

## Modelling self-heating solids

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Many powdered materials slowly oxidise with time which generates heat. If in a bulk form (such as during transport or storage) then heat generation can exceed heat loss, leading to ignition. Climate control and limiting packing amounts can reduce the risk but this increases the costs for the consumer through reduced logistical options, larger shipping volumes and disposal of additional packaging.

Laboratory tests are well established to determine a safe packing size. However, they are costly, especially for new products where limited amounts of material are available. The physics of the oxidation process can be simulated provided all the material properties are known.

Can these two approaches be combined? Given the measured material properties and results of laboratory thermal stability tests how certain are the unknown material properties, such as Activation Energy, which are key to predicting the stability at real world scales?

This paper will demonstrate a method to use the results of simulation studies to guide the order and type of thermal stability tests to carry out. It represents an alternative approach to using empirical correlations and extrapolations (such as a Leuschke plot) and is particularly relevant where test material is limited. It should be of interest to those who need to make decisions about safe handling, transport and storage of materials that undergo oxidative decomposition.

### Introduction

A porous solid can undergo slow oxidative decomposition generating heat. If the rate at which this heat is transferred through the bulk to the surroundings is too low, the internal temperature can rise rapidly, causing the reaction rate to increase further, leading to thermal runaway. For a given material and geometry there exists a critical temperature [ $T_{crit}$ ] above which thermal runaway occurs.

Previous work presented at this conference encouraged practitioners to include uncertainty when making extrapolations from basket line results (Puttick, 2011). In this work we want to highlight an alternative mindset to approaching this problem. Rather than trying to get enough data to extrapolate, the focus is on getting sufficiently good estimates of the relevant material properties. These estimates can then be used in the appropriate equations [i.e. Frank-Kamenetskii] to predict the stability at real world scales.

A motivating factor behind this approach is the limited quantities of material available when assessing the safety of new chemicals. A basket line requires a minimum of 5 litres of powder and can easily use over 20 litres. Prior to the pilot plant production, only 10's to 100's of kilos of material may exist globally which is also required for toxicology, registration, formulation and field trial studies. There is an additional desire to having a good understanding of the safe operating conditions before introducing the material to pilot scale manufacture.

Using this alternative approach, the required material properties can be determined using less than 2 litres of material whilst also giving the uncertainty in the critical temperature at real world scales.

### Thermal Explosion Theory

By the time a material is considered for basket line testing, it has already been pre-screened to check it is not an explosive and demonstrated it undergoes self-heating under laboratory conditions. A full basket line is not required for shipping, instead relying on the *UN Recommendations on the Transport of Dangerous Goods*, Division 4.2 (Nations, 2003). A series of up to 4 basket tests are carried out according to a flow chart to determine the packing group. This may classify some materials into restricted pack sizes, whereas the prediction based on basket line testing may demonstrate this restriction is not required. Additionally, the Division 4.2 information may not be enough for the design of bulk storage facilities.

The Frank-Kamenetskii method is the most widely used method for determining the critical temperature. The application is described in BS EN 15188:2007, a European standard which is used commonly in industry (2007). It has been refined based on inter-laboratory testing to ensure it is applicable beyond the area of carbonaceous materials in determining safe processing, packing and transportation conditions (Kunath et al., 2013, Frost et al., 2016).

Thermal explosion theory is covered in standard textbooks (Bowes, 1984) and so the derivation will not be covered here. However, Equations 1 to 3 need to be introduced for the subsequent discussion. By varying the oven temperature [ $T_o$ ] for different fixed basket sizes [ $r$ ], the values of P and M can be determined experimentally. This is helpful as the material properties in Equation 3 may not be known.

In turn these values of P and M can be used in Equation 1 and solved iteratively for the geometry of interest to determine safe storage conditions.

$$\delta = \frac{r^2}{T_0^2} \cdot e^{\left(M + \frac{-P}{T_0}\right)}$$

Equation 1: The dimensionless heat generation parameter [ $\delta$ ] is compared to the critical number [ $\delta_{crit}$ ]. If  $\delta > \delta_{crit}$  then thermal run-away occurs (Frank-Kamenetskii, 1939).  $\delta$  has different values for different shapes [for example 2.76 for equi-cylinders, 2.52 for cubes] (2007). Where  $r$  is basket radius,  $T_0$  is the oven temperature and  $P$  &  $M$  are defined below.

$$P = \frac{E}{R} \quad [K]$$

Equation 2: The slope from the Frank-Kamenetskii plot is labelled  $P$ . Where  $E$  is the activation energy of oxidative decomposition and  $R$  is the universal gas constant.

$$e^M = \frac{E}{R} \cdot \frac{\rho Q A}{\lambda} \left[ \frac{K^2}{mm^2} \right]$$

Equation 3: The intercept from the Frank-Kamenetskii plot is labelled  $M$ . Where  $E$  is the activation energy of oxidative decomposition,  $R$  is the universal gas constant,  $\rho$  is the powder density,  $Q$  is the heat from oxidative decomposition,  $A$  is the rate of oxidative decomposition and  $\lambda$  is the internal rate of heat transfer.

Finding the critical temperatures can be a time-consuming and resource intensive activity. For the smallest basket in the line a guess is made where the critical temperature might be. After testing at this temperature, the results are used to decide whether to increase or decrease the temperature depending on how close to the critical temperature the result appears to be.

This process is repeated until two temperatures are obtained 2 K apart, which at the higher temperature the material exhibits thermal runaway, and at the lower it does not. From Equation 1 it follows that increasing the basket size will decrease the critical temperature [to maintain the same value of  $\delta$ ]. Depending on the relative sizes and activation energy of oxidation, the critical temperature for the next basket size is around 10-30 K lower.

Once the critical temperature has been located for 4 or more basket sizes, linear regression is used to obtain  $P$  and  $M$ . Historically, the average of the two temperatures at each basket size is used to fit the line [dashed line, Figure 1]. However, the critical temperature could be located anywhere in the region between the maximum stable temperature and minimum temperature where thermal runaway is observed.

Bayesian linear regression can be used to obtain the confidence intervals on the plausible slopes that could lie in this region, but this is beyond the general practitioner. A simpler approach is to fit two lines which try to join the maximum stable temperature at the smallest scale with the minimum thermal runaway temperature at the largest basket size [and vice-versa]. The lines must be drawn however so that all the results of the same type [stable or thermal runaway] lie on the same side of the line [solid lines, Figure 1].

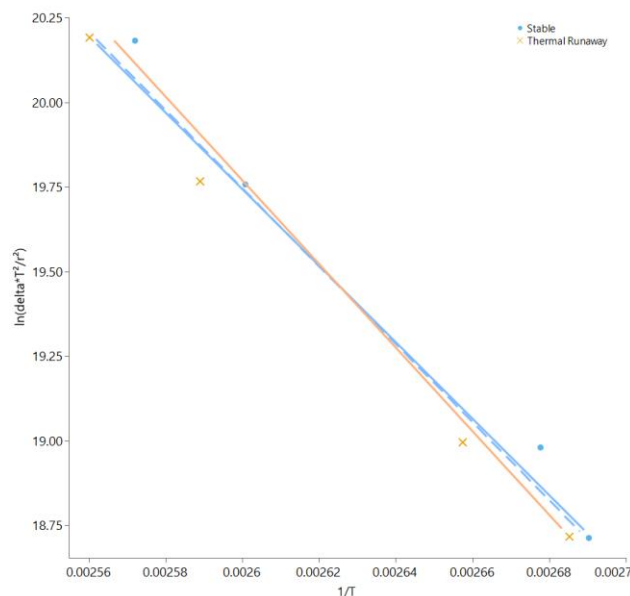


Figure 1: Frank-Kamenetskii plot of basket line results for Lignite taken from a round robin study (Frost et al., 2016). The dashed blue line is the historically used fit which considers only the maximum stable temperature for each size of basket. The solid blue line is the shallowest fit consistent with the data whilst the solid orange line is the steepest fit consistent with the data.

The equations for these two lines yield the plausible ranges for P and M. Rather than extrapolating from the laboratory data these values are used directly in Equation 1 which can be solved iteratively to obtain the critical temperature for the size and geometry of interest.

In Figure 2 the prediction uncertainties for a 1 m<sup>3</sup> package were calculated by fitting a mixed linear model to the data from multiple laboratories [pooled limit] and applying it to extrapolated predictions (Frost et al., 2016). The procedure in Figure 1 can be used to obtain the plausible ranges for P and M for each laboratory separately and then solve Equation 1 directly. This gives similar results and prediction uncertainties whilst only requiring the data from a single lab.

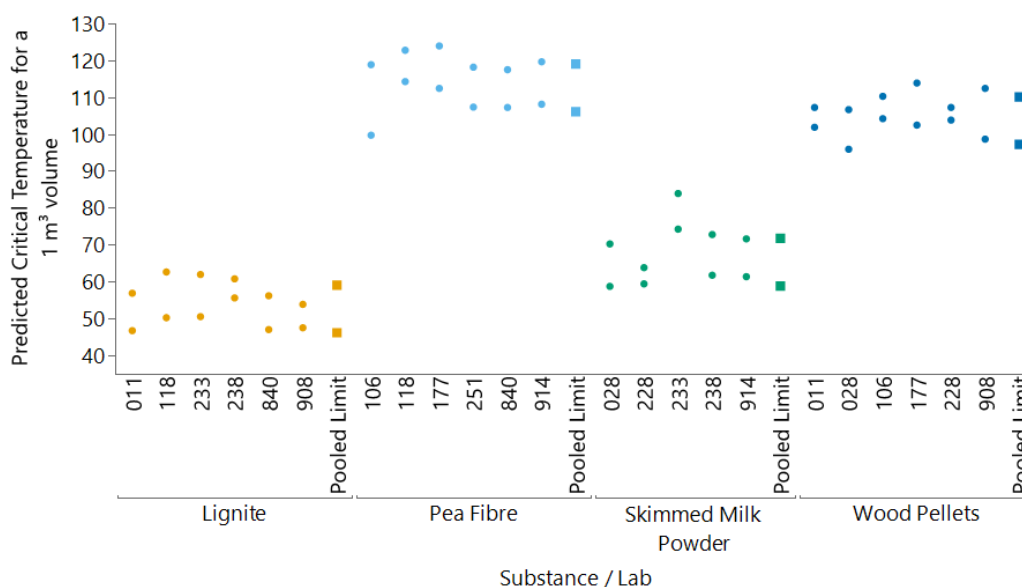


Figure 2: Comparison of plausible slope results with pooled estimates from round robin study. The pooled estimate was obtained by taking the robust mean of the laboratory maximum non-ignition results, for each basket size and extrapolating from the laboratory to real world scales using a Lueschke plot of  $\ln(V/S)$  versus  $1/T$  [where  $V$  = volume,  $S$  = surface area and  $T$  = temperature in K]. Precision parameters derived from the data via a mixed linear model were used to add uncertainty limits to the point estimate (Frost et al., 2016). Comparable results are obtained for other volumes.

### Why Use Simulations?

Since the underlying phenomena can be expressed mathematically, modern physics software has a high enough accuracy to reproduce the self-heating behaviour of materials via simulations (Azhar and Arbaee, 2018, Schmidt et al., 2003).

All simulations are biased by some unknown amount due to simplifications used in the model building process [in this case these are that the overall oxidation process follows zero order Arrhenius behaviour, material contains no trapped solvents, material doesn't melt or release vapour prior to thermal-runaway, and that material is not consumed in the thermal runaway]. Additionally, real world data is subject to noise, such that results obtained experimentally won't match the theory exactly.

Despite this, moving through the simulated chemical space and real chemical space, it is reasonable to expect the topography to be similar. The simulation becomes a map, if you knew where you were, it could guide your decision making.

Chemical space is large and whilst the terms in the thermal equation could take any number, only a limited range of values are plausible (Pearson, 2020). Some combinations of properties result in materials that are unstable at room temperature - these would never be tested. Others are explosive and screened out early in the testing process. Equally powders not observed to being self-heating under conditions that can be created in a laboratory oven are not of interest. This is summarised in Figure 3.

Rather than trying to produce simulations that match the experimental data [as has been the previous approach], this reduced chemical space is sufficiently small to allow detailed exploration. Utilizing experimental design and automation, simulations can be carried out for a range of fictitious materials which cover the entire space. There is also the potential to build surrogate or meta-models which link together the results from different simulated thermal tests. These meta-models allow generalisation to new materials which were not specifically simulated.

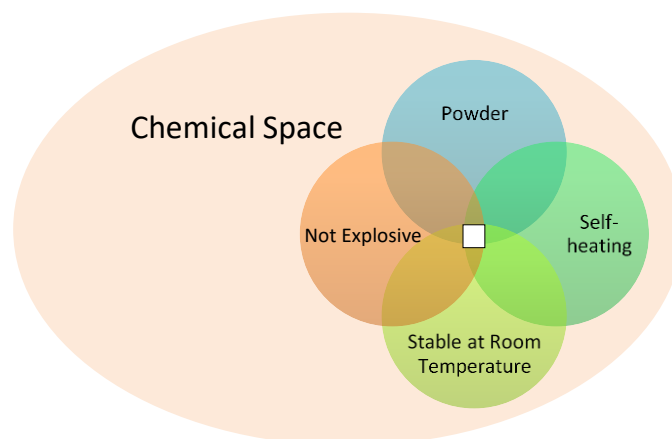


Figure 3: For a material to be subject to a basket line test, it must be a powder, stable at room temperature, not explosive and show evidence of self-heating [i.e. UN Division 4.2, Grewer-oven or similar]. The white square represents the sub-set of chemical space we wish to understand.

The results for 12,000 simulated materials from the square in Figure 3 are summarised below in terms of P and M. The space is bounded as materials to the left of the Packing Group II region are unstable at 298 K [25 °C] and materials to the right of the Not Division 4.2 region are stable to beyond 675 K [402 °C]. The top right corner of the chemical space is where most of the explosive materials are located.

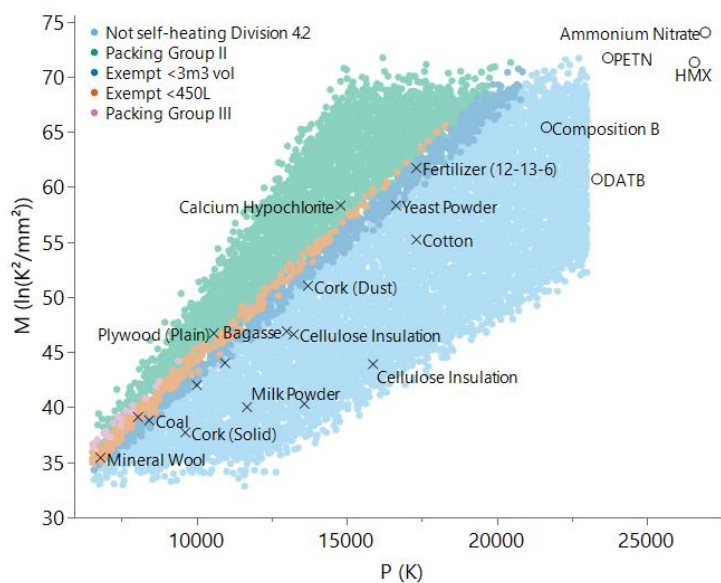


Figure 4: UN Division 4.2 results for 12,000 materials sampled from the reduced chemical space. The Frank-Kamenetskii method was used to locate  $T_{crit}$  for 25 and 100 mm cubes and thus categorise them. The M and P values determined experimentally for a range of materials have been added for context (Tamburello, 2011). Open circles indicate explosives.

### Putting It Together

The simulation results provide additional prior information to help guide the experimental programme. The activation energy, heat and rate of the oxidation is the key information gained from a basket line. The results of a thin layer or ramped thermal stability test depend heavily on the same material properties and so are strongly correlated. The correlations that exist between these tests can be estimated using simulations and the results of these meta-models then applied to laboratory data (Pearson, 2020).

Materials which undergo thermal runaway before 385 K in a ramped test or 425 K as a 5mm layer [112 and 152 °C] are likely to be in *Packing Group II*. Equally materials which exhibit thermal runaway above 500 K in a ramped test or 550 K as a 5mm layer [227 and 277 °C] are likely to be *Not Self-heating Division 4.2* [Figure 5].

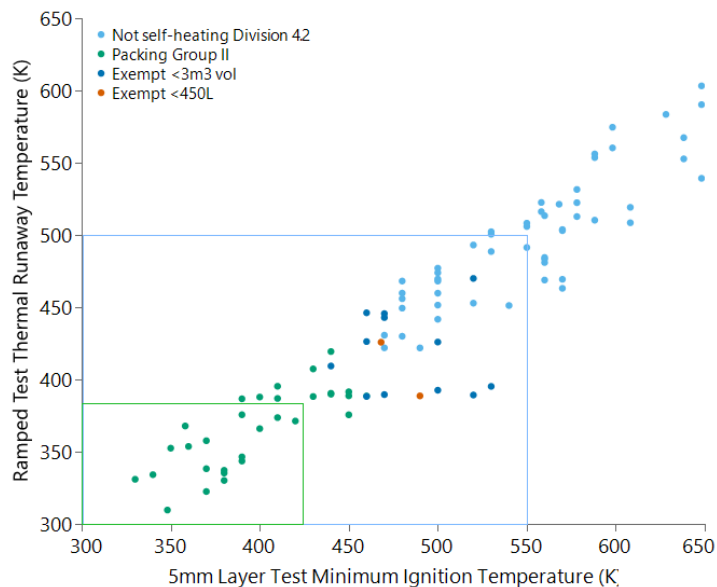


Figure 5: The simulated UN Division 4.2 results for 175 materials sampled from across the reduced chemical space. COMSOL Multiphysics® was used to locate  $T_{crit}$  for 25 mm and 100 mm diameter equi-cylinders of each material and thus categorise them. The minimum ignition temperature for a 5 mm layer and the thermal runaway temperature for ramped thermal stability test in a 50 mm diameter cylinder were also determined for each material via simulations (Pearson, 2020).

As discussed previously locating the result for the first basket in the line relies on trial and error and the number of tests needed depends heavily on how close the initial guess is. Using the correlations obtained from simulations, the results from a ramped temperature test can be used to give a starting temperature for the isothermal basket test.

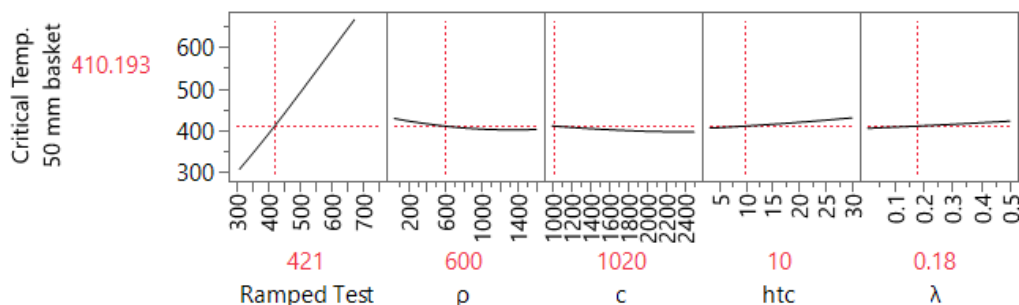


Figure 6: Predicted critical temperature for a 50 mm equi-cylinder of Lignite, using a meta-model built from simulation data (Pearson, 2020). Ramped Test and  $\rho$  are measured experimentally; heat capacity [c], heat transfer coefficient [htc], and  $\lambda$  are taken from the literature. Note the actual tests were carried out in 50 mm cubes and gave a result of 387 K [114 °C]. Variability in the exact dimensions of the cubic baskets means that predictions for an equi-cylinder are close enough to be useful.

Equally for the larger baskets, the search window is smaller but still sizeable. The results from a ramped temperature test can be used in conjunction with the results from the first basket in the line. The first basket critical temperature provides an anchor whilst the ramped test provides a direction to search in (by being a proxy for the activation energy). This helps cut down the number of tests required to locate the critical temperature at larger basket sizes.

Once the critical temperature has been located for two basket sizes, the plausible slopes approach can be used with a Lueschke plot to extrapolate to larger basket sizes [Figure 7]. The prediction window can then be used to guide further testing, rather than relying on experience or rules of thumb.

Using the plausible slope method there is no requirement to locate the critical temperature to within 2 K at every basket size. In the example in Figure 7, if the practitioner had been using the plausible slopes, the most efficient search method would have been to test the middle of the predicted range for the next size basket. This has the effect of halving the uncertainty in P and M each time.

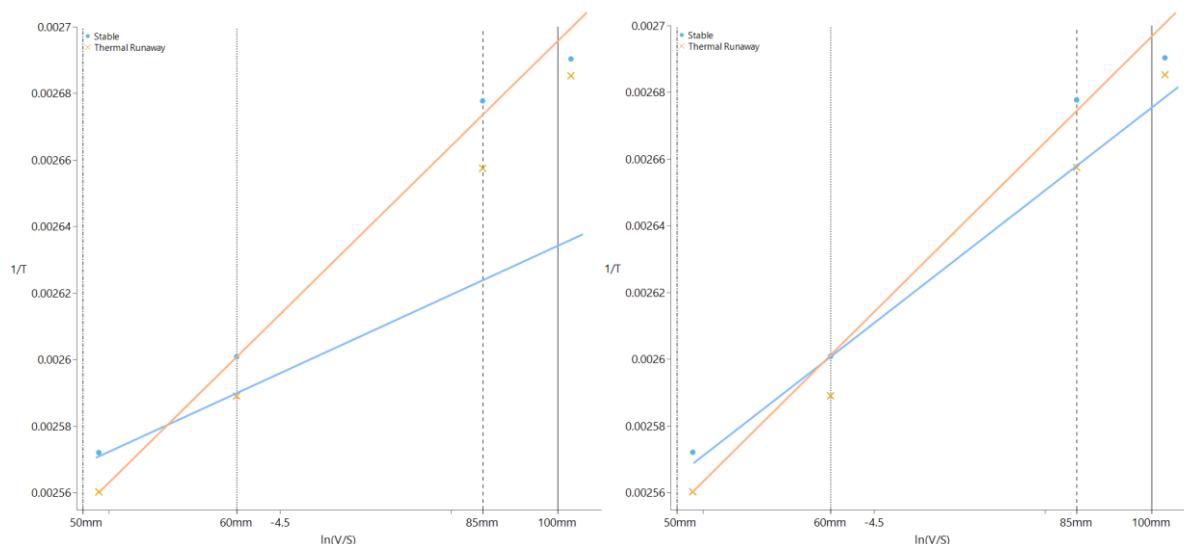


Figure 7: After using the simulation data to get a starting point for the smallest two baskets in the line, a Lueschke plot of  $\ln(V/S)$  versus  $1/T$  [where  $V$  = volume,  $S$  = surface area and  $T$  = temperature in K] can be used to extrapolate to larger basket sizes (Leuschke, 1981). Left; plausible slopes after locating critical temperature for 50 mm & 60 mm cubic baskets. Right; plausible slopes after locating critical temperature for 50 mm, 60 mm & 85 mm cubic baskets.

If material was limited, after completing one test at 85 mm, they could go straight to 100 mm using the updated range. Both these tests would have resulted in a thermal runaway if choosing temperatures based on the bisecting the prediction range. A second test at 85 mm, to obtain a result not leading to thermal runaway, would be advised to confirm the prediction range. This could be done by choosing the edge of the prediction range at 85 mm expected to not result in thermal runaway. This test doesn't improve the estimate of  $P$  and  $M$  but gives greater confidence in the results.

Finally, time and material allowing, bisecting the prediction range at 100 mm would result in no thermal runaway, halving the prediction range for  $P$  and  $M$ . Since estimates of  $P$  and  $M$  are available throughout this process [using Equation 1], the search could be terminated early. This might be triggered if the uncertainty in  $P$  reduced to less than 2400 K [20 kJ/mol] or there was strong evidence the material would be [un]stable at the size and geometry of interest.

## Conclusion

Results from ramped thermal stability tests can give estimates of key material properties. When combined with correlations derived from simulation studies it provides a map to explore the chemical space. After completing half of the basket line, the plausible slopes method [on a Frank-Kamenetskii plot] can be used to estimate the range containing the critical temperature at the geometry of interest. Subsequent tests in the line can then focus on improving the estimate to the required accuracy.

It represents a pragmatic way to apply Bayesian principles to update expectations without using arithmetic or complex modelling tools. This alternative approach allows the experimentalist to more efficiently plan future tests and adapt the programme to the available material. The critical temperature at real world scales can be reported with reasonable uncertainty limits whilst using less than 2 litres of material.

## Acknowledgements

Stephen Puttick, Process Hazards Specialist, Syngenta provided guidance on the research context, methods and data interpretation.

## Appendix

Substance	Lab	P	M	FIBC 1 m <sup>3</sup> [°C]	Ships Hold 27 m <sup>3</sup> [°C]
Lignite	11	11024	48.3	46.7	26.4
Lignite	11	13429	54.6	56.8	39.2
Lignite	118	11884	50.6	50.2	31.1
Lignite	118	15485	60.1	62.6	46.7
Lignite	233	12291	51.8	50.5	31.9
Lignite	233	15704	60.8	61.9	46.3
Lignite	238	13360	54.5	55.6	37.9
Lignite	238	14974	58.8	60.7	44.4
Lignite	840	11255	49.0	47.0	27.1
Lignite	840	13473	54.8	56.2	38.6
Lignite	908	11354	49.3	47.5	27.7
Lignite	908	12934	53.4	53.8	35.7
Pea Fibre	106	14394	52.7	99.7	78.6
Pea Fibre	106	20985	67.8	118.8	102.8
Pea Fibre	118	19152	63.7	114.3	97.1
Pea Fibre	118	23680	74.1	122.8	108.2
Pea Fibre	177	18019	60.9	112.4	94.4
Pea Fibre	177	23587	73.7	123.9	109.3
Pea Fibre	251	16783	58.3	107.3	88.5
Pea Fibre	251	21120	68.2	118.2	102.3
Pea Fibre	840	16621	57.9	107.2	88.2
Pea Fibre	840	20859	67.6	117.5	101.5
Pea Fibre	914	16773	58.2	108.1	89.2
Pea Fibre	914	21868	69.9	119.6	104.2
Skimmed Milk Powder	28	10151	44.5	58.7	35.1
Skimmed Milk Powder	28	12257	49.7	70.2	49.2
Skimmed Milk Powder	228	10487	45.5	59.4	36.4
Skimmed Milk Powder	228	11228	47.3	63.8	41.7
Skimmed Milk Powder	233	12561	50.2	74.2	53.2
Skimmed Milk Powder	233	15150	56.5	83.9	65.4
Skimmed Milk Powder	238	10841	46.3	61.7	39.2
Skimmed Milk Powder	238	13165	52.1	72.8	52.9
Skimmed Milk Powder	914	10815	46.3	61.3	38.8
Skimmed Milk Powder	914	12826	51.2	71.6	51.4
Wood Pellets	11	11830	45.7	101.9	75.9
Wood Pellets	11	12695	47.6	107.2	82.4
Wood Pellets	28	11061	44.1	95.9	69.0
Wood Pellets	28	12906	48.2	106.6	82.2
Wood Pellets	106	12678	47.8	104.2	79.8
Wood Pellets	106	13813	50.2	110.3	87.0
Wood Pellets	177	12207	46.7	102.4	77.2
Wood Pellets	177	14533	51.8	113.9	91.4
Wood Pellets	228	12384	47.0	103.8	78.8
Wood Pellets	228	13073	48.6	107.2	83.1
Wood Pellets	908	11501	45.1	98.6	72.5
Wood Pellets	908	14018	50.6	112.4	89.3
Lignite	Pooled Limit			46.1	25.9
Pea Fibre	Pooled Limit			106.1	87
Skimmed Milk Powder	Pooled Limit			58.8	35.4
Wood Pellets	Pooled Limit			97.2	70.3
Lignite	Pooled Limit			59	42.3
Pea Fibre	Pooled Limit			119	103.4
Skimmed Milk Powder	Pooled Limit			71.7	51.7
Wood Pellets	Pooled Limit			110.1	86.6

Table 1: Values of P and M used to calculate the results in Figure 2. The pooled limits are taken from (Frost et al., 2016) pages 47 and 48.

Data from (Frost et al., 2016) pages 96 to 99 was used to construct Frank-Kamenetskii plots to which the plausible slope method was applied to estimate P and M above. The thermal runaway temperatures were obtained by adding the *Difference between "Go" and "No Go"* to the reported maximum stable temperatures.

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