

BASKET LINE TESTING FOR THERMAL STABILITY AND PREDICTION CONFIDENCE

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Wire mesh baskets are used in isothermal oven tests to determine onset temperatures for solid exothermic decomposition/ignition. Using onset data from different size baskets allows extrapolation to different temperatures and scales; typically this is done using Frank-Kamenetskii or Thomas theory (Bowes, 1984) or simplified Leuschke (1975) analysis. This is all well established practice and is used to predict maximum bulk sizes for storage and transport. However, few authors document the uncertainties associated with such predictions. This is a major concern since in these cases we are concerned with extrapolations and not interpolations, and the uncertainties increase with distance from the measured data. It is also common practice to average the highest no-go temperature with the lowest go temperature to give the onset. This has the effect of throwing away information about the uncertainty since the two data points are effectively the low and high estimates respectively for the onset temperature.

This paper looks at extrapolation and uncertainty using standard statistical methods on both Frank-Kamenetskii and Leuschke style analysis. Extrapolation and uncertainty is also discussed in the context of the single point measurement transport classification tests associated with self-heating substances covered Division 4.2 of the UN (2009) regulations.

BACKGROUND

This work was in part triggered by some work by members of CEN/TC 305 WG1¹ on EN 15188 (Determination of the spontaneous ignition behaviour of dust accumulations). The standard was published in 2007, but the last inter-laboratory test before publication failed to achieve reasonable reproducibility between participants (the test results are shown in Figure 1). Syngenta and BAM have since carried out a joint programme to identify and understand some of the key experimental variables and improve reproducibility. One key question that arose from the work was how we measure whether results are significantly different. The other motivator has been concern around safety factors and extrapolated data, and can be phrased as “How confident or cautious should we be?”

SELF-HEATING AND SELF-IGNITION

Self heating is a well known phenomenon where accumulations of material release heat, increasing the local temperature, which in turn increases the rate of heat release. This process continues until an equilibrium is reached between heat generation and heat transfer away, at which point there is a peak in the material temperature above the prevalent ambient conditions. If a critical ambient temperature is exceeded no equilibrium will be reached and a thermal runaway will occur which can result in self ignition. The critical ambient temperature is dependent on the size

and shape of the accumulation and will decrease with increasing volume. This process has led to a number of incidents in transport storage and processing of various materials, some examples of which can be found in Bowes (1984) or the archives of the Fire Research Station. Literature searches will obviously find other examples. It is relevant to the setting of packing sizes for transport and storage, as well as safe conditions for processing such as drying, and maximum temperatures for packing off material.

Thermal explosion theory allows analysis of the problem or at least the derivation of kinetics from experiments and is covered in a variety of standard text books such as Drysdale (1998) and Bowes (1984). For accumulations of solid materials the Frank-Kamenetskii model is commonly applied; this assumes the main resistance to heat transfer is due to conduction in the solid, so there is a temperature gradient within the solid, but none at the boundary between the material and ambient conditions (infinite Biot number conditions). Thomas (1958) made modifications to this analysis to correct for conditions where there is also heat transfer resistance at the wall.

EXPERIMENTAL DETERMINATION

Powdered materials are packed into mesh baskets exposed to different constant oven temperatures. If ignition is observed the temperature is reduced in the oven and the experiment repeated until no ignition is seen, or conversely if no ignition is seen then the experiment is repeated at a higher oven temperature. The arithmetic average of the oven temperature for just critical (i.e. ignition) and just sub-critical conditions is often taken as the self-ignition temperature (Bowes and Cameron, 1971). Thermocouples are placed in the oven to monitor ambient oven temperature, in the centre of the sample to monitor for self-heating

¹CEN/TC 305 is a technical committee titled “Potentially explosive atmospheres - Explosion prevention and protection”, and WG1 is the working group responsible for writing and maintaining standards associated with “Test methods for determining the flammability characteristics of substances”

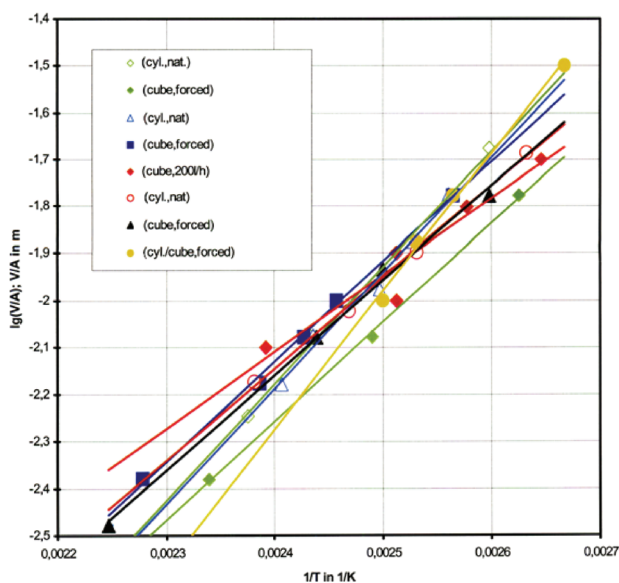


Figure 1. Previous Round Robin data for development of EN 15188

behaviour and runaway. Other thermocouples are often added at the sample edge and distributed across the cross section.

Once critical conditions have been determined for one size they can be repeated for a larger size of container. With several determined points one can then plot them on a graph for further analysis. Repeating the tests like this is often referred to as a basket line or the Bowes-Cameron Cage tests.

Since thermal explosion theory is covered in standard text books the derivation will not be covered here. Using Frank-Kamenetskii's model the dimensionless parameter δ can be defined where

$$\delta = \frac{E}{RT_A^2} \cdot \frac{r^2 Q \rho A}{\lambda} e^{-E/RT}$$

This parameter has different values for different shapes (for example 2.76 for equi-cylinders, 2.6 for cubes).

An Arrhenius plot of reciprocal absolute temperature ($\frac{1}{T_A}$) vs $\delta \frac{T_A^2}{r^2}$ can be made, the gradient of which will be $\frac{E}{R}$, hence we can have an estimate of the activation energy.

Leuschke (1975) empirically related $\left(\frac{1}{T_A}\right)$ to $\log\left(\frac{\text{volume}}{\text{surface area}}\right)$ for equi-cylinders of cork dust and found that this gave a reasonable fit for other shapes plotted on the same chart with plus/minus 5 degree temperature bands.

Examples of these two plots can be seen in Figures 2 and 3 using some of Bowes and Cameron's (1971) data, although not a complete set of the data, rather an abbreviated selection that appears in Drysdale. There is reasonable agreement between the two plots; certainly they cross the 27 m³ lines at predicted temperatures around 33°C.

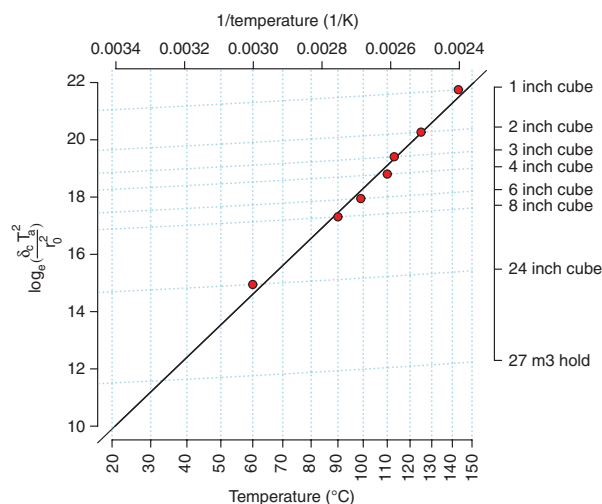


Figure 2. "Frank-Kamenetskii" Plot of Bowes and Cameron's data (27 m³ intercept at 33°C)

DISCUSSION AND CRITICISM OF REGRESSION ANALYSIS EMPLOYED

For linear regression the response variable is fitted as a function of the explanatory variable. Conventionally when plotted y is the response variable and x , the explanatory variable. This is convention rather than a requirement, but breaking convention has implications and requires extra care. On spreadsheet graphs adding a trend line will automatically use $y = f(x)$. When using a statistical package such as employed here (R Development Core Team, 2009) the user can specify which is response and explanatory variable for fitting, and plotting independently, but may need to transform some of the model parameters such as slope for use in plots. The predicted line will probably be similar, but will not be coincident if the variables are reversed and y is used to predict x .

In the two previous plots the plotted x variable has been reciprocal absolute temperature, however this is actually the response variable. Fixed size baskets are placed in an oven at different temperatures to measure the response, which technically is a sample over-temperature above the oven temperature. Ignition is commonly taken to be an over-temperature of more than 60 K, although for most materials it will be very clearly defined as a thermal explosion of hundreds of K above the oven temperature, with the maximum subcritical value being only a few tens of K. In Leuschke's paper this is plotted correctly with reciprocal temperature as the y axis response variable. It has been convention in the author's laboratory, and elsewhere to plot reciprocal temperature (with a human readable temperature scale) on the x axis, this then leads to expectations of being able to easily read the chart in this manner. Frank-Kamenetskii plots also use reciprocal temperature on the x -axis, probably because the slope can be used for an estimate of activation energy.

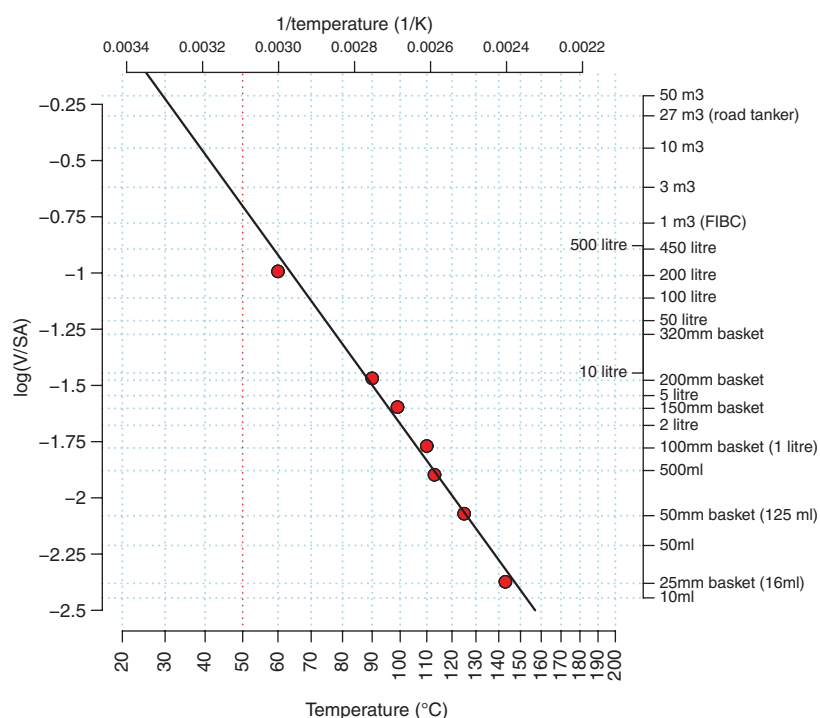


Figure 3. 'Leuschke' plot of Bowes and Cameron's Data (27 m³ intercept at 33°C)

What we are looking for is the critical ignition temperature which, as noted above, is conventionally taken as the arithmetic mean of the lowest determined ignition temperature, and the highest non-ignition temperature. However, it would serve us well to think of these as high and low experimental estimates of the actual critical ignition temperature, and use them as individual points. As such they then give us a measure of the variance of the ignition temperature. This variance will depend on the resolution with which we determine these values i.e. how close the highest non-ignition is to the lowest ignition temperature. Bowes and Cameron quote ignition temperatures as being ± 5 K or better, Cameron and MacDowell (1972) quote ± 3 K or better whereas Gray *et al.* (1984) claim to have determined this to within 0.5 K. Ramírez *et al.* 2010 claim ± 5 K, but since they tabulate their data it can be seen that the range 5 K which would mean the quoted values should be ± 2.5 K. This range will have implications on the confidence that can be claimed for the regression line. There is further variance that can be attributed to these points which relates to experimental variability. This is associated with the fundamental uncertainties in measurements and dimensions, and the treatments which may introduce slight variations in the final outcome (for example packing density). Methodologies for predicting and analysing the variance due to these contribution can be found in the Eurachem (2000) guide. The variance which becomes visible by using both the high and low estimates of ignition temperature reinforces the point that this is the correct response variable. Temperature appears on both axes in a Frank-Kamenetskii

plot which confuses the issue somewhat, but the variability is most visible in reciprocal temperature.

Least squares regression also assumes constant variance across the range. This is actually unlikely to be achieved in practice because

- i. Even if the resolution of ignition temperature is kept constant across the range this will not appear constant when using reciprocal temperatures
- ii. Perhaps more importantly the resolution will be narrowest for smaller test volumes simply due to the test duration and sample required meaning more tests can be carried out. This means larger test volumes will generally have a higher variance

It is possible that we should be considering weighted regressions, although this is outside the scope of the current paper.

CONFIDENCE AND SAFETY FACTORS

Bowes and Cameron performed a sensitivity analysis on the parameters based on their understanding of the variability of the data. Cameron and MacDowell in looking at various carbons used a safety factor choosing 50°C as the critical cut off temperature for a 27 m³ stow based on an assumed 38°C in the stow. Lueschke looked at the sensitivity of the regression slope by drawing lines through a high estimate of ignition through a low estimate of ignition at the other end of the size range of baskets, and vice versa. This gave possible bands either side of the predicted value. This

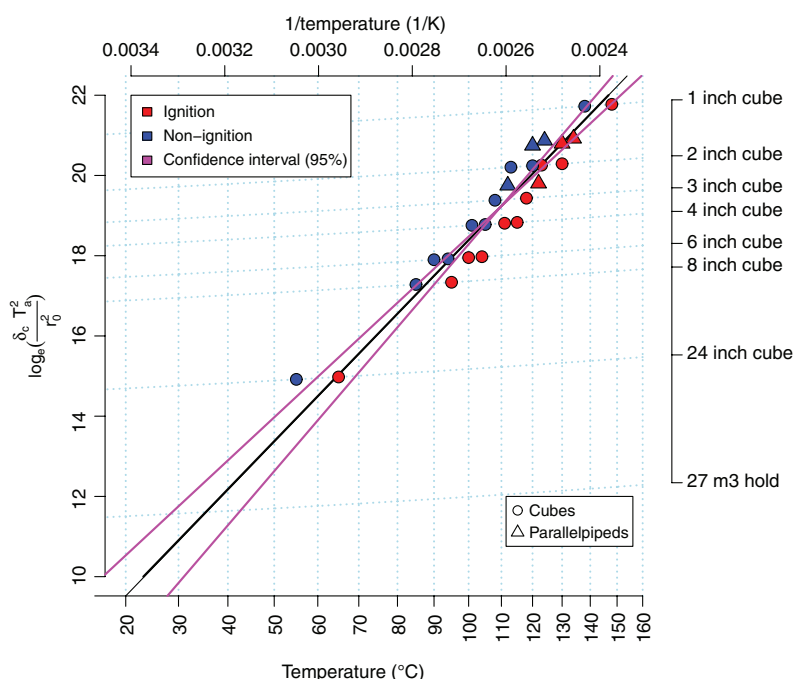


Figure 4. Bowes and Cameron Data showing best fit line with the lines of $\pm 95\%$ confidence on the slope

paper will use standard statistical methods to look at confidence intervals.

For a slope the confidence interval can be given by

$$\beta \pm t \times \text{standard error of slope}$$

where t is from the Student distribution, and depends on the width of the confidence interval required, and the number of degrees of freedom (i.e. how many data points are available minus the number of fitted parameters). An example of this is shown in figure 4 using Bowes and Cameron’s data (assuming there is a 10 K range on all the quoted ignition temperatures in their paper – the paper says ± 5 K or better, so some intervals will be wrong, but it will serve to illustrate the point). This leads to a 95% confidence interval on the slope of (90.3, 113.4) kJ/mol.

Alternatively we can use the prediction interval to give us a range where new data may be expected to lie. This is defined in the equation below

$$\hat{\alpha} + \hat{\beta} \pm t \sqrt{\frac{s^2(x_0 - \bar{x})^2}{S_{xx}} + \frac{1}{n} + l}$$

And involves the t statistic again, the number of points and the variance. An example of this for the same data set is shown in Figure 5. This shows how broad the prediction interval can be. For a 27 m³ stow this gives us an interval of about 24 to 47 °C for possible critical temperature.

Any true statistician will throw up their hands in horror at the thought of making predictions beyond the

scope of the available data, but that is exactly what we wish do. The prediction interval gets wider as we extrapolate away from the existing data reflecting increased

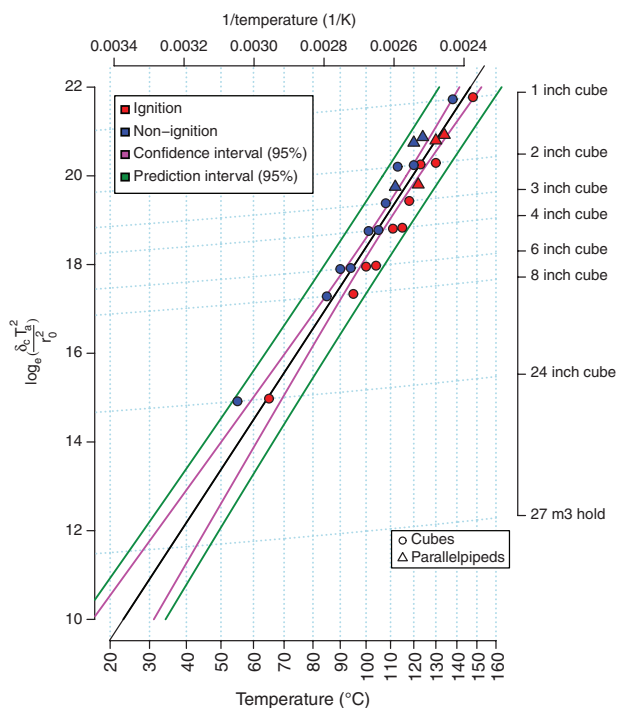


Figure 5. Bowes and Cameron data for activated Carbon showing the prediction interval for new data

uncertainty, although this is not particularly clear from this particular plot. This gives us a formal statistical method for looking at the kind of safety factors which we should employ. Even so there is still a health warning surrounding extrapolation, but we can alternate our scientific and statistical hats to help us manage this.

There are a variety of statistical tools for analyzing linear regressions in particular looking for potential outliers and points that have high leverages (i.e. points that individually make a significant contribution to the slope) and we shall use a couple (Kerns, 2010). Cook's distance is plotted in Figure 6 and one point stands out clearly. By looking at the values of the diagonal of the 'hat matrix' for leverage two values stand out, one of them is the same point as stands out in the Cook's distance plot and both of them correspond to the 24" (61 cm) basket. This is the largest basket tested, it is also the nearest size to the volumes of interest for extrapolation so arguably should be the most important point for our prediction. The reported critical temperature for this basket is 65°C, which is well below the 90°C reported for the next nearest size. All other points are above 100°C. It is common in this form of testing for all points to be above 100°C which means at ambient pressures that water effects (heat transfer and sorption generally, although possibly reaction solvent) will not occur at test temperatures, although they may be relevant. Bowes and Cameron acknowledge that water probably plays a role at ambient temperatures in this case. Griffiths *et al.* (1985), also discuss this issue and in the case of their paper, despite corrections allowing for variable non-infinite Biot number, failed to extrapolate correctly to safe pile sizes for cellulosic material.

Returning to Bowes and Cameron's data it is interesting to perform the regression without the data from the 24" basket, this is shown in Figure 7. This plot confirms the

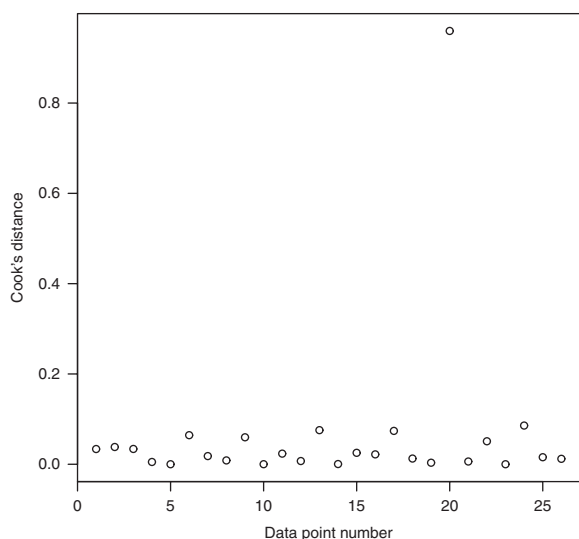


Figure 6. Cooks distance – an example of techniques looking at outlying or influential points

interpretation of the statistical tests, these points are very significant to our overall result, and the extrapolation from the other points fails to predict them. The best fit line falls on the unsafe (high) side of our lowest ignition temperature and the highest non ignition temperature does not even fall within the prediction interval. In this case it is highly likely that these are the actual extremes recorded by Bowes and Cameron due to the length of time and quantities of material required for this scale of test. At 27 m³ the predicted critical temperature is about 42°C which is above the assumed temperature range for the stows, although the prediction interval covers the temperature range for the stows. Without plotting the prediction interval this gives us an unsafe prediction, and it is worth noting that it is very rare for laboratories to carry out experiments at anything approaching this scale.

Our conclusion here should be that the 24" cube data probably do not fit with the rest of the data from a regression point of view, but that they are probably more important to us than most of the rest of the data. Without sufficient other data below 100°C to perform a regression on a second line the data should be left in our initial regression, and the prediction interval used.

One suggestion for applying a safety factor is to only use the highest non-ignition data when quoting data. This on the face of it has some appeal and is consistent with the reporting of values for flammability limits in European standards. For a single point value measure this would be

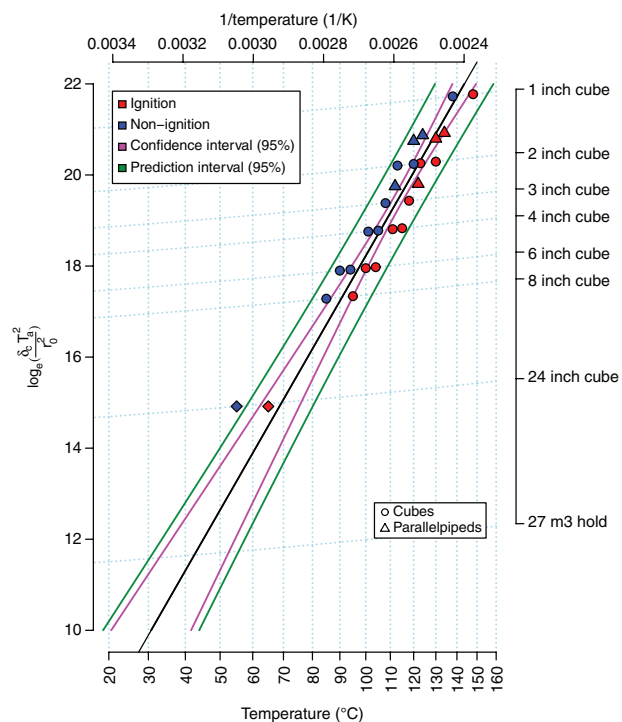


Figure 7. Regression on Bowes and Cameron's (1971) data excluding the largest basket size tested showing a failure to predict on the unsafe side

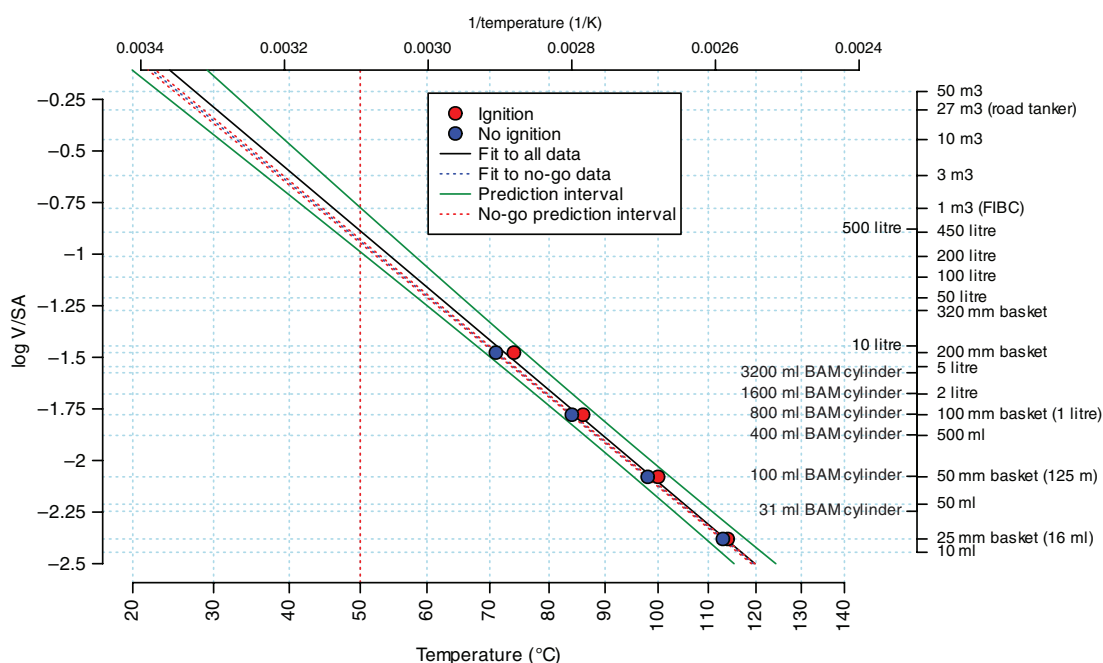


Figure 8. Plot showing fits and prediction intervals using full highest non-ignition to lowest ignition compared with just using highest non-ignition data

a legitimate approach erring on the safe side. For a point used with others in a regression this has effectively thrown away data about the variance, which would then lead to the calculation of a prediction interval that is much narrower than the true prediction interval (see Figure 8 for an example). Even without calculating the prediction interval the regression line could be less safe than expected at the range of interest, if a combination of points included the highest possible non-ignition temperature for the largest test volume, and the lowest possible non-ignition temperature for the smallest test volume.

TESTING FOR TRANSPORT CLASSIFICATION

The UN manual of tests and criteria (2009) allows for several single point tests in 100 mm side cubes at 140°C, 120°C and 100°C, and a 25 mm side cube at 140°C. See Figure 9 for graphical illustration. Failure to ignite at 140°C in a 100 mm basket leads to exemption from 4.2 classification (this assumes an extrapolation to 27 m³ at 50°C). Ignition at 140°C classifies the material. Ignition in a 25 mm basket at this temperature classifies the material as packing group II, otherwise the material is considered to be packing group III. If the material fails to ignite at 120°C in a 100 mm basket it may be exempted from classification provided that pack size does not exceed 3 m³; or if it ignites at this temperature but fails to ignite at 100°C then it can be exempted provided that packsize does not exceed 450 litres.

The origins of this testing is in the follow up to Bowes and Cameron's paper (which covered the testing of

a carbon following self-ignition incidents in ships' holds), by Cameron and MacDowall (1972), who tested a series of 10 carbons. Two of the carbons failed to meet the 50°C criteria, although we should bear in mind that this 50°C represents a safety factor over the assumed maximum of 38°C in a ships hold. The other carbons all had ignition temperatures which exceeded 140°C for a 10 cm basket. This test was originally for carbons, but has grown to cover all materials.

Jones (2000) has criticised the single test point nature of this test because it assumes an extrapolation at assumed activation energy. We will look at samples 2 and 9 near the classification temperature but still deemed to be safe. Sample 9 has a best fit at 27 m³ of just over 60°C (agreeing with the data quoted in the paper) and a prediction interval of about 50 to just over 70°C. Comparing this with the Bowes-Cameron data leads us to expect that a predicted temperature of 50°C derived from a reasonable set of data will probably have a prediction interval above the 38°C assumed maximum in a hold. Although this author's regression of sample 2 does not give the quoted 56°C (or 55 from the table) but rather 42°C, so this would cast doubt on the validity of the 140°C test even for carbons, although it is possible the data tabulated contains an error. Looking at the data in a different way the best fit slope for sample 9 gives an activation energy of about 93 kJ/mol and that for sample 2, 76 kJ/mol.

Figures 10 and 11 show data for other materials where the linear extrapolations do not work and the curvature of the plots is towards the hazardous side. One of these is a

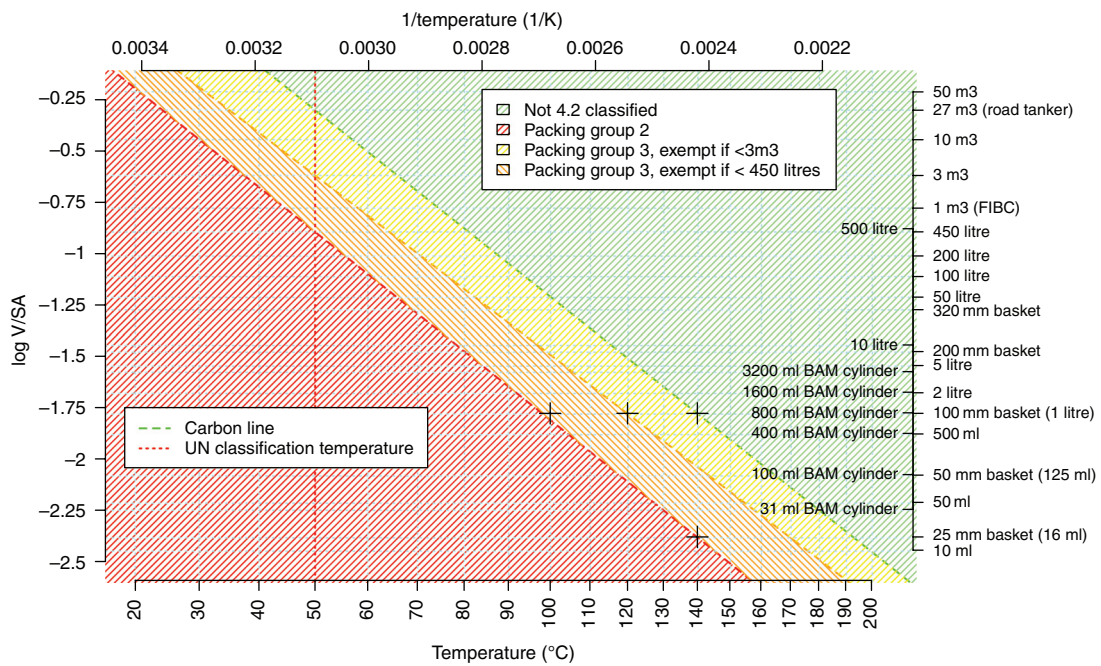


Figure 9. Illustration of the single point tests from the UN manual of tests and criteria and the UN classifications

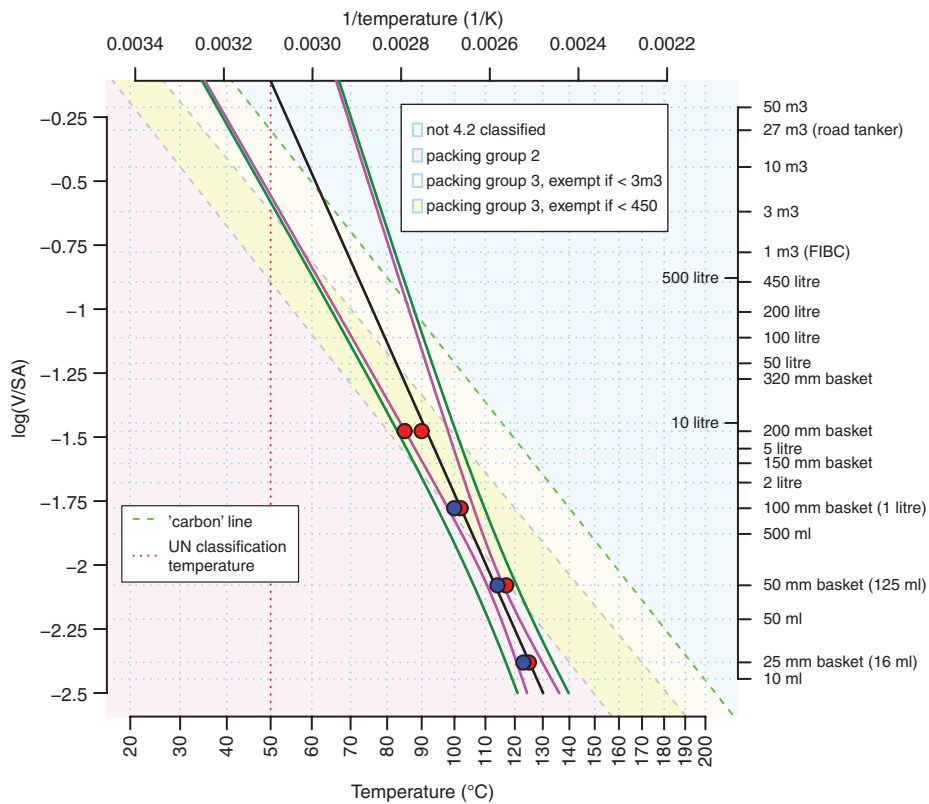


Figure 10. Basket line showing curvature, and no non-ignition for largest sample

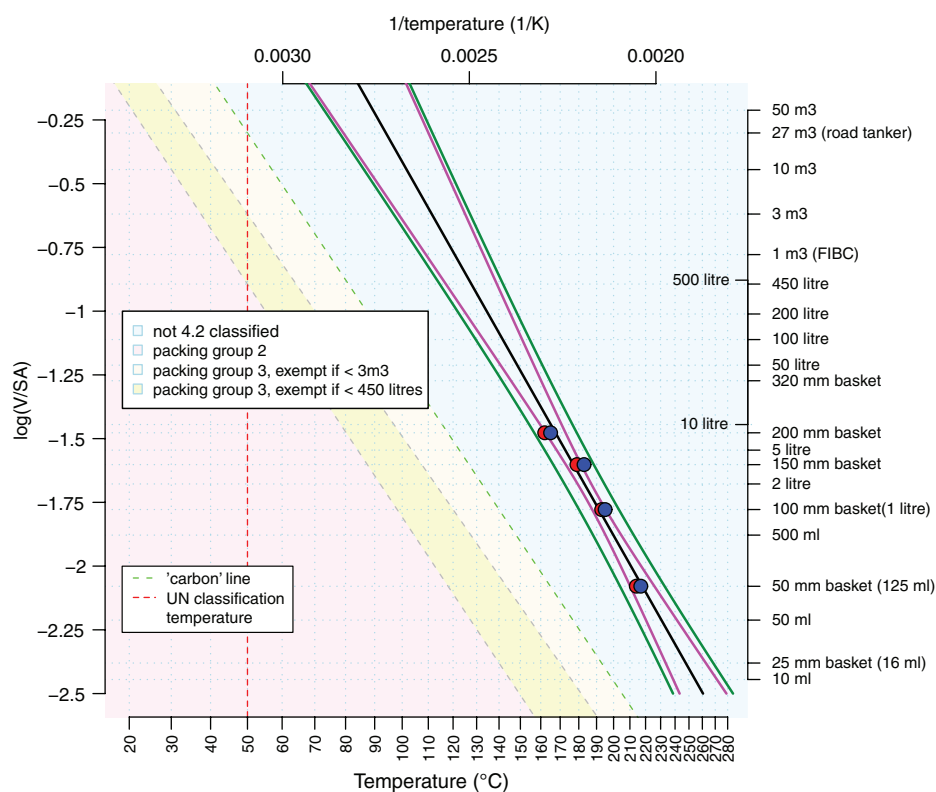


Figure 11. Basket line showing curvature – regression is likely to be a poor fit if the curvature continues and it is not just experimental variation

carbon which shows that even for a relatively simple material thermal explosion models may not be applicable. The other material shows much more complicated multistep decompositions, as the volume tested increases it looks as if the data points are curving towards an even more hazardous region. In fact at lower temperatures the behaviour changes altogether and the major exotherm does not occur, but to handle this safely requires in-depth analysis of the thermal properties and understanding of the chemistry of the decomposition. Simple testing cannot give this insight.

LIMITATIONS OF ANALYSIS

This particular statistical approach is suitable for the experimental data to which it is applied, because the variance is derived from the random variation and difference between the lowest ignition temperature and highest non-ignition temperature of specific experimental data sets. Experiments carried out in different types of ovens (i.e. natural convection) give different experimental ignition temperatures. These differences may be scale and sample dependent, since they are largely related to the Biot number and surface heat transfer. Corrections may be necessary to make data determined in different configurations comparable. Work on EN 15188 is focussing on improving consistency between laboratories.

CONCLUSIONS

Standard statistical tools can help give a feel for the uncertainty in predicted values and give a feel for appropriate safety factors. Tests such as the UN transport classification have some assumed safety factors built in to them (although the key assumptions on hold temperatures could be revisited to reflect modern shipping patterns, and locations where containers may be stored for extended durations). The simplistic notion of the single point test is potentially hazardous.

For other uses such as safe packing off temperatures and bulking of warm material on chemical plants it is well worth using prediction intervals to help set safety factors.

Other statistical tools can help us to examine the linearity of the plot, and look for 'problem' points which should make us think about the physics, or changing chemistry of what is happening.

One key problem area is the relevance of testing well above ambient temperatures and usually above the boiling point of water. This means that extrapolations are being made over long ranges away from where the data has been gathered. The physics and chemistry may be very different at processing or ambient conditions, possibly on the hazardous side. Water can play a role in heat transfer and physical and chemical processes that can generate heat at ambient temperatures. Gathering data at temperatures where water is not present can put us into unsafe

territory. Heat release or other methods may be necessary to look at the kinetic parameters at the temperatures of interest since increased basket sizes are unlikely to be practical.

There are other potential issues particularly with complex, multi-component materials such as formulations. Issues include multi-stage decompositions that cannot be adequately approximated by lumped parameters and melting behaviour. These will be covered in later publications.

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