) as meeting the criteria for self-heating set out by the GHS[11] for hazard communication and labelling purposes.

The test set-up consists of a hot-air circulating oven, cubic sample containers with sides of 25 mm and 100 mm made of stainless-steel net with a mesh opening of 0,05 mm, and thermocouples of 0,3 mm diameter for measurement of the oven temperature and the temperature of the centre of the sample. The sample container is housed in a cubic container cover made from stainless-steel net with a mesh opening of 0,60 mm and slightly larger than the test container. To avoid the effect of air circulation, this cover is installed in a second steel cage, made from a net with a mesh size of 0,595 mm and 150 mm × 150 mm × 250 mm in size.

The normal procedure is to start with a test at 140 °C with a 100-mm sample cube. The container is housed in the cover and hung at the centre of the oven. The oven temperature is raised to 140 °C and kept there for 24 h. A positive result is obtained if spontaneous ignition occurs or if the temperature of the sample exceeds the oven temperature by 60 °C. If a negative result is obtained, no further test is necessary.

If a positive result is obtained at 140 °C with a 100-mm sample cube, the substance is classified as a self-heating substance and further testing shall be made to find the correct classification (see 6.1.3).

The bulk density tested can influence the test results. The bulk density of the sample shall be adjusted according to EN 15188 to the respective practical conditions (if known) and the tested bulk density shall be recorded. The MTC contains no information on the bulk density to be tested.

6.1.3 Classification criteria — GHS

The classification criteria are given in chapter 2.11.2 of the GHS[11]. The criteria are summarized in Table 1.

Table 1 — Criteria in GHS for self-heating substances and mixtures

Category	Criteria
1	A positive result is obtained in a test using a 25-mm sample cube at 140 °C
2	a) A positive result is obtained in a test using a 100-mm sample cube at 140 °C, a negative result is obtained in a test using a 25-mm sample cube at 140 °C and the substance or mixture is packed in packages with a volume of more than 3 m^3; or b) A positive result is obtained in a test using a 100-mm sample cube at 140 °C, a negative result is obtained in a test using a 25-mm sample cube at 140 °C, a positive result is obtained in a test using a 100-mm sample cube at 120 °C and the substance or mixture is packed in packages with a volume of more than 450 l; or c) A positive result is obtained in a test using a 100-mm sample cube at 140 °C, a negative result is obtained in a test using a 25-mm sample cube at 140 °C and a positive result is obtained in a test using a 100-mm sample cube at 100 °C.

NOTE Hazard packing group classification is prescribed depending on flammability characteristics of the material, see GHS, Table 32.1.[11]

6.2 Classification criteria — IMO

Handling guidelines and hazard classifications for all cargoes, including SRFs, transported onboard ocean vessels are specified by the International Maritime Organization (IMO) in the International Maritime Solid Bulk Cargoes (IMSBC) Code[13]. This stipulates the MTC Test N.4 to be used for testing but includes additional criteria for solid possessing hazards compared to the GHS criteria in Table 1, as follows:

a) Does the material undergo dangerous self-heating when tested in accordance with Test N.4 in a 100-mm sample cube at 140 °C?

If yes, class 4.2 applies. Materials in this class are materials, other than pyrophoric materials, which, in contact with air without energy supply, are liable to self-heating.

b) Does the material show a temperature increase of 10 °C or more when tested in accordance with Test N.4 in a 100-mm sample cube at 140 °C?

If yes, test in a 100-mm sample cube at 100 °C and if temperature increase is 10 °C or more.

If yes, material hazardous in bulk (MHB) applies.

If no, neither class 4.2 nor MHB applies.

6.3 Applicability of MTC Test N.4 for solid recovered fuels

MTC Test N.4 will possibly be unsuitable for SRFs.

Experience from testing several SRF samples indicates that the CAT for this type of material in 1,0 l basket heating tests can be lower than 140 °C, especially when various materials, including inert ones, are present in the mixture, see Annex A and References [14] and [15].

The reasons that this test will possibly be unsuitable as a general test method for SRFs are as follows: i) the criteria in MTC Test N.4 is based on the fixed-reaction kinetics of coal, which are not directly transferable to SRFs; ii) there is no published information on the selectivity and the correlation to large-scale storage of this test for SRFs; iii) the self-heating process of SRFs can undergo multi-step reactions at different temperature ranges, including phase transitions (melting). Low-temperature reactions and phase transitions are not covered by tests according to the MTC N.4 method.

In the case of testing melting materials, sample preparation can be necessary. Corresponding instructions are given in 8.4.

7 Tests for determination of reaction kinetics

7.1 General

There are different basket heating tests available for the determination of reaction kinetics for self-heating of reactive materials. The most important of these methods are summarized in this clause.

7.2 Isoperibolic test methods

7.2.1 General

The original basket heating test method was developed in the UK and is sometimes referred to as the FRS method. This is a rather time-consuming method to use because of the large number of experiments needed for each material studied. This method does not exist in the form of a test standard but has been described in detail by Bowes[16] and Beever[9].

Several investigations and interlaboratory comparisons in the past have shown significant differences between the results of hot storage tests determined by different laboratories[17],[18]. Lab-specific differences have been identified as possible reasons for the deviations, such as:

a) oven ventilation (enforced, natural convection);

b) oven size;

c) sample baskets (shape, size, construction);

d) radiation effects;

e) measuring precision (temperature difference between tests with ignition and tests with no ignition);

f) minimum sample size.

For this reason, the original FRS method was modified and further developed in EN 15188. The main difference is the use of an additional wire-mesh screen and special volumes of the sample baskets (cubes) to normalize or harmonize the test conditions in the surrounding of the samples independent from the used oven type and size. This is, however, an important deviation from the Frank-Kamenetskii theory (see Annex C), which relies on a high Biot number of the test specimen to keep the boundary of the test specimen at the analysis (oven) temperature. On the other hand, the air-flow velocity in the vicinity of the sample is reduced to prevent convective mass and heat transport in the sample. For these reasons, the critical Frank-Kamenetskii parameter shall be corrected according to Annex C.1.3 if this method is used.

7.2.2 Test procedure

The general test procedure is to conduct the tests using a pre-heated oven with the sample placed in a wire-mesh container in the centre of the oven. These methods involve a number of separate, rather time-consuming, heating tests with at least three or four different sizes of sample containers. Thin thermocouples are used for measuring the temperature in the oven and the temperatures at the centre and the periphery of the sample. The CAT for each size of sample is determined by repetitive tests at oven temperatures successively closer to the critical temperature. In this way the critical value of the temperature can be bracketed in as closely as desired. It is usually found that ignition is very sharply defined and a difference in oven temperature of only 0,5 °C produces a sharp rise in the recorded central temperature[9]. The closeness with which the critical temperature is determined is reflected in the precision of the calculation of the lumped kinetic parameters. A maximum error of ± 0,5 K is recommended by Reference [9] if data are used for extrapolations over a wide range of sizes. The recommendation in EN 15188 is that the oven temperatures of the test just producing ignition and that of the test not producing an ignition differ by not more than 2 K. EN 15188 requires testing of four different volumes with a minimum sample size of 100 cm^3; the largest sample volume shall not be smaller than 1 000 cm^3.

7.2.3 Determination of reaction kinetics

The indirect evaluation of the Frank-Kamenetskii parameter (see also Annex C) is based on the determination of the critical temperature for a known size of a material in small-scale oven tests, as described in 7.2.2.

The Frank-Kamenetskii parameter δ is defined by Formula (1).

$$\delta = \frac{\rho QA}{\lambda} \cdot \frac{E_a L^2}{RT_0^2} \cdot \exp\left(-\frac{E_a}{RT_0}\right) \tag{1}$$

With Formula (2), Formula (1) can be rewritten as Formula (3).

$$P = \ln\left[\frac{E_a}{R} \rho \frac{QA}{\lambda}\right] \tag{2}$$

$$\ln\left[\frac{\delta T_0^2}{L^2}\right] = P - \frac{E_a}{RT_0} \tag{3}$$

If the critical value of δ is inserted, the ambient temperature is equal to the CAT. A plot of $\ln(\delta_c T_0^2 / L^2)$ versus 1/CAT for a number of tests with varying sample sizes (L) forms a straight line with $-E_a/R$ as the slope and P as intercept. The critical Frank-Kamenetskii parameters (δ_c) for the geometries tested can be calculated according to the principles discussed in Annex C. Thus, E_a and QA can be extracted from such measurements.

Once the material parameters are determined from the small-scale tests it is possible to predict the critical size for any full-scale configuration, see Formula (C.5) in Annex C, or to calculate the Frank-Kamenetskii parameter for any specific configuration and compare with the critical parameter to get an assessment of the criticality of such a configuration.

7.2.4 Applicability for solid recovered fuels

Isoperibolic tests of different sample volumes according to EN 15188 should be the most appropriate basket heating method for testing solid recovered fuels if the critical Frank-Kamenetskii parameter is corrected according to C.1.3. This recommendation is based on the following observations:

a) The CAT of each size of test portion is accurately determined.

b) The determination of the CAT is based on measurement of the centre temperature of the test portion, which shall reach thermal runaway, which means that the exact position of the thermocouple in the sample is less important (in comparison to the alternative crossing point method).

c) Convective heat and mass transport in the sample is reduced or prevented even in bulks with large gap volumes.

d) The method according to EN 15188 provides reproducible results independent of the type of furnace used.

In the case of testing melting materials, sample preparation can be necessary. Corresponding instructions are given in 8.4.

Studies on the self-ignition behaviour of various materials are presented in Annex A.

7.3 Crossing-point method

7.3.1 General

An alternative method for determination of the kinetic parameters in a self-heating substance is the method described by Chen and Chong[19], commonly referred to as the crossing-point temperature method. This method involves the periphery heating of an initially "cold" exothermic material being subjected to a hot environment with a constant temperature and is based on analysis of the non-steady solution of the energy conservation equation.

Consider a symmetrical sample specimen of a reactive material where the heat wave propagates towards the centre. Initially the centre temperature is lower than the periphery temperature and a temperature in the material a small distance from the centre. At a certain time, the centre temperature exceeds (by self-heating) the temperature measured a small distance from the centre. At that point where the centre temperature just exceeds the other temperatures in the sample specimen, the centre temperature is defined as the "crossing-point temperature" (T_p).

It has been shown[19] that the observation of T_p can be used as a physic-chemical property to indicate the propensity of a solid material to self-heat. If T_p is identified experimentally, and a temperature-time profile is recorded to determine the time derivate of the temperature at T_p, the kinetic parameters can be derived.

The main advantage of the crossing-point method is that instead of carrying out a series of time-consuming experiments with several sample sizes, as with the isoperibolic methods, each of the transient experiments only requires one sample size and in a rather short time produces a data point. In order to obtain several data points for the plot the initial temperature of the oven is varied within certain limits[19].

NOTE Cuzzillo[20] carried out a detailed error analysis of the crossing-point method and showed several advantages of this over the standard isoperibolic method. First, the previously mentioned advantage that every test result gives a useful data point. Second, there is no need to measure or estimate the Biot number in the laboratory tests as the theory does not have such a requirement. This means that the heat transfer properties of the oven and the conductivity of the sample need not be known in the laboratory tests for determining the kinetic parameters.

7.3.2 Test procedure

The following is an example of a test procedure from Reference [8]. The equipment used included a wire mesh basket (cubic) of 1,0 l volume made from 0,6-mm stainless-steel mesh and a temperature-controlled oven with a recirculating fan. Temperatures were registered by six thermocouples, five to record the temperature profile of the sample and one to measure the ambient gas temperature in the oven. The first measurement point was in the centre of the basket, the second 10 mm away from the centre, the third 10 mm further away, the fourth a further 15 mm away and the fifth located at the edge of the sample material close to the wire-mesh wall.

For a test, the thermocouples were attached to the basket (supported with a special frame to keep them in position) and the basket was filled with the sample material. The prepared basket with the test sample was then suspended in the centre of the oven, which had been preheated to the selected ambient temperature for the specific test. The test continued until the temperature in all measurement points inside the sample was higher than the one located at the edge of the sample material close to the wire-mesh wall. The crossing point temperature was subsequently determined from the temperature recordings at the time when the centre temperature exceeded the other temperatures between the centre and the periphery.

Tests with at least three furnace temperatures shall be conducted, but five tests at different furnace temperatures are recommended.

7.3.3 Determination of reaction kinetics

It has been shown[19] that the observation of this unique temperature can be used as a physic-chemical property to indicate the propensity of a solid material to self-heat. Consider the energy conservation formula for a one-dimensional slab, Formula (4).

$$\rho C_\mathrm{p}\frac{\partial T}{\partial t}=\lambda\frac{\partial^2 T}{\partial x^2}+Q\rho A\exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{4}$$

where the left-hand side is the rate of enthalpy change within the solid, the first term on the right-hand side is the conductive heat transfer, and the second term is the heat generation term of the lumped exothermic reactions.

The conductive heat transfer term in Formula (4) would initially have a value of zero in the centre of the periphery-heated slab. The second derivative of temperature against distance would take a positive increasing value initially as the slab is heated but would eventually decrease and become negative as the centre temperature advances towards the periphery temperature and passes it. It is thus evident that the conductive heat transfer term is zero at some point, and this is the stricter definition of the crossing-point temperature. Thus, at the crossing-point temperature (T_p), Formula (5) applies:

$$\frac{\partial^2 T}{\partial x^2}=0 \tag{5}$$

Formula (4) is reduced to Formula (6),

$$\frac{\partial T}{\partial t}=\frac{QA}{C_\mathrm{p}}\exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{6}$$

which can be rewritten as Formula (7):

$$\ln\left(\frac{\partial T}{\partial t}\right)=\ln\left(\frac{QA}{C_\mathrm{p}}\right)-\frac{E_\mathrm{a}}{RT} \tag{7}$$

Thus, if T_p is identified experimentally and a temperature-time profile is recorded to determine the time derivate of the temperature at T_p, the kinetic parameters can be derived from a plot of $\ln\left(\frac{\partial T}{\partial t}\right)$ at T_p against $\frac{1}{T_\mathrm{p}}$.

An example of calculating kinetic parameters from crossing point method tests can be found in Annex B.

7.3.4 Applicability for solid recovered fuels

Whereas tests using the crossing point method applied to solid biofuel[19] and solid biofuel pellets[8] have given credible results, information on experience with SRFs is not yet available.

A disadvantage of the crossing point method is that inaccuracies in the positioning of the thermocouples in the sample basket significantly affect the quality of test results.

In the case of testing melting materials, sample preparation can be necessary. Corresponding instructions are given in 8.4.

7.4 Adiabatic hot storage tests

7.4.1 General

Adiabatic hot storage tests can be an alternative to time- and material-consuming isoperibolic hot storage tests. If carried out with sufficient precision, adiabatic tests are volume-independent as no heat conduction takes place in the bulk material.

7.4.2 Test procedure

The test procedure is described in EN 15188:2021, Annex D.

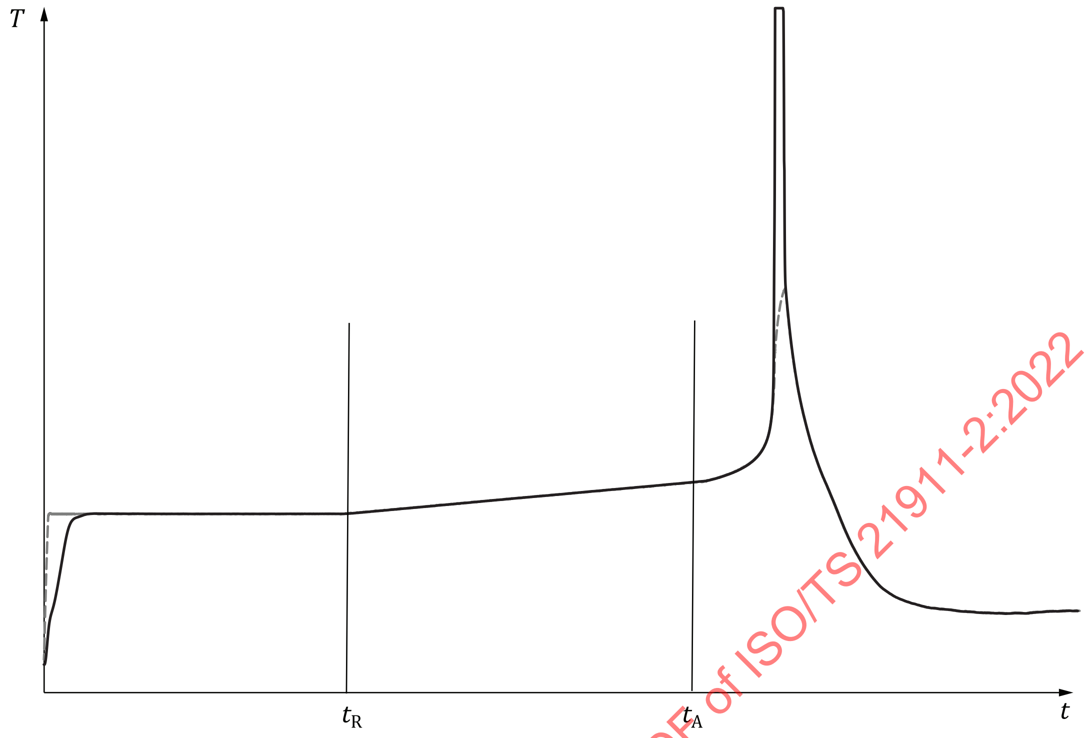
The test setup corresponds to that for isoperibolic hot storage tests. In addition, the set-up shall have a difference-temperature controller that enables the oven temperature to be adjusted to the temperature at the centre of the sample.

Wire-mesh containers (cubes or equidistant cylinders) with a volume of preferably 400 cm^3 to 1 000 cm^3 serve as sample containers. These are filled with sample material of a specified bulk density. The thermocouple for measuring the sample temperature is placed in the centre of the sample. The thermocouples, which register the oven temperatures, are located in the immediate vicinity of the wire basket. The temperature time curves of the sample and oven temperatures are recorded.

In the adiabatic hot storage test, the oven temperature is first set to a suitable start temperature. The self-ignition process starts if the temperature at the centre of the sample exceeds the oven temperature. From that point the oven temperature needs to be adjusted to the temperature at the centre of the sample. If no self-heating is detected, the furnace temperature can be further increased (e.g. temperature ramp of 1 °C/h) or the test can be repeated with an increased start temperature.

An oven temperature slightly below the self-ignition temperature of the sample volume should be chosen as the start temperature.

Figure 1 shows an example temperature profile of an adiabatic test.



Key

T	temperature (°C)
t	time (min)
t_R	start of temperature ramp
t_A	sample temperature exceeds oven temperature; oven temperature is adjusted to the temperature of the sample
- - - - -	oven temperature plot
———	sample temperature plot

Figure 1 — Temperature versus time plot of an adiabatic test

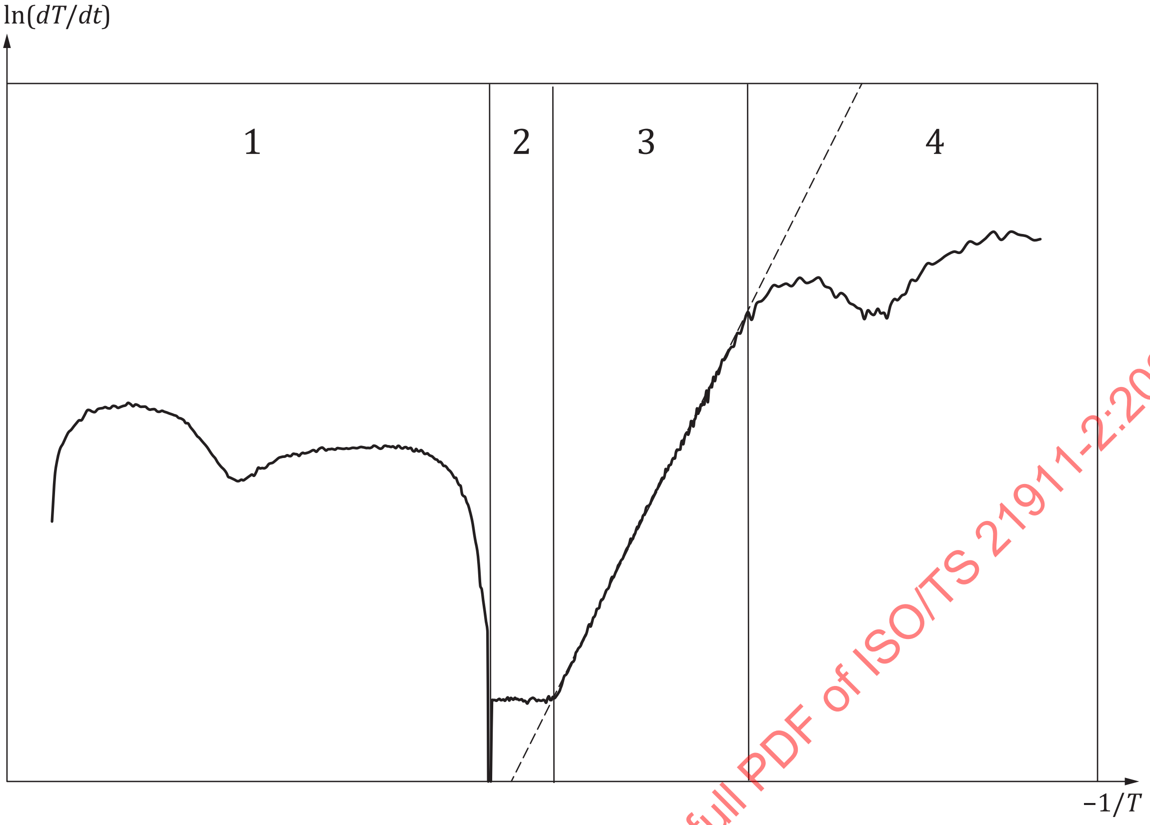
7.4.3 Determination of reaction kinetics

Adiabatic hot storage tests are used for the determination of reaction kinetics, such as pre-exponential factor and apparent activation energy.

To determine these values, the temperature rate dT/dt is first derived from the temperature time course of the sample by numerical differentiation. In a diagram, the natural logarithm of the temperature rate is plotted against the reciprocal sample temperature in Kelvin ($-1/T$) (Arrhenius diagram), see Figure 2. If zero-order conditions are assumed, the rate of temperature rise can be described as in Formula (8), see EN 15188.

$$\ln\left(\frac{dT}{dt}\right)=\ln\left(\frac{H_0}{C_p}A\right)-\frac{E_a}{RT} \tag{8}$$

The linear part of this function is approximated by a straight line. The slope of the straight line corresponds to the apparent activation energy. The pre-exponential factor can be determined from the intersection of the straight line with the ordinate $\ln\left(\frac{H_0}{C_p}A\right)$.



Key

T	temperature (K)
t	time (min)
1	heating up to start temperature
2	temperature ramp
3	self-ignition process with linear increase of the temperature rate
4	decrease of the temperature rate due to the diffusion resistance (no longer zero-order reaction conditions) due to lack of oxygen

Figure 2 — Arrhenius diagram of an adiabatic experiment

7.4.4 Applicability for solid recovered fuels

If it is executed correctly, a single test with a small sample quantity can be suitable to determine the reaction kinetic parameters of the sample. In combination with CAT of one volume determined by means of isoperibolic tests, it becomes possible to predict CAT of other volumes, see 7.2.3.

In the case of testing melting materials, sample preparation can be necessary. Corresponding instructions are given in 8.4.

8 Sample handling

8.1 General

Correct sample handling is important in maintaining the properties of solid recovered fuels. The transport and storage are of especial importance for self-heating properties as the reactivity of the sample can be reduced from prolonged exposure to air (oxygen). This is further accentuated at exposure to elevated temperatures.

The sample history and the conditions for sample handling should be stated as thoroughly as possible in the test report.

8.2 Sampling

Sampling of solid recovered fuel shall be made according to the procedures prescribed in ISO 21645.

The minimum size of the test sample for basket heating tests is normally 10 l, but larger sizes can be required for some tests.

8.3 Sample transport and storage

The laboratory sample shall be transported in a closed airtight sample container.

NOTE 1 An airtight container is used to limit the amount of available oxygen in order to reduce oxidation reactions with the sample.

The container shall be completely filled with the sample.

NOTE 2 A completely filled container limits the amount of air in the container (i.e. the amount of oxygen) and further reduces deterioration of the sample from physical wear (i.e. reduces the amount of fine fraction).

The time between sampling and analysis should be minimized and elevated temperatures shall be avoided.

NOTE 3 It has been seen that a sample can be stored for several months without any significant changes in reactivity if put in a freezer directly upon receipt at the analysis lab.

8.4 Sample preparation

The test portion shall be randomly taken from the test sample. The procedures from ISO 21646 shall be followed.

Especially in the case of melting materials, mixing with carrier materials can be necessary for an investigation (e.g. with powders or fibres) in order to be able to carry out the tests. This can lead to a more critical ignition behaviour even if inert substances are used as carrier material. As the risk of spontaneous combustion can be overestimated in this way, this should only be carried out if it also reflects the practical conditions (e.g. in the case of mixtures of different materials or possible impurities).

If particle size reduction is necessary for the tests, it shall be ensured that the properties of the sample are not altered (e.g. by excessive heating). This can be ensured, for example, by using slow-running mills.

8.5 Sample disposal

The test portion from a basket heating test is hot and often emits toxic combustion gases and shall be disposed of in a safe way.

NOTE A suitable method of safe disposal is to put the remaining sample material in a bucket of water.

9 Test report

The test report shall include the following information:

a) name and address of the test laboratory;

b) sample description:

   1) sample ID;

  2) type of product (and brand name if appropriate);
  3) classification if available;
  4) product data (if available: diameter, length, density, moisture content, material composition);
  5) sample selection process (e.g. random);
  6) product history (date of: production, sampling, transport and arrival at the test laboratory);
  7) type of package for the sample during transport;

c) sample state and preparation:
  1) sample storage prior to sample preparation (e.g. temperature);
  2) date and time of unpacking and sample preparation (hour, day, month and year);
  3) type of sample preparation before taking out test portions;
  4) moisture content;
  5) bulk density;

d) reference to this document (i.e. ISO/TS 21911-2):
  1) test method applied;
  2) use of the test results: screening tests or tests for calculation of kinetic parameters;

e) any unusual features noted during the determination which have possibly affected the result;

f) results of the test, including units and the basis they are given;

g) date of the test.

Annex A
(informative)

Self-ignition behaviour of selected materials suitable to be used as solid recovered fuels

A.1 General

In 2010, a research project on the self-ignition behaviour of different SRFs was completed. One aim was to determine the volume-dependent self-ignition temperatures according to 7.2[15].

A.2 Tested samples

Samples from different residuals were chosen for testing, see Tables A.1, A.2 and Figure A.1. The samples were reduced to fractions with particle sizes < 1 mm and 5 mm to 10 mm, respectively, using a cutting mill, see Figure A.2.

With the exemption of paper and textiles, the samples were mixed with diatomite (kieselgur) in a ratio of 4:1.

Table A.1 — Tested samples

Sample no.	Sample acronym	Description of sample
1	PP 1 mm	paper, cardboard < 1 mm
2	TEX 1 mm	textiles < 1 mm
3	P1 1 mm	cleaned plastics < 1 mm mixed with 20 % diatomite
4	P2 1 mm	cleaned plastics (>50 % foils) mixed with 20 % diatomite
5	P3 1 mm	uncleaned plastics < 1 mm mixed with 20 % diatomite
6	MB 1 mm	waste from mechanical-biological treatment < 1 mm (20 % diatomite)
7	TEX 10 mm	textiles 5 mm to 10 mm
8	P3 10 mm	uncleaned plastics 5 mm to 10 mm mixed with 20 % diatomite
9	MB 10 mm	waste from mechanical-biological treatment 5 mm to 10 mm (20 % diatomite)

Table A.2 — Material properties of tested samples

Sample no.	Sample acronym	Moisture content %	Calorific value (original sample) J/g	Elemental composition (original sample) %			Ash (water free) %
				N	C	H	
1	PP	2,7	14 247	0,285	37,35	5,454	19,7
2	TEX	5,4	22 645	4,673	52,25	6,624	15,3
3	P1	1,1	37 018	0,237	59,97	9,01	3,5
4	P2	0,7	36 325	0,188	58,00	8,419	8,9
5	P3	1,0	35 447	0,325	56,35	8,485	7,3
6	MB	3,2	27 608	0,629	45,41	6,575	16,3

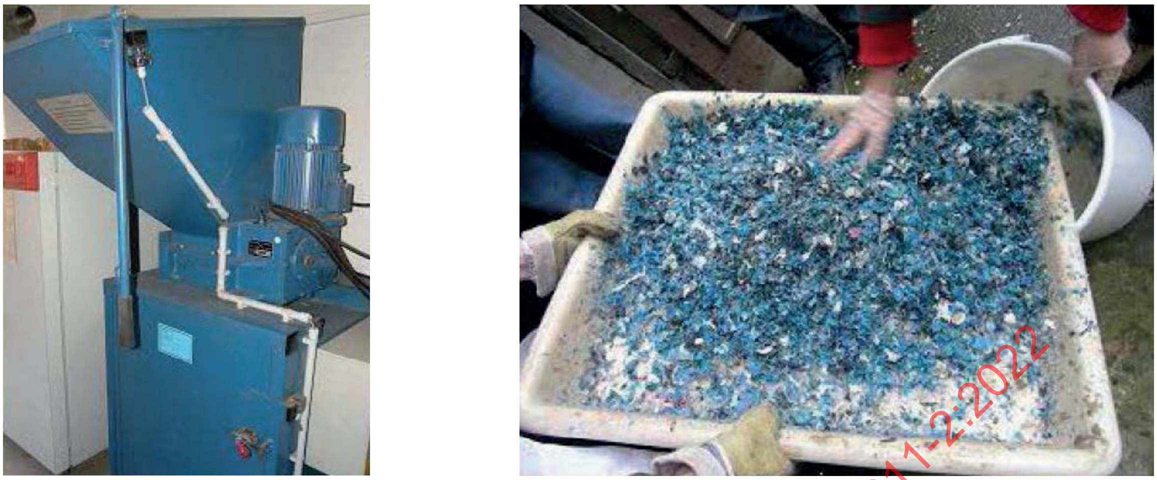
a) Textiles (samples 2 and 7)

b) Uncleaned plastics (samples 5 and 8)

c) Paper and cardboards (sample 1)

d) Waste from mechanical-biological treatment (samples 6 and 9)

Figure A.1 — Tested samples (selection)



a) Retsch cutting mill, particle size 5 mm to 10 mm

b) Retsch cutting mill 2 000, particle size ~ 1 mm

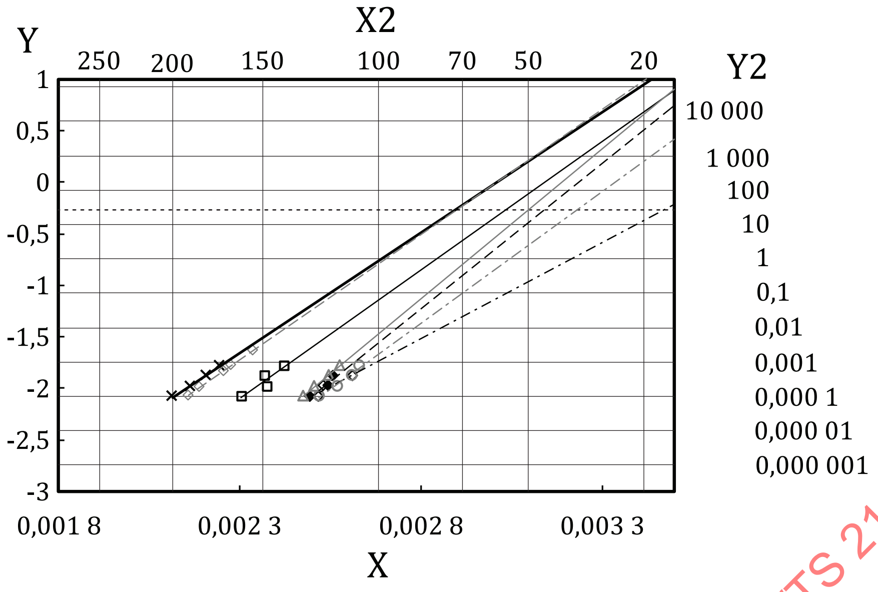
Figure A.2 — Sample preparation

A.3 Test results

To be able to assess the self-ignition behaviour of solid recovered fuels, wood pellets are used as reference material. In tests according to EN 15188 wood pellets show a moderate risk of self-ignition. The extrapolated CAT for a 1 000 m^3 pile was found to be in a range of 50 °C. Additional exothermic low-temperature oxidation processes are a precondition for self-ignition of wood pellet piles of this size. Without such additional exothermic processes, the risk of self-ignition is low for this storage volume. If much larger volumes are stored, as is often the case with wood pellets, spontaneous combustion can occur even without such additional exothermic processes. This applies equally to other materials.

Figure A.3 shows a comparison of all samples reduced to a particle size of < 1 mm. Paper and wood pellets show a similar self-ignition behaviour even if the sample consists of small particles.

All other samples showed a more critical self-ignition behaviour than wood pellets. In particular, plastics mixed with diatomite exhibit a higher risk for self-ignition. The extrapolated CAT for a 1 000 m^3 pile is lower than 20 °C for two samples.



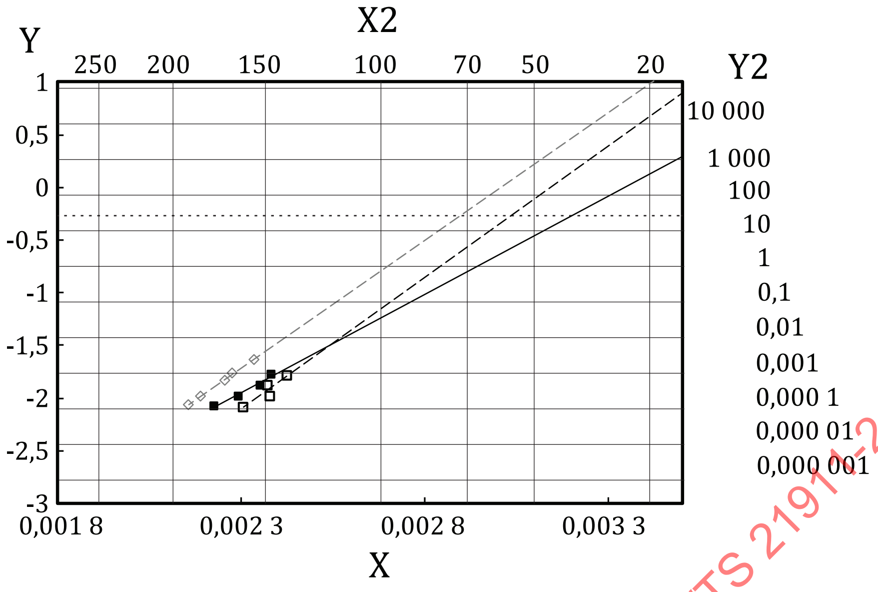
Key

X	reciprocal CAT in K^{-1}	X2	CAT in °C
Y	lg V/S (V/S in m)	Y2	volume (cylinder) in m^3
—×—	PP 1 mm	—□—	TEX 1 mm
--◇--	P1 1 mm	--◆--	P2 1 mm
--○--	P3 1 mm	—△—	MB 1 mm
--◇--	wood pellets		

Figure A.3 — Pseudo-Arrhenius diagram, samples < 1 mm

Figures A.4 to A.6 show a comparison of particle sizes < 1 mm and 5 mm to 10 mm for samples TEX, P3 and MB. For samples P3 and MB the self-ignition temperatures increase with particle size.

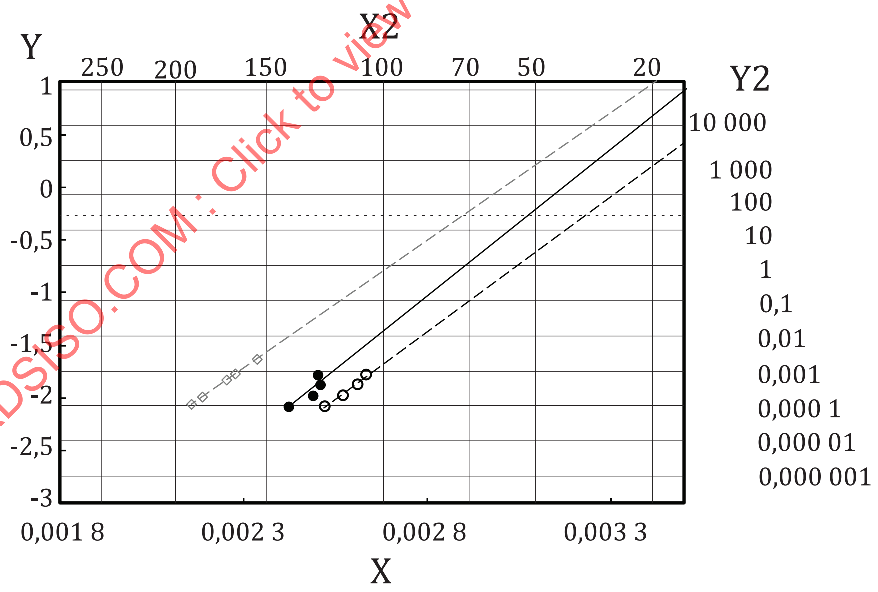
Sample TEX 10 mm and sample P3 (see Figure A.5) show an implausible dependence of the CAT on the volume. This behaviour can be explained by inhomogeneities of the samples. Inhomogeneities increase the uncertainty of the result of the extrapolation. One means of reducing the influence of inhomogeneities is to perform multiple tests with samples of each size.



Key

X	reciprocal CAT in K^{-1}	X2	CAT in °C
Y	lg V/S (V/S in m)	Y2	volume (cylinder) in m^3
--□--	TEX 1 mm	—■—	TEX 10 mm
--◇--	wood pellets		

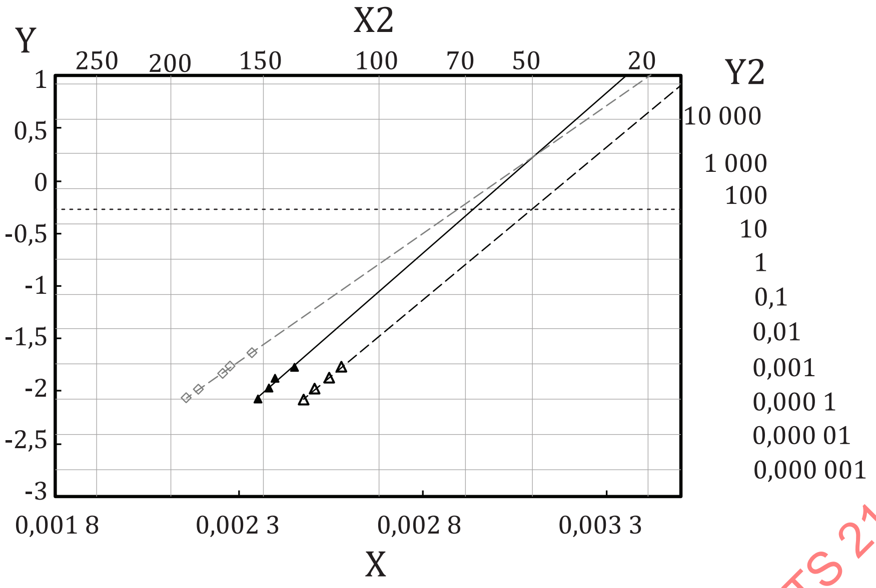
Figure A.4 — Pseudo-Arrhenius diagram, sample TEX



Key

X	reciprocal CAT in K^{-1}	X2	CAT in °C
Y	lg V/S (V/S in m)	Y2	volume (cylinder) in m^3
--○--	P3 1 mm	—●—	P3 10 mm
--◇--	wood pellets		

Figure A.5 — Pseudo-Arrhenius diagram, sample P3



Key

X	reciprocal CAT in K^{-1}	X2	CAT in °C
Y	lg V/S (V/S in m)	Y2	volume (cylinder) in m^3
‒ ‒△‒ ‒	MB 1 mm	‒▲‒	MB 10 mm
‒ ‒◇‒ ‒	wood pellets		

Figure A.6 — Pseudo-Arrhenius diagram, sample MB

In Table A.3 the extrapolated self-ignition temperatures are listed for deposits of 27 m^3, 100 m^3 and 1 000 m^3.

Table A.3 — Extrapolated self-ignition temperatures

Sample no.	Sample acronym	Extrapolated self-ignition temperatures T_{SI} °C		
		27 m^3	100 m^3	1 000 m^3
1	PP 1 mm	73	63	48
2	TEX 1 mm	57[a]	48[a]	35[a]
3	P1 1 mm	15	7	–7
4	P2 1 mm	46	39	28
5	P3 1 mm	37	30	18
6	MB 1 mm	50	43	32
7	TEX 10 mm	39[a]	30[a]	14[a]
8	P3 10 mm	52	45	34
9	MB 10 mm	67	60	49
10	wood pellets	74	65	50

Key

dark grey cells = high risk (self-ignition temperature ≤ 30 °C)

light grey cells = medium risk (30 °C < self-ignition temperature ≤ 40 °C)

white cells = low risk (self-ignition temperature > 40 °C)

[a] Implausible value (see Figure A.5).

According to Table A.3 a storage (pile) is divided into the following classes. This classification is only made to demonstrate the differences in self-ignition behaviour of the materials; the actual risk shall be determined considering the present storage conditions.

As for wood pellets, an additional exothermic low-temperature reaction (oxidation, microbial processes) considerably increases the risk of self-ignition.

A.4 Findings and conclusions

Recovered fuels can contain a large number of different materials. Some materials or combinations of materials exhibit an increased risk of self-ignition. Also, mixtures of combustible and inert materials can undergo self-ignition processes. Under certain circumstances the addition of inert materials or materials with a high surface (porous materials, textiles) can promote self-ignition, especially of melting materials, see ISO 21912.

Exothermic low-temperature reactions (oxidation, microbial decomposition) considerably increase the risk of self-ignition.

To evaluate the risk of self-ignition of recovered fuels the following is recommended:

a) determine the volume-dependent self-ignition behaviour (basket tests according to EN 15188);

b) identify low-temperature reactions using isothermal calorimetry;

c) consider testing mixtures of combustible materials with inert materials or further carrier materials depending on possible material combinations;

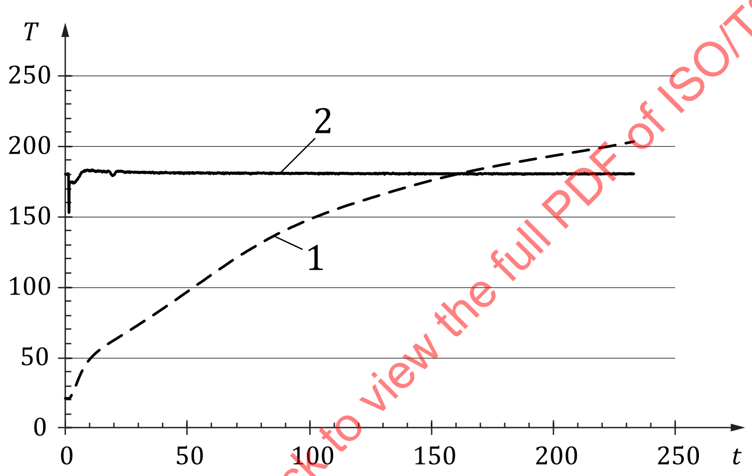
d) consider testing different particle sizes depending on present conditions.

The test results show that quality of determined data is low for some materials, for example implausible results for sample TEX or low coefficient of determination R^2 for regression lines of samples P1 1 mm and P3 10 mm, see Figure A.3 and Figure A.5. Hence, focus should be put on sample preparation to generate representative and homogeneous test samples. In addition, it is recommended that larger sample volumes are tested.

Annex B
(informative)

Example of calculating kinetic parameters from crossing point method tests

Whereas tests using the crossing point method applied to solid biofuel[19] and solid biofuel pellets[8] have given credible results, experience with SRFs is not yet available. Therefore, this example shows how kinetic parameters have been calculated using the crossing point method for a wood pellet batch called 5.2. Basket heating tests were performed at six different furnace temperatures: 160 °C, 170 °C, 180 °C, 185 °C, 190 °C and 200 °C. An example of measured data at 180 °C is given in Figure B.1. Only the centre temperature is given, even though temperatures were measured at several locations inside the basket.



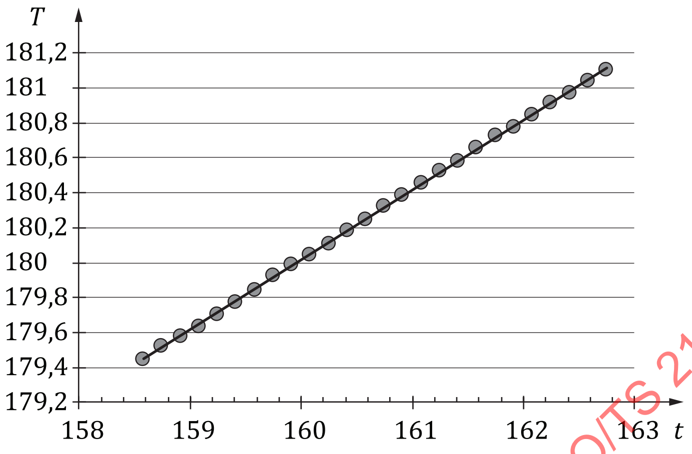
Key

T	temperature (°C)
t	time (min)
1	centre temperature
2	furnace temperature

NOTE After 161 min the centre temperature in the basket crosses the furnace temperature (180,3 °C at this point).

Figure B.1 — Example of basket heating test with the crossing point method for wood pellet batch 5.2 at 180 °C

From Figure B.2 the slope of the temperature-time graph at the crossing point ln(*dT*/*dt*) is calculated. Here the slope has been calculated by finding the linear fit for data within ± 2 min from the time of crossing point.



Key

T temperature (°C)

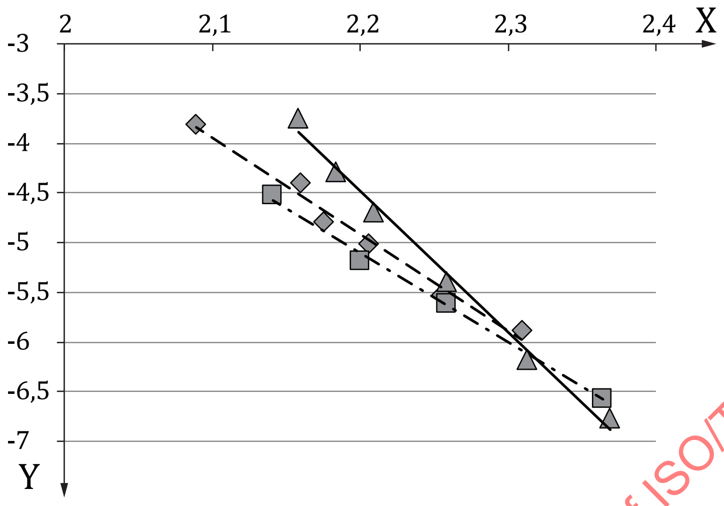
t time (min)

● centre temperature

—— linear fit of A ($T = 0{,}399\,3t + 116{,}12$, $R^2 = 0{,}999\,8$)

Figure B.2 — Determination of the slope of the temperature-time graph at the crossing point ln(*dT*/*dt*) for wood pellet batch 5.2

The slope of the temperature-time graph at the crossing point, ln(dT/dt), is plotted against the inverted crossing point temperature, 1 000/T_p, for all furnace temperatures, see Figure B.3. For comparison plots for two more batches, 10.2 and 17 are given.



Key

X	1 000/T_P
Y	Ln dT/dt
◆	5.2
■	10.2
▲	17
– – –	linear fit of 5.2 ($y = -9{,}703\,7x + 16{,}435$, $R^2 = 0{,}984\,6$)
- · -	linear fit of 10.2 ($y = -9{,}0245x + 14{,}75$, $R^2 = 0{,}995\,9$)
——	linear fit of 17 ($y = -14{,}219x + 26{,}793$, $R^2 = 0{,}991\,7$)

Figure B.3 — Plot of ln(dT/dt) versus 1 000/T_p for each ambient temperature for wood pellet batches 5.2 and comparison with two other batches

By using the data in Figure B.3 and Formula (7) in 7.3.3, the kinetic parameters E_a and QA can be calculated, see Table B.1. The activation energy E_a can be obtained from the coefficient in the linear expression $-E_a/R$ and heat of reaction QA can be calculated from the constant ln(QA/C_p). However, for the calculation of QA the specific heat of the wood pellet bulk C_p shall also be known.

Table B.1 — Kinetic parameters of wood pellets, calculated with test data from basket heating tests

Wood pellet	**Pellet bulk** C_p J/kg/K	E_a kJ/mol	$Q \times A$ J/kg/s
Batch 5.2	1 370	81	$1{,}9 \times 10^{10}$
Batch 10.2	1 390	75	$3{,}5 \times 10^{9}$
Batch 17	1 460	118	$6{,}3 \times 10^{14}$
NOTE For comparison data for two more batches, 10.2 and 17 are given.			