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

Part 2: Basket heating tests

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

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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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.

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[6] 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 ISO 20049-1, 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 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, the CAT is found for a 1 l sample portion in the range 150 °C to 200 °C.

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[7].

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[8].

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, for example, cottonseed meal, bagasse and milk powder[9]. The principle used in this type of tests 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].

Basket heating tests are useful for assessment of self-heating of solid biofuel pellets. 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 pelletized biofuels is provided.

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

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

Part 2:
Basket heating tests

1 Scope

This document specifies basket heating tests for the characterization of self-heating properties of solid biofuel pellets.

This document includes:

a) a compilation of basket heating test methods;

b) guidance on the applicability and use of basket heating tests for solid biofuel pellets;

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

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 for use in quality control and in hazard and risk assessments related to the procedures given in ISO 20024.

The described methods can be used for other substances than solid biofuel pellets (e.g. wood chips).

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*

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

— IEC Electropedia: available at http://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 temperature of a storage] where the internal temperature of the *test portion* (3.6) or the stored material increases significantly (due to *self-heating* (3.4))

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>" has been deleted from the beginning of the definition.]

3.5
spontaneous ignition
ignition caused by an internal exothermic reaction

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

[SOURCE: ISO 13943:2017, 3.24, modified — "spontaneous ignition" has replaced auto-ignition" has the preferred term and the other terms have been deleted. Notes 1 to 3 have been deleted and a new Note 1 to entry has been added.]

3.6
test portion
sub-sample either of a *laboratory sample* (3.8) or a *test sample* (3.7)

3.7
test sample
laboratory sample (3.8) after an appropriate preparation made by the laboratory

Note 1 to entry: In this document, the test sample is typically a representative sample from a batch of solid biofuel pellets.

3.8
laboratory sample
combined sample or a sub-sample of a combined sample for use in a laboratory

[SOURCE: ISO 16559:2014, 4.124]

4 Symbols

Symbol	Quantity	Typical unit
A	pre-exponential factor in Arrhenius expression	s^{-1}
B	dimensionless adiabatic temperature rise	dimensionless
Bi	Biot number, ($\mathrm{Bi}=\frac{hL}{\lambda}$)	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}
h_c	convective amount on heat transfer coefficient	W m^{-2} K^{-1}
L	characteristic length	m
n	order of reaction	dimensionless
P	constant, see Formulae (2) and (3)	dimensionless
$\dot{q}'$	heat generation term, see Formula (B.1)	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	Rayleigh number	dimensionless
t	time	s
T	temperature	K
T_0	ambient temperature	K
T_p	crossing point temperature	K
x	length coordinate	m
δ	Frank-Kamenetskii parameter, see Formula (B.4)	dimensionless
δ_c	critical value of δ	dimensionless
ε	activation energy parameter, ($\varepsilon=\frac{RT_0}{E}$)	dimensionless
Φ	oxygen diffusion parameter, see Formula (B.13)	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[5].

Basket heating tests are based on the Frank-Kamenetskii theory of criticality of a self-heating isotropic slab (see Annex B) and have been developed to determine the reaction kinetics of the global reaction responsible for heat production in a self-heating material.

NOTE 1 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, it is recommended to keep the air flow in the vicinity of the sample at a low level and to correct the critical Frank-Kamenetskii parameter (see B.1.3) or to prevent convective transport within the sample by further measures (e.g. finer mesh wire of the basket).

NOTE 2 The CAT for the test portion in a basket heating tests 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 laboratory size basket heating test has a very high surface area-volume ratio and has 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 (UN) Globally Harmonized System of Classification and Labelling of Chemicals (GHS)[11] is the international convention for hazard communication and labelling of gases, vapours, solid and liquid substances, and mixtures. The GHS defines limit values, classes and categories and related measures in relation to the level of hazards during transportation, handling and storage.

The UN Manual of Tests and Criteria (MTC)[12] prescribes specific test procedures in support of the GHS.

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

Test N.4 is described in the UN 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 of it to air at temperatures of 100 °C, 120 °C or 140 °C in a 25 mm or 100 mm wire mesh cube.

The Test N.4 basket heating test is not intended for determination of self-heating kinetics but rather prescribed to classify a material (e.g. solid biofuels) 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 of 25 mm and 100 mm sides made of stainless-steel net with a mesh opening of 0,05 mm, and thermocouples of 0,3 mm diameter for the 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 is 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 cube sample. 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 cube sample, the substance is classified as a self-heating substance and further testing shall be made to find the correct classification (see 6.1.3).

NOTE The bulk density tested can influence the test results. prEN 15188 suggests adjusting the bulk density of the sample to the respective practical conditions (if known) and recording the tested bulk density. The UN 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 the GHS for self-heating substances and mixtures

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

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

6.2 Classification criteria — IMO

Handling guidelines and hazard classifications for all cargoes, including solid biofuels, transported onboard ocean vessels are specified by the International Maritime Organization (IMO) in the International Maritime Solid Bulk Cargoes Code[13]. The code stipulates UN MTC Test N.4 to be used for testing but adds 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 check the temperature increase is 10 °C or more:

   1) if yes, material hazardous in bulk (MHB) applies;

   2) if no, neither Class 4.2 nor MHB applies.

NOTE Wood pellets containing no binder and additives are given the designation MHB (OH) as a result of a high emission of carbon monoxide and not MHB (SH), since wood pellets are not classified as self-heating in accordance with the criteria specified under the GHS and the MTC.

6.3 Applicability of UN MTC Test N.4 for pelletized biofuels

Experience from the testing of wood pellets indicates that the CAT for this type of material always is higher than 140 °C in 1,0 l basket heating tests; see, for example, Reference [8]. The 140 °C criterion seems thus not to be generally applicable for solid biofuel pellets.

The reasons that this test is unsuitable as a general test method for solid biofuel pellets are the following:

a) the criteria in Test N.4 is based on fix reaction kinetics of coal, which is not directly transferable to solid biofuel pellets;

b) experience shows that the UN criteria based on self-ignition of the analytical sample in a 100 mm sample cube test at 140 °C is not valid for solid biofuel pellets since the CAT of 1000 cm^3 wood pellets is normally higher;

c) there is no published information on the selectivity and the correlation to large scale storage of this tests for solid biofuel pellets;

d) the self-heating process of wood pellets can undergo multi-step reactions at different temperature ranges. Low temperature reactions are not covered by tests in accordance with the Test N.4 method.

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 7.2 to 7.4.

7.2 Isoperibolic test methods

7.2.1 General

The original basket heating test method was developed at the Fire Research Station in 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 that is 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[14] 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[15][16]. Laboratory-specific differences have been identified as possible reasons for the deviations, for example:

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 no ignition);

f) minimum sample size.

For that reason, the original FRS method was modified and further developed in the European standard EN 15188. The main difference is the use of an additional mesh wire screen and special volumes of the sample baskets (cubes) to normalize/harmonize the test conditions in the surrounding of the samples independent from used oven type and size. This is, however, an important deviation from the Frank-Kamenetskii theory (see Annex B), which relies on a high Biot number of the test specimen to keep the boundary of the tests 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 in accordance with B.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 to 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 will produce 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 should be used for extrapolations over a wide range of sizes. The recommendation in prEN 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. prEN 15188 requires to test 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 B) is based on the determination of the critical temperature for a known size of a material in small-scale oven tests as described above.

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

$$\delta = \frac{\rho Q A}{\lambda} \cdot \frac{E L^2}{R T_0^2} \cdot e^{-E/RT_0} \tag{1}$$

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

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

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

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

Once the material parameters are determined from the small-scale tests, it would be possible to predict the critical size for any full-scale configuration, see Formula (B.5), 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 pelletized biofuels

Isoperibolic tests of different sample volumes in accordance with prEN 15188 should be the most appropriate basket heating method for testing solid biofuel pellets if the critical Frank-Kamenetskii parameter is corrected in accordance with B.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 in accordance with prEN 15188 provides reproducible results independent of the type of furnace used.

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[17], 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 formula.

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[17] 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 could 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 in the isoperibolic methods, each of the transient experiments with the crossing-point method where only one sample size is needed produces a data point in a rather short time. In order to obtain several data points for the plot, the initial temperature of the oven is varied within certain limits[17].

NOTE Cuzzillo[18] has evaluated the crossing-point method in detail. A detailed error analysis of the method was made and Cuzzillo shows several advantages of the crossing-point method over the standard isoperibolic method. First, the above-mentioned advantage that every test result gives a useful data point. Further, it eliminates the 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 to be known in the laboratory tests for determining the kinetic parameters.

An example of calculating kinetic parameters using the crossing-point method is given in Annex A.

7.3.2 Test procedure

An example of a test procedure from Reference [8] is given in this subclause. The equipment used includes a wire mesh basket (cubic) with 1,0 l volume made from 0,6 mm stainless steel mesh, a temperature-controlled oven with a re-circulating fan, and six thermocouples to register the temperature: 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 was 10 mm away from the centre, the third was 10 mm further away, the fourth was additionally 15 mm further away and the fifth was 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 exceeds 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[17] 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, see Formula (4):

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

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;

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:

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

and Formula (4) is reduced to Formula (6):

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

which could be rewritten as Formula (7):

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

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 could be derived from a plot of $\ln\left(\frac{\partial T}{\partial t}\right)$ at T_{p} against $\frac{1}{T_{\mathrm{p}}}$.

7.3.4 Applicability for pelletized biofuels

Tests using the crossing-point method applied to solid biofuel[17] and solid biofuel pellets[8] have given credible results and, in one case, correlation with large-scale validation tests has been demonstrated[20].

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.

NOTE There is most probably a lower limit of the size of the test basket in relation to the size of the pellets. A 1,0 l basket has proved to give credible results for standard 6 mm and 8 mm wood pellets[8]. However, less accurate results have been given for abnormally long pellets tested.

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 prEN 15188:2019, Annex D[5].

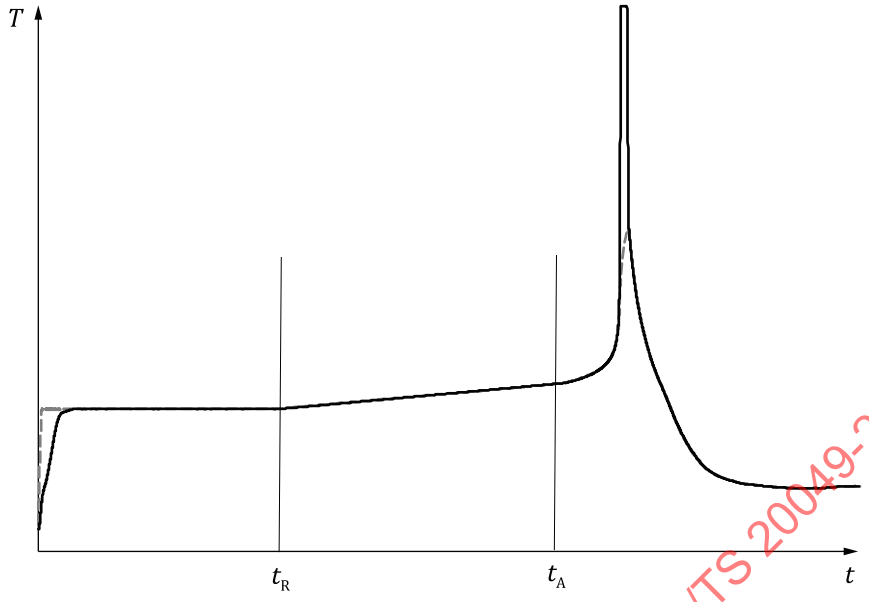
The test setup corresponds to that for isoperibolic hot storage tests. In addition, the set-up shall have a difference-temperature controller that enables the oven temperature to be adjusted to the temperature at the centre of the sample.

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. For a 400 cm^3 volume of wood pellets, a suitable start temperature can be in the range of 120 °C to 140 °C.

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

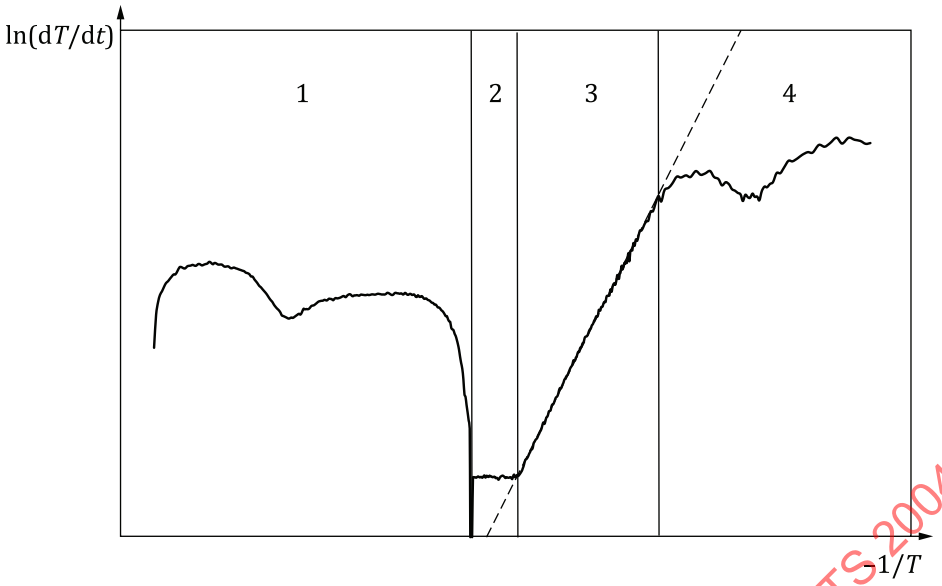
7.4.3 Determination of reaction kinetics

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 shown in Formula (8)[5].

$$\ln\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)=\ln\left(\frac{H_0}{C_\mathrm{p}}A\right)-\frac{E_\mathrm{a}}{RT} \tag{8}$$

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 $\ln\left(\frac{H_0}{c}A\right)$.



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 pelletized biofuels

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 the CAT of one volume determined by means of isoperibolic tests, it becomes possible to predict the CAT of other volumes, see 7.2.3.

8 Sample handling

8.1 General

Correct sample handling is important in maintaining the properties of solid biofuel pellets samples. Transport and storage are of especial importance for self-heating properties, as the reactivity of the sample will 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 biofuel pellets shall be made in accordance with procedures prescribed in ISO 18135.

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 sample.

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

The time between sampling and analysis should be minimized. 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 it is put in a freezer directly after being received at the analysis laboratory.

8.4 Sample preparation

Any fine fraction shall be removed from the test sample before extracting test portions. The fine fraction can be removed by gentle hand sieving using sieve size 3,15 mm in accordance with ISO 18846.

NOTE 1 The fine fraction is removed to avoid any fine fraction produced during handling and transport being included in the test portion.

The test portion shall be randomly taken from the test sample. Procedures from ISO 14780 shall be followed.

8.5 Sample disposal

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

NOTE A suitable way for 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, e.g. in accordance with ISO 17225-2;

   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, year);

3) type of sample preparation before taking out test portions;

4) moisture content;

5) bulk density.

d) a reference to this document, i.e. ISO/TS 20049-2;

1) the 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 that could affect the result;

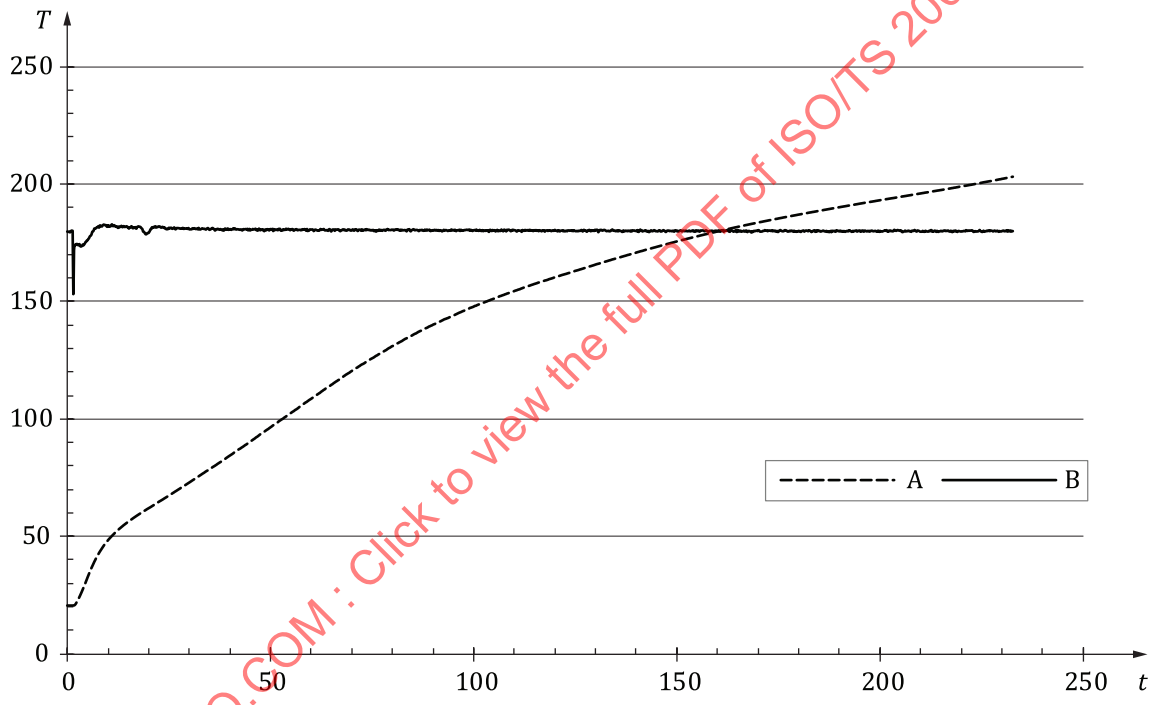
f) results of the test, including the units and the basis they are given;

g) the date of the test.

Annex A
(informative)

Example of calculating kinetic parameters from crossing-point method tests

This example shows how kinetic parameters have been calculated for a pellet batch called "5.2" using the crossing-point method. 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 A.1. Only the centre temperature is given even though temperatures were measured at several locations inside the basket.



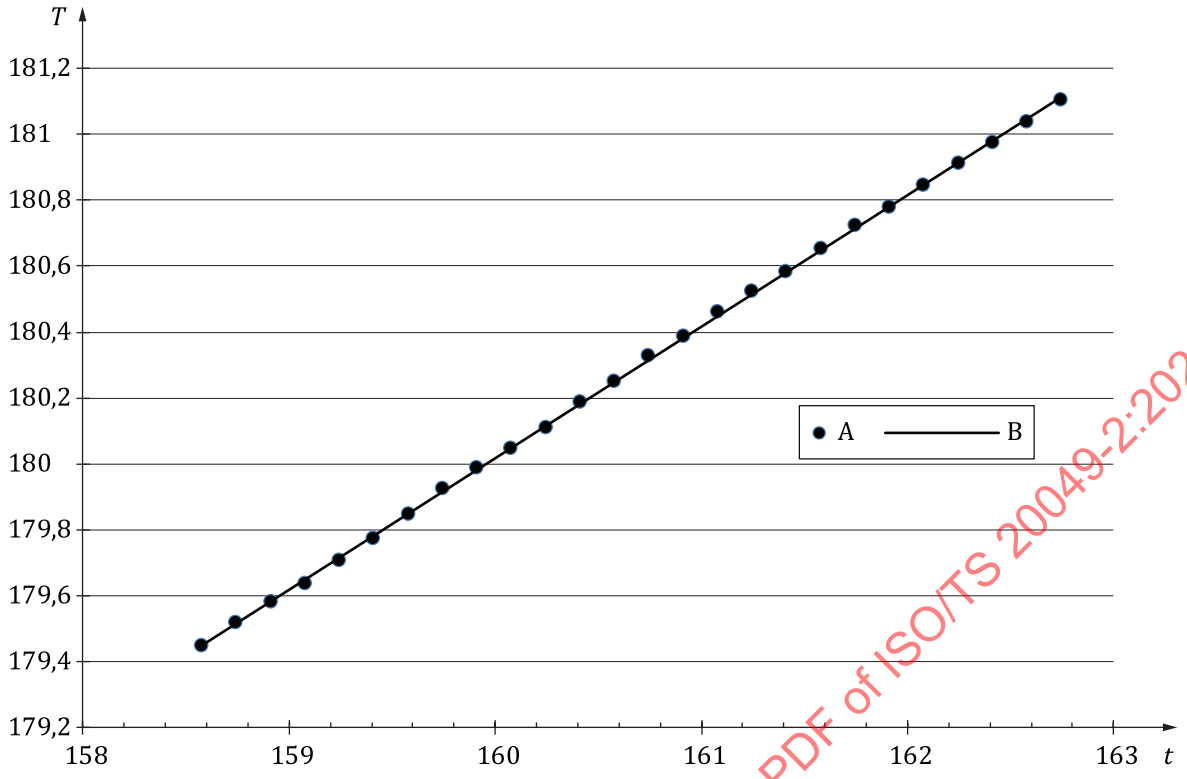
Key

T temperature (°C)
t time (min)
A centre temperature
B furnace temperature

NOTE After 160,6 min, the centre temperature in the basket crosses the furnace temperature (180,3 °C at this point).

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

From Figure A.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)

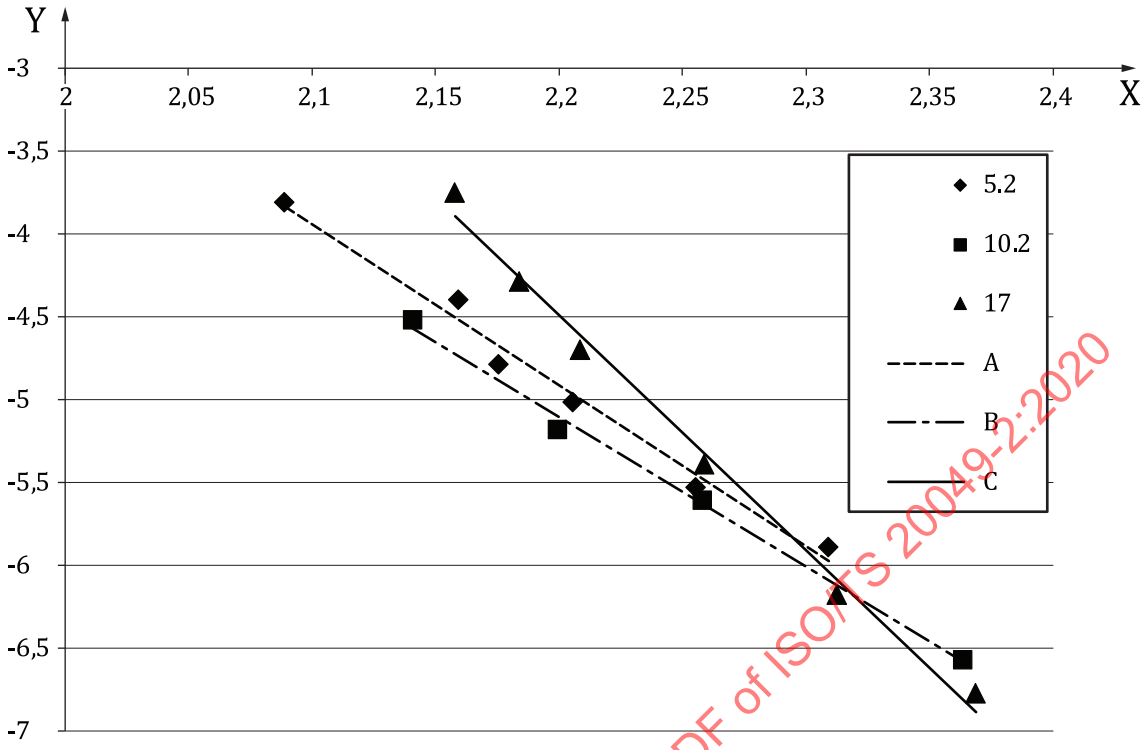
t time (min)

A centre temperature

B linear fit of A (T = 0,399 3t + 116,12; R^2 = 0,999 8)

Figure A.2 — Determination of the slope of the temperature–time graph at the crossing point $\ln(dT/dt)$ for 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 A.3. For comparison, plots for two more batches, 10.2 and 17, are given.



Key

Y $\ln(dT/dt)$

X $1\,000/T_p$

A linear fit of 5.2 ($Y = -9{,}703\,7X + 16{,}435$; $R^2 = 0{,}984\,6$)

B linear fit of 10.2 ($Y = -9{,}024\,5X + 14{,}75$; $R^2 = 0{,}995\,9$)

C linear fit of 17 ($Y = -14{,}219X + 26{,}793$; $R^2 = 0{,}991\,7$)

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

By using the data in Figure A.3 and Formula (7) in 7.3.3, the kinetic parameters E and QA can be calculated, see Table A.1. The activation energy E can be obtained from the coefficient in the linear expression E/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 pellet bulk C_p must also be known.

Table A.1 — Kinetic parameters, calculated with test data from basket heating tests

Wood pellet	C_p, pellet bulk (J/kg/K)	E (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.			

Annex B
(informative)

Use of data for calculations of critical conditions in storages

B.1 The Frank-Kamenetskii stationary model

B.1.1 General

In theoretical work on self-ignition problems, infinite slab geometry is often used, because of the relatively simple formula for energy conservation compared to more complex geometries. The results for the slab can, however, normally be generalized to other geometries by various techniques[14].

Consider the energy formula for a slab given in Formula (B.1):

$$\rho C_{\mathrm{p}} \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \dot{q}' \tag{B.1}$$

where

the left-hand side	is the rate of enthalpy change;
the first term on the right-hand side	is the conductive heat transfer;
$\dot{q}'$	is the heat generation term.

The solution of Formula (B.1) would give the temperature distribution as a function of the distance and time. Solving the formula for a material liable to self-heating within the temperature limits of ignition would yield a slow steady increase in temperature with an abrupt transition to a large and rapid raise at the moment of ignition.

There are computational methods available to solve Formula (B.1), but the method introduced by Frank-Kamenetskii for finding a stationary solution of the energy formula is often used as an engineering tool to make assessments of the risk for spontaneous ignition.

The stationary theory is based on the time-independent heat conduction formula with distributed sources of heat. Under the steady (time-independent) assumption, Formula (B.1) becomes Formula (B.2):

$$\lambda \frac{\partial^2 T}{\partial x^2} = -\dot{q}' \tag{B.2}$$

The solution of Formula (B.2) gives the stationary temperature distribution in the slab. The initial conditions under which such a stationary distribution becomes impossible (i.e. where there is no solution for the formula) are interpreted as the critical conditions for ignition.

Most existing methods for the prediction of spontaneous ignition are related to the Frank-Kamenetskii (F-K) theory, and therefore this method is reviewed in some detail here. A brief summary of the basic assumptions is given in B.1.2. Appropriate corrections and limitations are discussed in B.1.3 and B.1.4, respectively.

B.1.2 Basic assumptions

A requirement for spontaneous ignition to occur is that the material is sufficiently porous and reactive so that adequate fuel and oxygen are available throughout the whole self-heating process. The following assumptions constitute the basis of the stationary F-K theory[9].

a) Heat is generated by a single (global) reaction whose rate at a given temperature is not a function of time. The rate of internal heating is assumed to be a function of temperature in accordance with the Arrhenius equation, i.e. Formula (B.3):

$$\dot{q}' = Q\rho A\, e^{-\frac{E}{RT}} \tag{B.3}$$

b) The activation energy is assumed to be sufficiently high such that $\varepsilon = \frac{RT_0}{E} << 1$ (here, T_0 is a reference temperature, usually the ambient temperature).

c) Heat transfer through the body is by conduction only.

d) Heat transfer at the boundaries to the surrounding takes place through convection and radiation. The Biot number $\mathrm{Bi} = \frac{hL}{\lambda}$ is sufficiently high so that the surface temperature of the body equals the ambient temperature, where:

   1) h is the effective heat transfer coefficient, i.e. including both radiation and convection;

   2) L is a characteristic length of the body;

   3) λ is the heat conductivity of the solid material.

e) The material is assumed to be isotropic and homogeneous with constant physical properties.

f) The F-K parameter δ is defined by Formula (B.4):

$$\delta = \frac{\rho Q A}{\lambda} \cdot \frac{EL^2}{RT_0^2} \cdot e^{-E/RT_0} \tag{B.4}$$

The critical value of the F-K parameter δ_c (T_0 = CAT) depends on the geometry of the sample or storage. For simple geometries, solutions for δ_c have been developed for Bi → ∞[14][21], see Table B.1.

Table B.1 — Critical values of δ for different simple geometries

Geometry of deposit	δ_c for Bi → ∞
Sphere	3,32
Equidimensional cylinder	2,76
Cube	2,52
Infinite cylinder	2,00
Infinite slab	0,88

Once the value of the critical F-K parameter (δ_c) is known, the kinetic parameters appearing in the definition of δ in Formula (B.4) can be obtained by indirect experimental methods (e.g. basket heating tests) for any material. Alternatively, the kinetic parameters can be determined by direct experimental methods (e.g. isothermal calorimetry).