Per Blomqvist, Bror Persson

Spontaneous Ignition of Biofuels - A Literature Survey of Theoretical and Experimental Methods

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Abstract

Methods for assessing the risk of spontaneous ignition are reviewed. The most widely used engineering method today, the Frank-Kamenetskii method, is reviewed in detail. Further a new improved experimental method, the so-called crossing-point method, is reviewed. This new method considerably speeds up the testing procedure. The Frank-Kamenetskii theory is best suited for application on materials that do not have excessive moisture content and where the reactions can be sufficiently well described by a single order reaction of the Arrhenius type.

It was found that a serious limitation in the classical F-K theory is that no account is taken to moisture transport and the accompanying phenomena of hydrolysis, evaporation and condensation. Furthermore, the role of water-mediated reactions cannot be handled by the Frank-Kamenetskii method. A further serious limitation to present engineering methods, regarding application to storage of biofuels, is that no consideration is taken to the low-temperature processes that take place before the oxidative reactions commence. Hence, a more complete model must also include the initial production of heat by microorganisms.

A survey of the potential risk for spontaneous ignition in various biofuel storages in Sweden has further been made. It was found that the largest risk for spontaneous ignition would be in storages of moist biofuel. The types of biofuels that would induce the highest risk for spontaneous ignition in storage, and that can be found in large quantities in storage, would be wood chips, sawdust and bark, if using moisture content as criteria. Dry refined wood fuels as pellets, briquettes and pulverized wood would thus give a low risk for spontaneous ignition.

Key words: spontaneous ignition, Frank-Kamenetskii, crossing-point method, biofuels, experimental methods.

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SP Sveriges Provnings- och Forskningsinstitut
SP Arbetsrapport 2003:18

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SP Swedish National Testing and Research Institute
SP AR 2003:18

Postal address:
Box 857,
SE-501 15 BORÅS, Sweden
Telephone: +46 33 16 50 00
Telex: 36252 Testing S
Telefax: +46 33 13 55 02
E-mail: info@sp.se

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Nomenclature

A	pre-exponential factor in Arrhenius expression (s^{-1})
B	dimensionless adiabatic temperature rise (-)
Bi	Biot number, ($Bi = \dfrac{hL}{\lambda}$) (-)
c_0	ambient oxygen concentration by volume (-)
C	specific heat of the reaction products (J kg^{-1} K^{-1})
C_p	specific heat of the bulk material (J kg^{-1} K^{-1})
D	diffusion coefficient (m^2s^{-1})
E	activation energy (J mol^{-1})
h	heat transfer coefficient (W m^{-2} K^{-1})
L	characteristic length (m)
n	order of reaction (-)
P	constant, equation (11) (-)
$\dot{q}'$	heat generation term, equation (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})
t	time (s)
T	temperature (K)
T_0	ambient temperature (K)
x	length co-ordinate (m)

Greek symbols

δ	Frank-Kamenetskii parameter, equation (3) (-)
δ_c	critical value of δ (-)
ε	small parameter, ($\varepsilon = \dfrac{RT_0}{E}$) (-)
Φ	oxygen diffusion parameter, equation (9) (-)
λ	thermal conductivity (W m^{-1} K^{-1})
ρ	bulk density (kg m^{-3})

1 Introduction

Spontaneous combustion of long-term storage is a long-standing practical problem that, in spite of extensive and intensive studies, has proved to be so intractable that there is still need for a definitive-working model capable of prediction of ignition behaviour with accuracy. An accurate prediction of fire risk requires an adequate description of the initiation and development of a fire. The problem is compounded by the uncertain physical and chemical behaviour involved at ambient conditions and presents difficulties of practical control to restrict the temperature increase in storage.

The dominant source of heat is the hydrocarbon oxidation governed essentially by the rates of diffusion and convection of air from outside, however there can also be significant influence of heat of wetting from adsorption of the inherent moisture. Various exothermic processes such as low temperature oxidation, microbial metabolism, the adsorption-desorption of water due to the difference between real and equilibrium moisture concentration in a storage and air and oxidation of volatile and reactive compounds can contribute to self-heating of materials in storage and spontaneous combustion.

As Sweden aligns itself with the EU Waste Directive, there will be some major changes in the disposal of waste in the next few years. After 1st January, 2002, it is prohibited by law to place combustible waste in a landfill. Similarly in 2005 it will be prohibited to place organic waste in a landfill. In preparation for these changes Sweden has been working with collection and sorting of a variety of waste for the past 5-10 years. The waste is first divided into a number of fractions, which can then be disposed of in different ways. In many cases this waste will be stored for varying periods of time in anticipation either of material or energy recycling. These storage sites present enormous potential environmental and safety problems.

With the anticipated increase in storage volumes of combustible waste, a research programme has been initiated by CECOST (Centre for Combustion Science and Technology) with founding from the Swedish Energy Agency (STEM), the Swedish Rescue Services Agency (SRV) and the Swedish Board for Fire Research (Brandforsk). The major participants in the project are: the Department of Fire Safety Engineering at Lund University, the department of Fire Technology at SP Swedish National Testing and Research Institute and Växjö University. The aim of the project is to conduct research on spontaneous ignition processes in storages of combustible materials and to develop computational tools for accurate simulation of such processes.

A literature review has been made on present theories and methods for prediction of spontaneous ignition. The results from this review are presented in this report. The review has mainly concentrated on engineering models and the small-scale methods required to produce input data for such models. Shortcomings of the models and specific problems associated with the applications to biofuels have been addressed. Further, a survey of the potential risk for spontaneous ignition in various biofuel storages in Sweden has been made.

2 Evaluation of small-scale methods

2.1 Frank-Kamenetskii theory

In theoretical work on self-ignition problems one has often worked with the infinite slab geometry, because of the relatively simple equation for energy conservation compared to more complex geometries. The results for the slab can however normally be generalized to other geometries by various techniques [1].

Consider the energy equation for a slab:

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \dot{q}' \tag{1}$$

where the left hand side is the rate of enthalpy change, the first term on the right hand side represents the conductive heat transfer and $\dot{q}'$ is the heat generation term. The solution of equation (1) would give the temperature distribution as a function of the distance and time. Solving the equation for a material liable to spontaneous combustion 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 equation (1), but the method introduced by Frank- Kamenetskii for finding a stationary solution of the energy equation is often used as an engineering tool to make assessments of the risk for self-ignition.

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

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

The solution of equation (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 equation) are interpreted as the critical conditions for ignition.

Most existing methods for prediction of spontaneous ignition are related to the Frank-Kamenetskii theory (F-K for short) and therefore this method is reviewed in more detail here. A brief summary of the basic assumptions is given and limitations and appropriate corrections are discussed.

2.1.1 Basic assumptions

A requirement for self-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 Frank-Kamenetskii theory, [2]:

1. Heat is generated by a single 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 according to the Arrhenius equation, i.e.,

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

   where Q is the heat of reaction, ρ is the bulk density of the material, A is the reaction frequency, R is the universal gas constant, and E is the activation energy.
2. 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).
3. Heat transfer through the body is by conduction only.
4. Heat transfer at the boundaries to the surrounding is taking place through convection and radiation. The Biot number $Bi = \frac{hL}{\lambda}$ is sufficiently high so that the surface temperature of the body equals the ambient temperature (here h is the effective heat transfer coefficient i.e. including both radiation and convection, L is a characteristic length of the body, and λ is the heat conductivity of the solid material).
5. The material is assumed to be isotropic and homogeneous with constant physical properties.

The Frank-Kamenetskii parameter δ is defined by

$$\delta = \frac{\rho Q A}{\lambda} \cdot \frac{E L^2}{R T_0^2} \cdot e^{-E/RT_0} \tag{4}$$

Once the value of the critical F-K parameter (δ_c) is known from independent calculations (see Section 2.1.2), the kinetic parameters appearing in the definition of δ in equation (4) can be obtained by indirect experimental methods for any material. Alternatively the kinetic parameters could be determined by direct experimental methods. Appropriate experimental methods are summarised in Section 2.2.

A self-ignition map for the system can be provided by rewriting equation (4) as

$$L = \sqrt{\frac{\delta_c \lambda}{\rho Q A} \cdot \frac{R T_0^2}{E} \cdot e^{\left(E/2RT_0\right)}} \tag{5}$$

Equation (5) gives the critical size above which the material will self-ignite as a function of the ambient temperature. However before equation (5) can be applied corrections to the critical parameter δ_c need to be applied to account for e.g. low activation energy and finite Biot number (finite heat transfer coefficient).

2.1.2 Corrections to the critical F-K parameter

Critical values of the Frank-Kamenetskii parameter δ_c can be theoretically calculated as the limit when no steady state solution to the stationary heat conduction equation is available. Values of δ_c for different geometries are compiled in e.g. Beever [2]. The interpretation is that if $\delta > \delta_c$ then self-ignition occurs.

<u>Activation energy</u>

If the activation energy parameter ε is not sufficiently small a correction of δ_c will be necessary according to the following expression derived by Boddington [3].

$$\delta_c(\varepsilon) = \delta_c(\varepsilon = 0) \cdot (1 + 1.07\varepsilon) \tag{6}$$

<u>Finite heat transfer coefficient</u>

The assumption in the F-K theory that the surface temperature of the body equals the ambient temperature implies that the heat transfer coefficient h is very large i.e. $Bi \to \infty$. Usually this is not the case in reality and the F-K parameter need to be corrected. For finite values of Bi the following formula according to Barzykin et al [4] can be applied

$$\delta_c(Bi) = \delta_c(Bi \to \infty) \cdot \frac{Bi}{2}\left(\sqrt{Bi^2 + 4} - Bi\right) \cdot e^{\left(\frac{\sqrt{Bi^2+4}-Bi-2}{Bi}\right)} \tag{7}$$

<u>Reactant consumption</u>

In the F-K theory it is furthermore assumed that the reaction is sufficiently exothermic for negligible reactant consumption to have occurred at the point of ignition. The parameter that governs the effect of reactant consumption is the dimensionless adiabatic temperature rise, B, given by

$$B = \frac{E}{RT_0^2} \cdot \frac{Q}{C} \tag{8}$$

where C is the specific heat of the reaction products. Highly exothermic reactions have high B values, while a low heat of reaction results in a low B value. The correction to be applied also depends on the order of reaction, n, where the rate of reaction depends on reactant concentration, c, such that

$$rate \propto c^n \tag{9}$$

The parameters B and n must be determined before a correction can be made. Beever [2] lists a number of different correction formulas depending on the magnitude of the parameter B and the activation energy parameter ε. Additional information on this subject can be found in Tyler et al [5], Adler et al [6] and Carter et al [7].

Oxygen diffusion

The effects of limited oxygen diffusion on the critical conditions for spontaneous ignition have been investigated by e.g. Takeno and Sato [8]. The effects of oxygen diffusion were found to be governed by a parameter, Φ, defined by

$$\Phi = \frac{nkT_0}{c_0 Q_0 D} \tag{10}$$

Here c_0 is the ambient concentration of oxygen by volume, Q_0 is the heat of reaction by volume of oxygen, and D is the mass diffusion coefficient.

Classical F-K theory assumes that $\Phi \ll 1$. Takeno and Sato show that as Φ is increased, the critical F-K parameter δ_c increases also. From equation (10) it is then concluded that low concentrations of oxygen, low heat of reaction, and low diffusivity increase δ_c. Takeno and Sato present an analytical method for determination of $\delta_c(\Phi, \varepsilon)$.

The uncertainty of the different corrections listed above is also discussed in Beever [2].

2.1.3 Limitations of methods based on ‘classic’ F-K theory

A serious limitation in the classical F-K theory is that no account is taken to moisture transport and the accompanying phenomena of hydrolysis, evaporation and condensation. It is clear that when moisture transport is present the central assumption in the F-K theory is not always met i.e. the adiabatic region where ignition occurs might not coincide with the midpoint of the system, see e.g. Akgun and Essenhigh [9], and Krishnaswamy et al [10]. The role of water-mediated reactions under certain circumstances, are clearly evident in work by Back [11] and Gray et al [12].

It does not seem feasible to introduce corrections for moisture effects into the F-K model. Attempts to formulate a more complete theory of self-ignition can be found in e.g. Krishnaswamy et al [10] and Gray et al [12].

A description of these more advanced models will be given in a separate document.

2.2 Methods for obtaining reaction kinetics parameters

Most methods used for analysis of a materials tendency for self-ignition are based on the Frank-Kamenetskii theory. The theory was described in the previous section.

There are two possible routes to determine the material parameters needed for evaluation of the Frank-Kamenetskii parameter. One approach is to actually measure the reaction kinetics parameters, *E* and *A*, and the heat of reaction, *Q*, or take the values from literature data if possible. The methods commonly applied for measurement of these parameters are thermo-analytical methods as differential scanning calorimetry (DSC) in combination with thermo-gravimetric analysis (TGA). Beever gives some references to these methods [2]. Complications arise however when analysing naturally occurring materials with various possible decomposition routes.

The most common approach is instead to obtain groups of parameters (in equation (4)) by searching for critical behaviour in a material under controlled ambient conditions. The normal procedure is to conduct small-scale tests using a pre-heated air oven with the sample placed in a wire-mesh container in the centre of the oven. In order to comply with the condition of a high Bi-number in the F-K theory the air in the oven is re-circulated to create high convection from the sample surface. Critical conditions within the sample are determined from temperature measurements using fine thermocouples.

2.2.1 The 'Frank-Kamenetskii method'

This indirect evaluation of the Frank-Kamenetskii parameter is based on the determination of the critical temperature for a known size of a material in small-scale oven tests. If rewriting equation (4) as shown below

$$\ln\left[\frac{\delta T_0^2}{L^2}\right] = P - \frac{E}{RT_0} \tag{11}$$

where,

$$P = \ln\left[\frac{E}{R}\rho\frac{QA}{\lambda}\right] \tag{12}$$

it can be seen that a plot of $\ln(\delta_c T_0^2 / L^2)$ versus $1/T_0$ 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 F-K parameters (δ_c) for the geometries tested have to be calculated according to the principles discussed in Section 2.1.2. Thus E and QA could be extracted from such measurements.

Once these material parameters are determined from the small-scale tests it would be possible to predict the critical size for any full-scale configuration (see equation (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.

In practice the „F-K method" involves a number of separate, rather time consuming, heating tests with at least two different sizes of sample containers. Thin thermocouples are used for measuring the temperature in the oven (T_0) and the temperatures at the centre and the periphery of the sample. The critical temperature (T_0) for each size of sample container is determined by repetitive tests at oven temperatures successively closer to the critical temperature. In this way the critical value of the temperature may 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 [2]. The closeness with which the critical temperature is determined is obviously reflected in the precision of the calculation of the lumped kinetic parameters. A maximum error of ±0.5°C is recommended if data should be used for extrapolations over a wide range of sizes.

2.2.1.1 Examples of applications

There are several examples where the „F-K method" has been applied successfully for the storage safety of coal [13] and other materials liable to spontaneous combustion, e.g. animal feedstuff and milk powder [2].

Further some applications with biological materials normally used as fuels have been reported in the literature. One of the most detailed studies of the self-ignition propensity of a biofuel using the F-K methodology is that of Gray et al. [14]. They conducted small-scale experiments with bagasse using a pre-heated re-circulating air oven. Bagasse is the residue from sugar cane processing, which is used as a fuel in boilers. Bagasse is a cellulosic material, with the main components: cellulose (ca 40%), hemi-cellulose (ca 30%) and lignin (ca 20%). The bagasse leaves the production plant with high water content (ca 50% by wt) and at a temperature of 50-70°C. In these tests sieved (3 mm mesh) bagasse pit was used to get a homogeneous material.

The tests were conducted with the samples in stainless steel, wire-mesh baskets of different sizes and shapes. The sample shapes tested and discussed in the paper were cubes, and cylinders. The cubes were of the sizes 50 mm and 100 mm. The types of cylinders were equicylinders, "squat" cylinders and "long" cylinders. Diameters of the cylinders varied between 20 mm for the long cylinder and 150 mm for the equicylinder. The critical Frank-Kamenetskii parameter was calculated for these different geometries. There was no correction applied for reactant consumption, other corrections applied in the calculations can be found in the paper [14].

A series of experiments was conducted at different oven temperatures for the various geometries to establish the critical temperature in each case. Different degrees of packing and water content were further investigated.

The temperature development found in the tests might be divided into two periods. First there was a fore period during which the sample was brought uniformly to the oven temperature (T_0). During this period the sample exhibited a quasi-stationary central temperature (61-75°C) that was associated with the evaporation of water. The packing density affected the temperature attained during this period, and the duration of the period was controlled by the amount of water present. The second period was presumed to be that of self-heating due to exothermic oxidation.

The results from the tests can be summarized as follows:

- Once T_0 was achieved uniformely throughout the sample, the same rate and extent of self-heating followed regardless of the amount of water initially present.
- The critical temperature in each case was established reproducible with very high precision (±0.25 K).
- The distinction between subcritical and supercritical conditions was absolutely clear.
- The critical temperature was sensitive to both the size of the sample and its packing density.
- A higher packing density resulted in a lower critical temperature.
- A rise of approximately 4.5 K was found for the surface temperature of the sample at the critical temperature. This finding was interpreted as an indication that it might be necessary to investigate the criteria for criticality (δ_c) in some particulate or fibrous systems (the Frank-Kamenetskii assumption is $Bi \rightarrow \infty$).

The collected data from the tests were plotted for an indirect evaluation of the kinetic parameters using the Frank-Kamenetskii relationship as described in Section 2.2.1. The plot included data for all geometries investigated, both with natural packing density and greater densities. Included in the plot were also additional results from tests with woodflour (Beever, P., unpublished results).

The results from the assessment of the experimental results showed that:

- A least-mean-square line through the data points showed a good fit (including the data on woodflour), and the gradient ($15 \pm 0.7\times 10^3$) yielded effective activation energy of 125 ± 6 kJ/mol.
- Using the determined activation energy in a calculation of the critical temperature excess in the experiments conducted showed a good consistency between the experimental measurements and the theoretical interpretations founded on conductive heat transfer.
- Correction for reactant consumption did not seem to be necessary.

There are other examples where researchers have applied the „F-K method" to wood materials. One such example is the work of Jones et al. [15] were seventeen different samples of leaves, wood shavings and forest floor litter were tested. In these tests cubic steel gauze baskets were used ranging in size from 4 cm side to 10 cm, resulting in values of the critical temperature in the range 172 – 217°C. Conclusion of this work was:

- Supercritical temperature-time behaviour was clearly distinguishable from subcritical.
- The samples of both forest litter and live vegetation showed good conformity to the principles of the theory.
- Consistency was shown by each sample gathered from a small area, but considerable variation was shown by samples gathered from different areas.
- The measured activation energies for the various samples were in the range 82 – 140 kJ mol^{-1}, however, it was seen that the pre-exponential factor varied much.

2.2.2 The 'crossing-point method'

An alternative method for determination of the (lumped) kinetic parameters in self-heating substances is the method described by Chen and Chong [16], 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 material where the heat wave propagates towards the centre. Initially the centre temperature is lower than the periphery temperature (which rather quickly exceeds the ambient temperature) and a temperature in the material a small distance from the centre (a few millimetres). At a certain time the centre temperature exceeds the temperature measured a small distance from the centre. At that point where the centre temperature just exceeds the other temperature in the material, the centre temperature is defined as the „crossing-point temperature".

It has been shown [16] 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 equation for a one-dimensional slab

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + Q \rho A \exp(-E/RT) \tag{13}$$

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 (cf. the discussion in Section 2.1).

The conductive heat transfer term in equation (13) 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 more strict definition of the „crossing-point temperature". Thus at the crossing-point temperature (T_p)

$$\frac{\partial^2 T}{\partial x^2} = 0 \tag{14}$$

and equation (13) at the centre of the slab is reduced to

$$\frac{\partial T}{\partial t} = \frac{QA}{C_p} \exp(-E/RT) \tag{15}$$

which could be rewritten to

$$\ln\left(\frac{\partial T}{\partial t}\right) = \ln\left(\frac{QA}{C_p}\right) - \frac{E}{RT} \tag{16}$$

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 $\ln(\partial T/\partial t)$ at T_p against $1/T_p$.

The main advantage of the crossing-point method is, that instead of carrying out series of time-consuming experiment with several sample sizes to obtain the data for the steady-state F-K plot, each of the transient experiments with the „crossing-point method" where only one sample size is needed, in a rather short time produces a point on the plot of $\ln(\partial T/\partial t)$ versus $1/T_p$. In order to obtain several data points for the plot the initial temperature of the oven is varied.

Cuzzillo has evaluated the „crossing-point method" in detail in his thesis [17]. A detailed error analysis of the method could be found here. Cuzzillo shows several advantages of the „crossing-point method" over the standard „F-K method". First, the already discussed advantage, that almost every test results in a data point on the graph. Further, it eliminates the need to measure or estimate Bi in the laboratory tests because δ_C need not to be evaluated in these tests. 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.

The kinetic data extracted from the laboratory tests can then be used according to what was discussed for the F-K theory in Section 2.1.1. Once the kinetic parameters are evaluated by the „crossing-point method", the Frank-Kamenetskii parameter, δ , can be calculated for any geometry according to equation (4), and be compared to the condition for criticality (δ_C) of the object.

The practical experimental procedure applied for the „crossing-point method" is illustrated in the examples in the next section.

2.2.2.1 Examples of applications

One recent application of the „crossing-point method" is a study of low-temperature oxidation of coals conducted by Nugroho et al. [18]. In this study the results from the „crossing-point method" was compared with that of the traditional F-K approach and a good agreement between the methods was found. It was concluded that the crossing-point method was more convenient to use than the F-K approach, and yet sufficiently reliable for the determination of the activation energy and the heat release times reactivity (QA).

Chong et al. [19] applied the „crossing-point method" to determine the thermal ignition kinetics of sawdust. Two types of sawdust were investigated, one treated with copper-chromate-arsenic, and one untreated. The sawdust was sieved to remove any particles larger than 5 mm. The moisture contents in the treated and the untreated wood was 6% and 2% respectively.

The cubical sample containers used in the tests were made of No. 30 stainless steel mesh, and three sizes of the containers were used (5, 6 and 7 cm). The majority of the tests were conducted using the 5 cm container. It should be noted that it is not necessary to use different sizes of sample containers for the crossing-point method. The authors do not discuss the reason for using several sizes in this case, however, the results does not indicate any influence of the container size. K-type thermocouples were inserted into the sample to measure the temperature at three locations. The first measurement point was in the centre of the sample, the second at 4 mm from the centre, and the third another 4 mm away. All thermocouples were aligned in a straight line.

The oven temperature in the tests ranged from 170 to 213°C for the treated sawdust, and from 180 to 215°C for the untreated sawdust. Crossing-point temperatures for the 5 cm basket in the range between 183°C and 226°C were found for the treated sawdust, and in the range between 181°C and 227°C for the untreated sawdust. The temperature in the oven was controlled to within ±2°C of the temperature set-point. Each sample was heated until the temperature measured at the centre become higher than the temperatures measured at the other two locations. A temperature-time plot was constructed for each test. From this plot the crossing-point temperature and the corresponding rate of change in temperature were determined.

The authors report twelve tests for the treated sawdust with 5-cm cubes, one test for the 6-cm cubes, and five tests with 7-cm cubes. The graph for this data yielded an activation energy of 106±4 kJ mol^{-1}, and using a C_p of 1700 J kg^{-1}K^{-1} gave a QA value of 2.47×10^{13} J kg^{-1}s^{-1}. The activation energy for the untreated sawdust was 90±3 kJ mol^{-1} with a QA value of 3.19×10^{11} J kg^{-1}s^{-1}. The data for the untreated sawdust was based on nine tests with 5-cm cubes and four tests with 6-cm cubes. The authors further draw the conclusion that the results indicate that there was only one dominant exothermic reaction present in the temperature range. They do not, however, discuss how this conclusion can be made.

These values can be compared with e.g. the activation energy of 102 kJ mol^{-1} calculated by Bowes [1] for softwood fibres. Bowes further states that for oxidative self-heating of carbonaceous materials, a value for E of 100 kJ mol^{-1} is usually a reliable estimate. The QA values for the sawdust were however significantly higher compared to the result for softwood boards (with an E of 101 kJ mol^{-1} recalculated using Bowes data [1]) that was about 1.54×10^7 J $kg^{-1}s^{-1}$.

2.2.3 Other oven heating methods

A method often referred to as the „heat release technique" has been developed by Jones [20] and shows many similarities to the crossing-point method. This method is however not so widely used. The two methods differ only in the way the centre temperature is defined when the heat conduction term is neglected. This will result in a slight difference concerning the determination of the slope of the temperature-time curve and the corresponding centre temperature.

In the „heat release technique" the heat conduction term is neglected when the centre temperature of the sample exceeds the oven temperature while in the crossing point method the heat conduction term is neglected when the temperature difference between two neighbouring points at the centre of the sample becomes zero. At elevated temperatures the difference between these two centre temperatures can be substantial. This has led to a dispute between the inventors of the two methods but it seems that the matter has been at least partially settled as described in a note by Chen [Letter to the Editor, Fuel Vol. 79, 2000, pp 855-857].

Björkman and Keski-Rahkonen have developed a transient method in a project sponsored by Nordtest [21]. The method shares many features of the normal F-K methods, however the temperature in the oven is continuously increased until self-ignition occurs. Two thermocouples are placed in the sample, and a special computer program control the heating and calculates the self-ignition temperature in the test. This method was developed to reduce the number of tests compared to the normal F-K approach but still requires several sizes of test containers. At the best case only three measurements are needed for determining the material parameters of a material. A number of tests with oat meat and bleaching powder samples are reported. However, the results are not compared to those of other methods, and there is no discussion of possible errors.

The concept of the „Frank-Kamenetskii method" is further used as a simplified general method to assess the safety in shipping of bulk materials. The method is described in the UN "Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria – Part III" [22]. In this test method („UN transport method" for short), tests are performed to determine if a substance in a 25 mm or 100 mm sample cube, at test temperatures of 100°C, 120°C or 140°C, undergo spontaneous ignition or dangerous self-heating, which is indicated by a 60°C rise in temperature over the oven temperature within 24 hours. These criteria are based on the self-ignition temperature of charcoal, which is said in the standard to be 50°C for a sample cube of 37 m^3. The method is however used as a general method for all types of materials, and not only for charcoal. Some implications of application of the method to cellulosic materials are discussed in the next section.

2.3 Predictions on large-scale systems

All of the methods discussed in the preceding sections are design to give input data for more or less accurate assessments of storage safety of materials liable to spontaneous ignition. Below some examples are given on such analyses specific for cellulosic materials

The use of the „UN transport method" for various materials apart from charcoal has been criticized. Bowes [1] point out that the use of a single point test implies an activation-energy common for all materials to which the test might be applied, and that this in fact is 77 kJ mol^{-1}. Jones et al. [23] has shown that the activation energy for peat is 134 kJ mol^{-1} and that the use of the test method on peat would give a hugely erroneous answer, however on the safe side. Thus, the conclusion would be, that there is a need for a more appropriate general small-scale method for assessment of transport safety for peat and other cellulosic materials.

Gray et al. [14] analysed the applicability of the results from the „F-K method" for predictions of real sized stockpiles of bagasse (residue from sugar-cane extraction). They identified some major questions to be answered that would be of importance for any application with real stockpiles of biofuels.

i) Can useful quantitative prediction be made from the small-scale F-K based data?
ii) Is the simple kinetic interpretation appropriate and may fuel consumption be ignored?
iii) Are variations in thermal diffusivity to be expected?
iv) What part is played by water in the stored material?

In order to answer the first question (i) the authors calculated the maximum non-critical mass for a stockpile of bagasse at normal ambient temperatures. The stockpiles in this calculation had the form of a rectangular rod with a base width of 18 m and a height of 4 m. The prediction of critical conditions at an ambient temperature of 40 °C gave a depth (or length) for the pile of 66 m. The same calculation for an ambient temperature of 20 °C gave a depth of 276 m. Experience from actual incidents, however, show according to the authors, that these calculations vastly over-predicts the safe storage dimensions. Further, inclusion of reactant consumption in the calculations would further increase the predicted dimensions. The authors thus identifies that spontaneous ignition occurs in these types of stockpiles by mechanisms not described in the theoretical model applied (the F-K method).

On the question of the simple kinetic interpretation in the present model (ii) the authors conclude that a more complex approach has to be used. They believe that the description of the temperature coefficient for the heat-release rate by a single Arrhenius term in a wide range of temperatures is an over-simplification. They further say: "A pre-requisite for assessing critical criteria in large stock-piles is thus to determine heat-release rates by calorimetric methods at temperatures much closer to those usually encountered in normal climatic conditions."

The question about thermal diffusivity (iii) has a strong coupling to the presence of water in the material (iv).

The laboratory tests were all carried out at a temperature above 100 °C and thus the influence of water in the sample was not included these tests. Normal piles of biofuel are however not dry but have moisture content that varies within the pile. The authors summarize possible effects of the water content of the material:

- Evaporation and loss of water is endothermic and would tend to stabilize the system.
- Completely dry cellulosic materials are hygroscopic. The condensation of water vapour and evolution of its latent heat can be sufficient to cause self-heating.
- Movement of water by evaporation and condensation do not give any net effect on the system but may locally cause hot spots to appear.
- Balanced internal movement of water do not lead to identical conditions for criticality of wet and dry masses. The thermal diffusivity within wet material is greater than that within dry material. Thus the stability of the wet mass is enhanced.
- Net loss of water from the system results in a gradual decrease in thermal diffusivity (and thus stability).
- As long as water remains in the system, liquid-phase oxidation and acid hydrolysis of hemicellulose may take place, making additional contributions to the heat-release rate.

Mehaffey et al. [24] have investigated the spontaneous ignition of insulating fibreboard panels. The background was that several serious fires have occurred in Canada when insulating fibreboard panels were being transported. Critical temperatures for the spontaneous ignition of 75, 190 and 305 mm cubes of fibreboard were measured in small-scale laboratory tests employing the „F-K method". The critical temperatures found for these sample sizes were 174 °C, 148 °C and 139 °C, respectively. There are, however, relatively large uncertainties in the critical temperatures reported, as a temperature difference of 5 K was applied between successive tests. By applying the F-K theory it was determined that the critical temperature for spontaneous ignition of a 1.2 m cubical pallet of fibreboard is 104 °C and for a tractor trailer full of fibreboard 89 °C.

In the manufacturing process of the specific fibreboards studied precaution were taken against spontaneous ignition of piles of boards. The boards are produced during elevated temperatures (200-300 °C), but were allowed to cool to below 74 °C before packed in piles for transportation (after a subsequent 2-days cooling period). In spite of these efforts there had been incidents of spontaneous ignition in the transport chain.

The results from the laboratory tests evaluated according to the F-K theory could thus not identify the cause of spontaneous ignition for e.g. a 1.2 m cubical pallet. It is not realistic that oxidative reactions would be the initiating factor for the self-heating process as the critical temperature for these processes was determined to 104 °C. The authors speculates that the initiating factor for the self heating process in this case would be due to condensation of water from a humid atmosphere. Research by Back [11] demonstrated that if a fibreboard product suddenly absorbs a significant amount of water vapour from the atmosphere so that its moisture content increases by about 4.5 %, the temperature of the product may increase to 100 °C, provided that adiabatic conditions prevail.

2.4 Other small-scale methods

In addition to the small-scale methods described in detail above, there are a number of different methods for studying spontaneous ignition processes in materials presented in the literature. For most part, the application of these methods has not been widely spread for the study of spontaneous ignition or the intention of the method is in some cases for measurements of comparative nature only. These different small-scale methods are discussed briefly below.

Different calorimetric methods can be used for analysing the heat producing processes in spontaneous combustion of materials. The calorimetric methods used can be classified as isothermal, adiabatic and thermo-analytical. The thermo-analytical methods were briefly discussed above (Section 2.2) and more information is given by Bowes [1].

In isothermal calorimetry the sample material is contained at a fixed temperature and the produced heat is conducted away for quantification, most isothermal calorimeters measure thermal power. Heat flow from the sample trough a thermal resistance to a heat sink establishes a temperature difference across the thermal resistance, which after calibration provides a measure of the rate of heat generation. Rates of heat generation that can present a self-heating hazard are, however, very low and micro calorimeters capable of measuring thermal powers of order 10^{-6} W or less are required [1].

Micro-calorimeters normally require small amounts of sample, which can induce errors when working with inhomogeneous biological materials like biofuels. Sophisticated micro calorimetry equipment is at present available in Sweden at e.g. Lund University (Lars Wadsö, Institution for building technology). There is additionally another type of isothermal calorimeters that can handle larger quantities of sample materials. An example of this type of calorimeter is the one constructed by Walker and Harrison [25], which relied on the calculation of the rate of heat generation from the observed temperature rise, i.e. an indirect procedure. The calorimeter consisted of a round-bottomed glass flask (different flasks between1L to 10 L were used) that contained the sample (they worked with wool) and was immersed in an electrically heated water bath that was stirred vigorously. The flask had a sealed inlet in the bottom, which acted as a gas inlet and also provided access for a thermocouple for measuring the temperature between the centre of the sample and the water bath.

Another example of an isothermal calorimeter is the fix-bed isothermal flow reactor of Krishnaswamy et al. [26]. They conducted experiments in order to study the low-temperature oxidation of low-rank coals including measurements of oxygen consumption and carbon dioxide production. The isothermally operated flow reactor consisted of four U-shaped copper tubes (i.d. 9.5 mm) 1,9 m long. About 100 g of coal was loosely packed in each tube. The four reactors could be run simultaneously in parallel, or in series to achieve a longer reactor. The tubes were immersed in a water bath. Metered air, humidified by passage through a humidifier also immersed in the water bath, was allowed to flow through the reactors. Experiments were run at different temperatures (but within a rather narrow temperature range) and the gas after the reactor was analysed for CO_2, O_2, N_2 and CO by gas chromatography.

In adiabatic calorimetry no heat transfer is allowed over the boundaries of the experimental system, i.e. one strives to work with a perfectly insulated system. In practise, an „adiabatic" calorimeter consists of a reaction vessel (sample vessel) with walls of low thermal conductivity immersed in a bath whose temperature is controlled by a differential temperature sensor between the interior of the vessel and the bath to follow the temperature of the reaction in the vessel as closely as possible. By this method, heat losses can be kept to a minimum in relation to the rate of heat generation in the reaction vessel. Thus, the system is effectively, but not perfectly adiabatic.

Work by Vance et al. [27] can serve as an example of an adiabatic device used for studies of spontaneous ignition processes. In this work the effect of the moisture content of coal on its spontaneous ignition in oxygen was investigated. The experimental set-up consisted of a 500-mL vacuum thermal flask, a pre-heated re-circulating air oven, and a temperature control system. The flask was mounted on the inner side of the oven door and the top of the flask was fitted with an airtight Teflon plug. An inlet for pre-heated conditioning air, thermocouple for temperature measurement in the centre of the sample and gas outlet was mounted by sealed fittings trough the top plug. To investigate spontaneous heating the oven was pre-heated to 40 °C and nitrogen was flowed trough the vessel to allow stabilization of the coal. The gas supply was then switched to oxygen flow to start the oxidation process and the oven was simultaneously switched to automatic mode to follow the heating and letting the oven temperature follow the temperature of the coal as closely as possible.

Another example of studies of spontaneous heating using an adiabatic test set-up consisting of a sample vessel within an oven with a temperature controlled to follow the sample temperature is the work of Briseid and Eidså [28] on both biological and chemical processes in hay and straw.

Further, there is a standardized small-scale test method by ASTM [29] for determination of the self-heating tendency of liquid and solid chemicals. A small quantity of the sample material held within a loosely packed inert material is heated in a thermostatically controlled (fixed temperature) chamber and the sample temperature is monitored to determine the temperature rise due to exothermic reactions. Bath temperature, sample quantity, and particle size of solids are varied to obtain the relative self-heating temperature of the material. The method is, however, designed for very small amounts of samples and would not be especially suitable for studies of inhomogeneous biofuels.

3 Large-scale systems

This section contains information specifically on biofuels; types and quantities encountered in Sweden, storage configurations, and a summary of the processes that leads to self-heating and possibly can lead to spontaneous ignition. Further, information is given on practical measures that are sometimes taken today in storage to avoid degradation of fuel quality due to heating processes or in the worst case ignition of the pile of fuel. Additionally, references are given to the few large-scale tests found in the literature on self-ignition of stored biofuels.

3.1 Biofuels

Biofuels include a large group of fuels which all originates from biological materials. The division into sub-groups are based on the origin of the specific fuel, but also on production methods and fuel fraction sizes. In Sweden this group of fuels mainly include [30]: wood fuels (wood, bark, chips, sawdust, “energy-wood”), spent liquor (from pulp-mills), straw, waste and peat. Here, only wood fuels will be treated.

The total energy production in Sweden during the year 1999 was 615 TWh. Biofuels contributed with 94 TWh (15 %). Of the total biofuels consumption, 60 % was from industries, 30 % from district heating power plants, and 10 % from small-scale domestic heating. In year 2001 the production of energy from biofuels had increased to 98 TWh (16 %). The contribution from biofuels to the total energy production has increased from 9 % to 16 % between the years 1970 and 2001 [31].

3.2 Wood based fuels

Biofuels originating from forest are normally divided into wood fuels (wood, bark, chips, etc.) and refined wood fuels (pellets, briquettes). The total production of wood fuels during 1998 was approximately 45 TWh [32]. The amount of wood fuel for sale on the Swedish market during the year 1999 corresponded to 23 TWh. District heating power plants used 16 TWh of the wood fuel on the Swedish market during this year. An interesting fact is that the use of wood fuel in district heating power plants has increased by four times during a ten-year period.

The types of wood fuel used vary between different parts of Sweden. In the northern part the production consisted of 74 % sawdust and bark, whereas in the southern part 54 % consists of fuel-chips.

Refined wood fuels (pellets, briquettes) constitute only to a minor but increasing part of the total amount of wood fuels on the market. The amount of refined wood fuel was approximately 4 TWh in 1998.

A summary of quantities and some storage related data for wood based fuels is shown in Table 1 below. More details can be found in subsequent sections of this report.

Table 1 Summary of data (Sweden) for wood based fuels including some alternative storage configurations and a coarse estimate of relative risk for heat build-up in storage.

Fuel	Approx. moisture content (%)	Quantities	Storage	Risk for heat build-up
Wood fuels:				
Wood chips	50-55	Major	Outdoor or shielded, large piles	High
"Dry wood chips"	< 20	(No data available)	Outdoor or shielded, large piles	Intermediate
Sawdust	45-60	Major	Outdoor or shielded, large piles	High
Cutter shavings	15	~1000 Kton/year	Outdoor or shielded, large, piles	Intermediate
Bark	55	Major	Outdoor or shielded, large piles	High
Refined wood fuels:				
Pellets	8-10	1000 Kton/year[1]	Indoor, large amounts to small sacks	Lower
Briquettes	10	260 Kton/year [2]	Indoor	Lower
Pulverised wood	< 10	205 Kton/year [2]	Indoor, silos	Lower

[1] 1997, [2] 1996

3.2.1 Wood fuels

A major part of the information presented in this section has been extracted from the excellent report by Lehtikangas [30].

The main types of wood fuels that are stored in stacks and might impose problems with spontaneous heating are: wood chips, sawdust and cutter shavings, and bark.

Wood chips come basically from two sources. The main source is residues from timber-cutting (GROT) or alternatively from intermediate thinning. The other source is by-products from sawmills. Wood chips from GROT have moisture content of 50-55 %, which decreases during storage and wood chips from sawmills have a moisture contents of 50-55 % for fresh chips and < 20 % for dry chips.

The total production of cutter shavings is approximately 7 million m^3/year (1000 ton). 34 % of this is used as fuel. Cutter shavings have an average moisture content of 15 %, whereas sawdust which is produced in much larger quantities have a moisture content of 45-60 %.

Almost all bark is used as fuel (98%) and the total production of bark is large. The moisture contents vary over a wide range with storage conditions etc. The average value over the year is approximately 55%.

3.2.2 Refined wood fuels

The main types of refined wood fuels are pellets, briquettes and pulverized wood. These fuels are mainly produced for easier handling specifically for smaller sized plants and domestic use.

Pellets are made from various compressed forest by-products. The raw material can consist of wood-chips, sawdust, cutter shavings, bark, or not as commonly, grass or straw. Pellets are produced from the finely divided raw material that in some cases is dried (< 15% moisture) before compressed into pellets. There are approximately 25 production plants operating in Sweden (2002). The production in Sweden is approximately 1 million tons per year (2001) and the absolute main part is produced from coniferous tree (spruce and pine) Approximately 90 % is used in district heating power plants with an effect > 20 MW. In large power plants the pellets are normally finely grinded before introduced in to the boiler. A pellet has a maximum diameter of 25 mm, in Sweden normally between 6 and 12 mm. The moisture content of the end product is in the range 8-10 %. Pellets are delivered in bulk quantities, in large sacks of approximately 800 kg or in small sacks with 15-20 kg pellets.

Briquettes are defined as compressed biofuels with a diameter above 25 mm. In Sweden the normal sizes are between 50 and 75 mm. The moisture content of a briquette is approximately 10 %. The production in Sweden was approximately 260 000 tons during the year 1996.

Various wood fuels can be used in the production of pulverized wood. Storage and transport of wood powder is difficult. Large boilers often buy pellets and briquettes and convert these fuels to wood powder before combustion. The moisture content of pulverized wood is normally < 10 %. The production was approximately 205 000 tons in 1996.

3.3 Storage of wood based fuels

Microbial growth results in a deteriorated quality of the fuel (reduced heating value) and a temperature increase in the stored fuel with possible risk of self-ignition.

Mainly various funguses cause microbial degradation of the fuels. The optimal temperature span for most microorganisms is between 20 and 40 °C. Mould fungus can tolerate temperatures up to 70 °C during shorter time periods. Microorganisms cause a temperature increase in storage piles in the range of 5-60 °C. The degradation processes are promoted by smaller particle sizes of the fuel. The various types of fungus prefer different components of the wood (cellulose, hemi cellulose or lignin). The green parts of the tree (needles and leafs) have a high content of nitrogen and are therefore preferred by fungus. Further, wood chips from broad-leaf tree have a higher tendency to be affected by fungus compared to chips from spruce and pine.

Chemical degradation starts to have some influence at 40 °C, and at temperature above 50 °C these processes becomes dominating. Research has shown that oxidative processes are faster in wood containing higher amounts of lignin [33]. It can be noted that the content of lignin is higher for softwoods (e.g. 29 % for pine and spruce) compared to hardwoods (e.g. 21 % for Scandinavian birch) [34]. As the heat producing processes proceeds, heat is transported from the interior of the pile towards the surface. The centre of the stack is drying and water is transported out from the centre. If the stack is compressed, i.e., the air circulation (convective heat transfer) within the stack is low, heat build-up in the stack might cause auto ignition.

The main factors influencing the temperature in the stack are: moisture content, the size of the pile and density; more information can e.g. be found in a report by Thörnqvist [35].

There are some practical advices available regarding storage of wood fuels [30]:

- If possible store dry fuels to avoid microbial growth (< 20 %).
- Fuels of different qualities should never be mixed when stored.
- Store preferable in small piles and during a short time.
- Do not compact the material.
- Avoid metal objects in the pile.
- Build the stored material in elongated stacks with a base-width of twice the height of the stack.
- Examples of recommended stack-heights: wood chips from core wood – 15 m, GROT – 7 m, bark – 7 m sawdust – 6 m.

Storage of refined wood fuels requires a protected environment to maintain the low moisture contents and the structure of the fuel. Thus, the storage conditions for these types of fuels are entirely different from the storage of “wet fuels” as wood chips etc. Due to the low moisture content the growth of microorganisms are limited, which reduces the possibility for any temperature build-up in the stored material.

3.4 Experimental storage data found in the literature

Most studies of spontaneous ignition in storage of larger quantities of materials found in the literature is on coal. One example of such a study is the large-scale tests with coal stockpiles [36]. Investigations on self-heating were carried out with five test piles (2000-3000 tons). The effect of periodic compaction, use of a low angle slope of the side of the slope in the wind direction, pile protection by artificial barriers and covering with artificial barrier were investigated. Stainless steel probes with thermocouples and sampling ports were positioned in the piles to measure temperature and collect samples of gases (O_2, CO_2, CO and CH_4). Pile temperatures were additionally measured using an infrared camera. This work was mainly focused on the transport of oxygen in the piles, and measures to reduce the ventilation. It was found that all three methods were effective in reducing heat build-up in the piles, and thus reducing deterioration of the fuel. It was further found that it was possible with the IR-camera to detect hot spots that would have been difficult to identify with the common thermocouple technique.

The storage effects on wood chips stored in open piles have been studied by Lehtikangas [30]. In this study, piles with a height of seven meters and a base length of 60 meters were studied, both regarding the influence of density of the stack and a sheltering roof. It was found that the condition that deteriorated the fuel most, and that could promote auto-ignition was a compacted fuel stored in the open. In this type of stack, temperatures above 300 °C were found in the lower part of the stack. Pyrolysis had occurred in this part of the stack and the material was partly carbonised. Other storage studies can be found in [30] and additional information can be found in [37-44]

Generally for the storage of wood fuels, there are few problems with dry wood chips due to the low moisture content compared to fresh wood chips. Cutter shavings have also low moisture content, which implies lesser problems during storage. Sawdust has higher moisture content, and there might be problems associated with storage, however, very few studies have been made on storage of sawdust. Storage of bark, on the other hand, often gives problem due to the high moisture content and the quality of the fuel is often deteriorated during storage.

The documented knowledge on the storage effects on refined wood fuels is limited. Lehtikangas [45] reports, however, on an experimental study on the storage effects of different types of pelletised wood fuels. In this study nine types of pellets were produced on a large scale. The assortments of pellets included base materials of fresh and stored sawdust, bark and logging residues. The pellets were stored for five months in plastic bags in an unheated barn (the average ambient temperature was 0 °C). The volume of pellets stored varied between 0.7 to 1.3 m^3. The major findings from this study were:

- The moisture content of the pellets varied between 10 and 19 % after 5 month. The pellets produced from bark had a moisture content of 21 % after production and showed the highest value after storing.
- A general tendency for the moisture content of the pellets during storage was to approach the ambient moisture content (11 % in this case).
- The temperature of the fuel coincided with the ambient temperature. No tendency of heat build-up was noticed.
- Bark pellets (wet) allowed some microbial growth.
- Fine particulates (even in dry sawdust) developed local microbial growth.

However, it is mentioned in the article by Lehtikangas that fungal growth and heat build-up have been observed in pellet piles at some production plants. To minimise these effects it is important that one bring about proper cooling of the pellets after production and try to avoid fine particulates to ensure a high durability of the pellets. Finer fractions have a higher water absorption capacity, which increases microbial growth.

4 Conclusions

Methods for assessing the risk of spontaneous ignition have been reviewed. The most widely used engineering method today is the Frank-Kamenetskii method. During the years numerous applications have been published on various materials and scenarios. There is large backlog of information on how to apply the method and of data for reaction parameters obtained by the method. Traditionally this method has been hampered by the tedious experiments necessary for obtaining kinetic parameters. Recently a new improved method, the so-called crossing-point method, has been introduced which considerably speeds up the testing procedure. The Frank-Kamenetskii method is best suited for application on materials that do not have excessive moisture content and where the reactions can be sufficiently well described by a single order reaction of the Arrhenius type. Furthermore it is advisable to be able to determine the kinetic parameters and transport properties in experiments as close as possible to the real full-scale conditions expected. With all its shortcomings it is nevertheless clear that this method will still be of use also in the near future at least for preparatory purposes. However, care must be exercised when the predicted critical sizes become several orders of magnitude greater than the samples used for obtaining reaction data.

A general comment on the use of theoretical methods for calculating critical conditions for spontaneous ignition in large stock-piles is the necessity of determining heat-release rates by calorimetric methods at temperatures much closer to those usually encountered in normal climatic conditions.

A serious limitation in the classical F-K theory is that no account is taken to moisture transport and the accompanying phenomena of hydrolysis, evaporation and condensation. Furthermore, the role of water-mediated reactions that has been noticed under certain circumstances cannot be handled by the Frank-Kamenetskii method. Consequently there is a need for a more refined formulation where the energy equation is extended to include terms for the heat released by evaporation and condensation, for heat generated by a moisture dependent reaction in addition to the conventional oxidation reaction. In addition the model need to include separate equations describing the transport of water, vapour and oxygen. Such methods are available today e.g. in work published by Grey et al [12].

A further serious limitation to present engineering methods, regarding application to storage of biofuels, is that no consideration is taken to the low-temperature processes that take place before the oxidative reactions commence. Hence, a more complete model must also include the initial production of heat by microorganisms.

Also reviewed in this report are different experimental methods for obtaining reaction parameters. There are various calorimetric methods that can be used for this purpose. The calorimetric methods used can be classified as isothermal, adiabatic and thermo-analytical. Efficient methods working with small amounts of sample are thermo-analytical methods as differential scanning calorimetry (DSC) in combination with thermo-gravimetric analysis (TGA) for obtaining the reaction kinetics, and isothermal micro calorimetry for measurement of the very low rates of heat generation developed from e.g. biological reactions. It is, however, important to make certain that the small amounts of sample material used does not induce any significant errors. There are further a number of calorimetric methods (both isothermal and adiabatic) working with larger sample sizes described in the literature. Methods of this kind can be valuable in that the possibility of studying a representative sample is greater, and that results can in some cases be used to confirm results from the small sample-size analytical techniques discussed above. Furthermore, it would be possible to use results from such tests for comparison to simulations in development of mathematical models.

A survey of the potential risk for spontaneous ignition in various wood stock storages in Sweden is presented here. It is found that the largest risk for spontaneous ignition would be in storages of moist biofuel. Storage of fuel with high moisture content gives suitable conditions for growth of bacteria and fungus that produces heat in the low temperature regime. Heat produced from microorganisms is normally a prerequisite for attaining the temperature regime where oxidative processes commence. The types of biofuels that would induce the highest risk for spontaneous ignition in storage, and that can be found in large quantities in storage, would be wood chips, sawdust and bark, if using moisture content as criteria. Dry refined wood fuels as pellets, briquettes and pulverized wood would thus give a low risk for spontaneous ignition. There would, however, be a risk associated even with these fuels if not stored properly, allowing the material to get moist initiating microbial growth.

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