Using JMP® Simulation Tools to Prevent Supply Chain Fires

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Abstract

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.

Using JMP® we will demonstrate how to combine these two approaches to reduce the amount of thermal stability testing required: 1) generate a constrained spacing-filling experimental design; 2) control the simulation software [COMSOL Multiphysics®] via JMP Scripting Language [JSL]; 3) build meta-models; 4) simulate the outcome for new materials.

By obtaining estimates of different material properties with each test, the prediction uncertainty can be updated to suggest the range of suitable packaging given the available data. This enables a data driven approach to the selection of laboratory tests.

Introduction

Many materials (raw materials, final active ingredients, granular formulations & seeds) have the potential to slowly oxidise which generates heat. If the total amount of material is small, heat loss from the pack surface exceeds any heat generated by oxidation. When the material is packed in bulk, heat transport is limited by the internal rate of heat conduction. The temperature at the centre of the sample can exceed the ignition temperature of the material resulting in thermal run-away. This is illustrated in Figure 1.

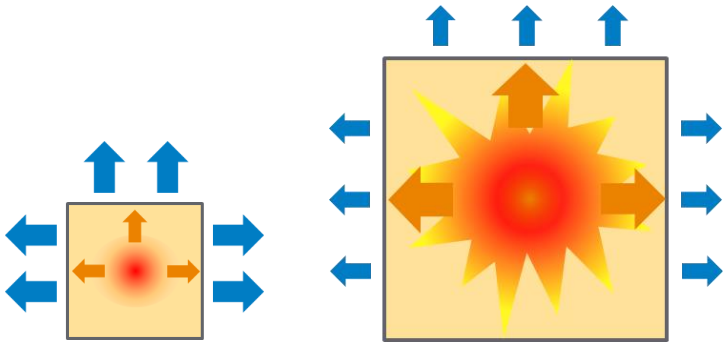

Figure 1: Effect of packing size on heat loss. Left, the surface area is high relative to the heat generated by oxidation, so heat loss exceeds heat generation and the pack temperature remains stable. Right, the heat generated by oxidation is limited by internal heat conduction. This causes the temperature at the centre of the pack to rise, which increases the rate of oxidation, generating even more heat which produces a thermal run-away to ignition.

The UN *Recommendations of the Transport of Dangerous Goods* states that substances for which the spontaneous combustion temperature is higher than 50 °C for 27 m^3 should not be classified in Division 4.2 (Nations, 2003). The classification of a flammable solid determines the types and sizes of

packaging which can be used for shipping. Tests are carried out at small scale [16 & 1000 ml] and the results are extrapolated to 27 m^3 based on the assumption that the oxidation process has the same activation energy as carbon [97.4 kJ/mol] (Bowes and Cameron, 1971).

Materials can be classified as not in Division 4.2 for transport but still spontaneously combust. Failure to understand this behaviour has serious consequences which were experienced with the widespread adoption of wood pellets as a renewable fuel (Hedlund, 2018, 2004).

Figure 2: Consequences of Oxidation. Left, Silobrand Härnösand [8-13 Sept 2004]. Right, Hallingdal Trepellets [10 July 2010]. These are just a couple of the reported incidents that occurred in wood pellet silos where self-heating lead to ignition.

An alternative approach to such extrapolations is possible if all the material properties are known. Equation 1 is comprised of heat dispersion, heat movement and heat generation terms and describes the self-heating physics. With the appropriate software this equation can be solved with time to determine if thermal run-away occurs (Azhar and Arbaee, 2018). This is computationally expensive and requires a good idea of what the critical temperature is.

$$\boldsymbol{\rho c \cdot \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \rho Q A e^{-\frac{E}{RT}}}$$

Equation 1: Heat equation describing the self-heating phenomenon. R is the gas constant, 8.314 $J \cdot K^{-1} \cdot mol^{-1}$, t is time in seconds, and the other terms in the equation are defined in Table 1.

Fortunately, Equation 1 can be approximated to give one which can be solved iteratively (Frank-Kamenetskii, 1946). Equation 2 bifurcates at the critical temperature and has no solution. Different values of T_O can be entered into Equation 2 which will give values much larger or much smaller than δ_{crit}. A hunting procedure can be used to find the pair of temperatures that bound δ_{crit}. The lower of two temperatures is the maximum non-ignition temperature for a material of the given size and properties.

$$\boldsymbol{\delta_{crit} = r^2 \cdot \frac{\rho Q A}{\lambda T_o} \cdot \frac{E}{R T_o} \cdot e^{-\frac{E}{R T_o}}}$$

Equation 2: Frank-Kamenetskii model (Frank-Kamenetskii, 1946), where the dimensionless parameter δ has different values for different shapes [for example 2.76 for equi-cylinders, 2.6 for cubes] (Boddington et al., 1971).

The critical value for equi-cylinders is defined in Equation 3 which accounts for surface effects at small scales.

$$\delta_{crit} = \frac{0.8047}{0.2830 + \frac{0.7292}{Bi}}, \; Bi = \frac{htc}{\lambda} \cdot r$$

Equation 3: The Thomas approximation (Thomas, 1960) modifies the Frank-Kamenetskii parameter δ to account for heat transfer at the surface which is important for small sample sizes such as the laboratory basket tests. This equation is for an equi-cylinder.

This open-ended problem can now be defined in terms of a bounded chemical space based on the capability of laboratory equipment and published material properties (Table 1). This brings the problem into the realm of designed experimentation.

Symbol	Description	Min	Max	Units
E	Activation Energy	66512	191222	J/mol
QA	Heat of Reaction x Rate of Reaction	$1x10^{10}$	$1x10^{22}$	J/kg/s
ρ	Density	50	1600	kg/m^3
λ	Internal Heat Transfer	0.01	0.5	W/m/K
c	Heat Capacity	1000	2500	J/kg/K
r	Radius of equi-cylinder (height = 2·r)	0.0125	0.1	m
htc	Heat Transfer between Surroundings and Body	5	30	$W/m^2/K$
T_o	Ambient Temperature	293.15	673.15	K

Table 1: Bounded chemical space based on the conditions physically possible to generate in the laboratory and those previously observed in powdered solids.

Initially 10,000 materials in this bounded space were generated in JMP (2017) using a space filling design and Equations 2 and 3 were solved for T_O. Many of these materials were found to have critical temperatures inaccessible to laboratory equipment. By plotting $\log_{10}$(QA) versus E the disallowed combinations [see code snippet below] of these parameters can be visualised.

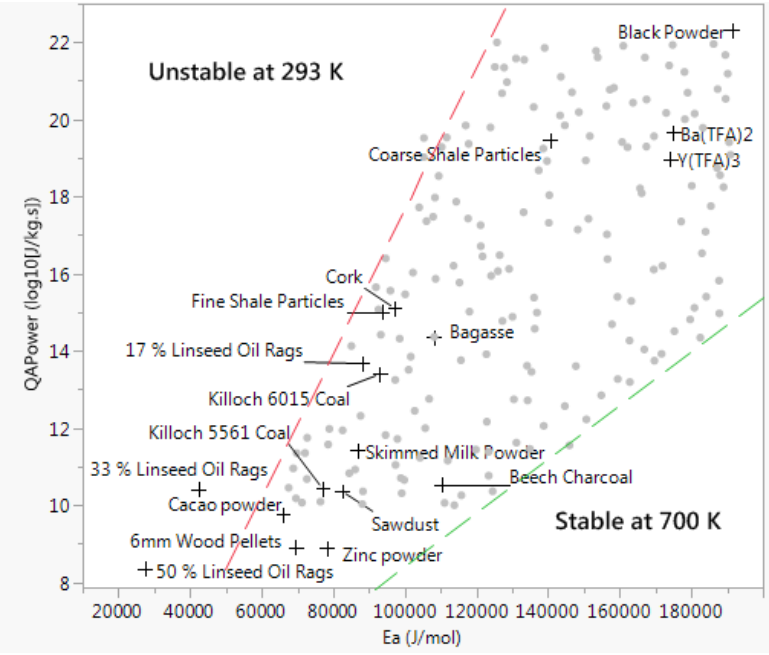

Figure 3: Bounded chemical space showing the location of previously tested substances (Jones, 1998, Worden, 2011, Everard et al., 2014, Cocchi, 2014, Frost et al., 2016, Blomqvist et al., 2007, Janes et al., 2008, Gross and Robertson, 1958).

Space-filling Experimental Designs

A computer simulation is a deterministic system which produces results which are biased from the real-world value but not subject to noise. They can be very complex and expensive to run. As a result, we may wish to build a simpler empirical model which describes the system well over a limited range of the factors.

If the number of runs is less than 500, a Gaussian Process model can be used to approximate the system. These models use spatial correlation to interpolate between data points, and effectively contain a copy of your data set. Alternatively, a Neural model can be built.

A rule of thumb [derived from simulation studies] is the number of runs needs to be at least 10 times the number of factors, to build an adequate model (Babyak, 2004). An additional consideration is when some combination of factors doesn't make sense or are disallowed. The Fast Flexible Filling option (Lekivetz and Jones, 2015) is a space filling design that can handle this situation [Figure 4].

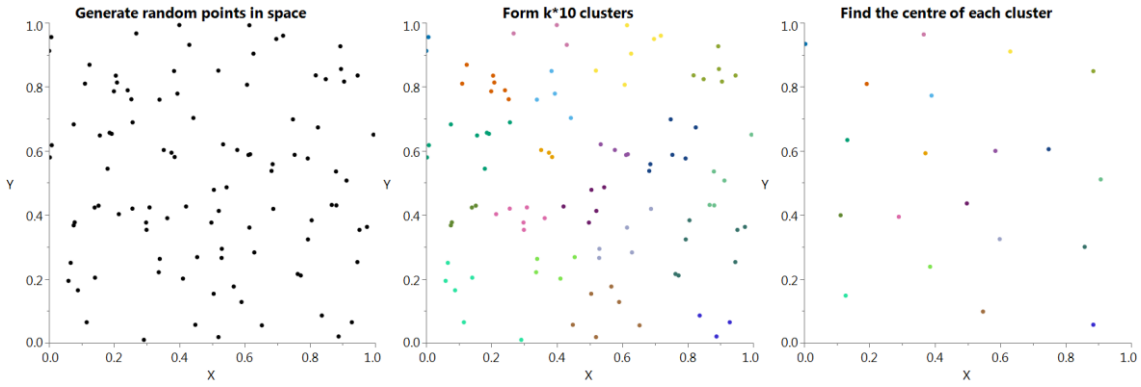

Figure 4: Simplified Example of Fast Flexible Filling. The Fast Flexible Filling algorithm generates 10,000 random points within the specified design region, then clusters them to give the Number of Runs specified. This is done in a way to maximise the spread of points within multidimensional space and for each factor.

A total of 175 materials were generated in the allowed chemical space using a space filling design. The minimum required runs were 60 but additional runs were chosen based on the available simulation time.

DOE(Space Filling Design,

{Add Response(Maximize, "Y", ., ., .),

Add Factor(Continuous, 0.01, 0.6, "lambda", 0),

Add Factor(Continuous, 1000, 2500, "c", 0),

Add Factor(Continuous, 50, 1600, "rho", 0),

Add Factor(Continuous, 5000, 23000, "EaPerR", 0),

Add Factor(Continuous, 8, 22, "QAPower", 0),

Add Factor(Continuous, 5, 30, "htc", 0), Set Random Seed(1556752215),

Disallowed Combinations(

*0.0016247 * EaPerR - QAPower < 2.5 | 0.0007113 * EaPerR - QAPower > 0.5*

), Simulate Responses(0), Set Run Order(Randomize), Make Table});

Controlling Simulation Software via JSL

The heat generation, geometry and heat transfer [Equation 1] for a laboratory oven were programmed in COMSOL Multiphysics® (2015). An equi-cylinder was chosen for the basket geometry as this greatly reduced the computational time required. The simulation results for the virtual thermocouple at the centre of the sample were set to write to an external text file.

The experiments were set-up to run for 76 hours of simulation time [5 minutes of processor time]. If the simulation resulted in a thermal run-away, then the experiment would terminate early. Once each run had finished the text file was read into JMP and saved as a data table.

To give initial temperature values for the simulations Equations 2 and 3 were solved for T_O for the 175 materials with basket sizes of 25, 50, 75, 100 and 200 mm. Starting from this point if a simulation was considered a thermal run-away, the simulation temperature was lowered, else the temperature was raised.

The temperature was stepped in 8 K increments [until both critical and sub-critical temperatures were located], then 4 K [to back fill the gaps], then finally 2 K. This was continued until two simulations were achieved with temperatures 2K apart, the lower of which completed the simulation whilst the upper temperature terminated early. Locating the critical temperature for all five basket sizes took 15-20 simulations per material.

The sample code below shows how COMSOL Multiphysics® can be controlled using the JSL command *RunProgram*. The *Read Function()* option causes the JSL code execution to pause whilst the simulation is run.

```
// Load Parameters From File

dtParam = Open( “SpaceFillingDesign.jmp" );

parameterList = dtParam << Get As Matrix;

Close( dtParam, NoSave );

// Loop Over Parameter List and Load Into Memory

...

// Send COMSOL Command

outputText = RunProgram(Executable( "C:\...\comsolbatch.exe" ),

Options(

{"-inputfile Basket.mph","-pname lambda,Cp,rho,EaPerR,QA,basketLen,Toven,htc,Tamb",

Concat("-plist ",Char( lambda ),",",Char( Cp ), ",",Char( rho ), ",",Char( EaPerR ), ",",Char( QA ),
",",Char( targetLen ),",",Char( Ttarget ), ",",Char( htc ), ",",Char( Tamb ) ),

"-Dosgi.locking=none"}),

Read Function( "text" ));
```

The results in the text file are as a series of uneven timestamps with temperatures at selected locations in the sample. More data is recorded in regions of greater change. The results can also be exported visually as slices across the material with time. Figure 5 shows the evolution of the temperature gradients within a sample which undergoes self-heating to ignition.

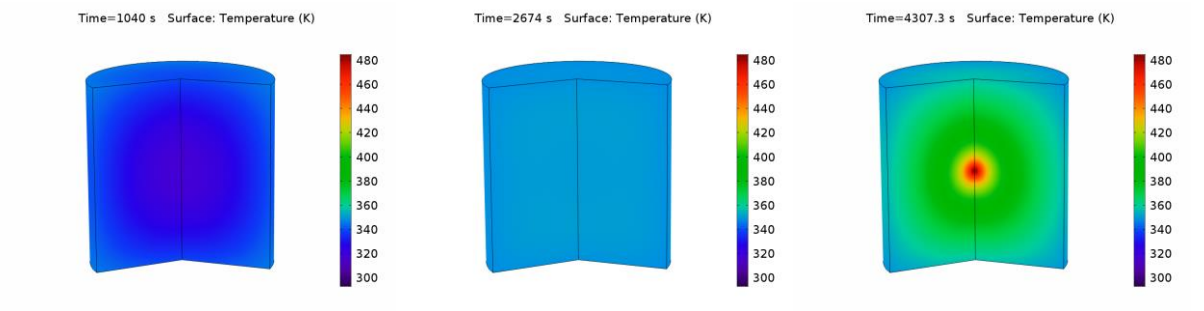

Figure 5: Temperature gradients during testing of self-heating solids. Initially heat is transferred from the oven to the sample surface, whereby it moves inward until eventually the whole sample is at the same temperature. If the oxidation process generates enough heat, then the temperature at the centre of the sample will exceed to the oven and eventually ignite.

The *File – Open Multiple…* option was used to combine the results files into a single table. The file names contained the material ID, basket size and oven temperature, and were included in the joined table.

Building Meta-models

For each material and basket size the simulation results were checked to ensure it had located the critical temperature. This required results 2K apart, the lower of which completed the simulation whilst the upper temperature terminated early.

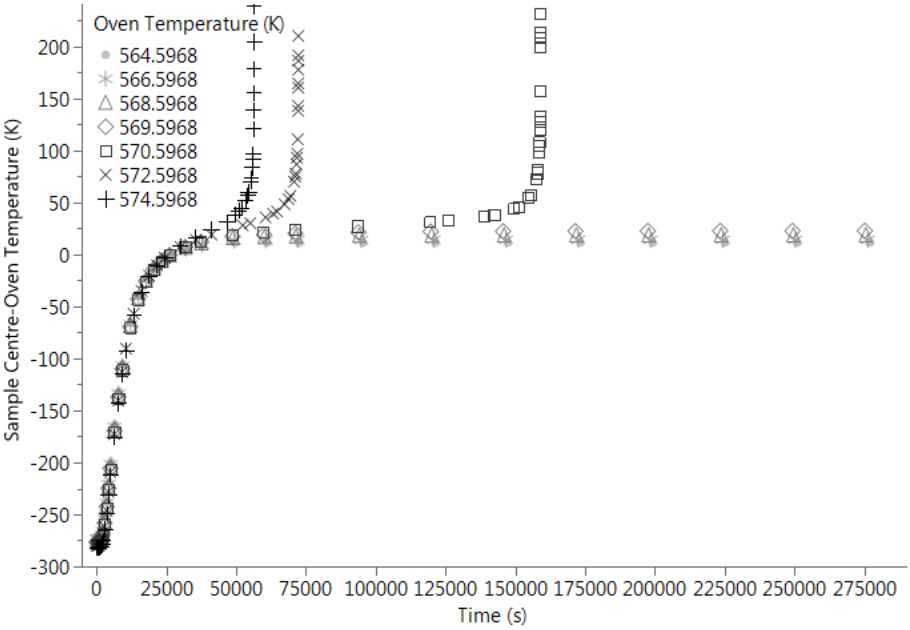

Figure 6: Example results for a material at a single basket size. The temperature at the centre of the sample is plotted relative to the oven temperature. A small increase in oven temperature [569.6 K to 570.6 K] alters the system from being stable to unstable. Further increasing the oven temperature rapidly decreases the time until thermal run-away is observed.

The maximum non-ignition temperature was then tabulated by material and basket size. These were then joined with the original space filling design containing the material properties. Gaussian Process and Neural models [TanH(3)] were fit to the simulation data. The residuals for these models along with the original predictions from the Thomas approximation are shown in Figure 7.

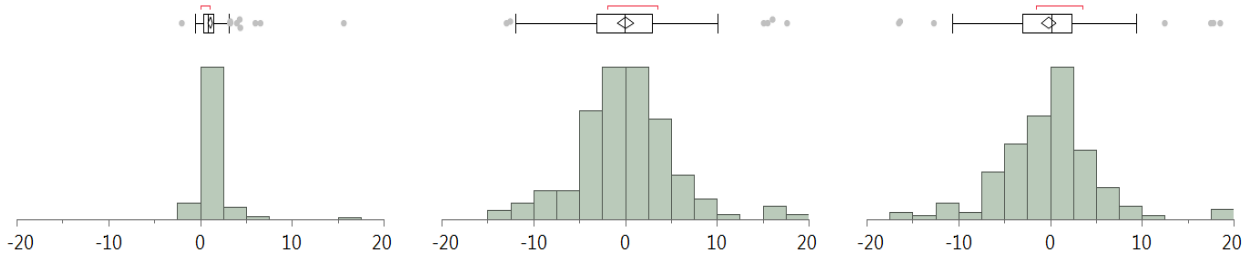

Figure 7: Residuals in maximum non-ignition temperature [K] relative to the simulation results. Left, $T_{simulation}$-T_{Thomas}; Middle, $T_{simulation}$-$T_{Gaussian}$; Right, $T_{simulation}$-T_{Neural}. The Thomas model is a better fit to the simulations than can be achieved by either the Gaussian Process or Neural meta-models

Using the same approach, simulation studies in COMSOL Multiphysics® were completed for these 175 materials on two related thermal stability tests. These tests require less material than the basket tests to give an estimate of the activation energy and reaction rate.

The diffusion cell is a screening test in which 60 ml of powder, in a 50 mm diameter glass cylinder, is heated at 0.5 K/minute [under air] from room temperature to 675 K. If the solid is self-heating, then during the test the sample temperature will exceed the oven temperature and proceed to thermal run-away.

The thin layer test involves a 5 mm layer of powder, 100 mm in diameter, on a hot surface. The surface is set to a temperature and the sample monitored via a thermocouple in the sample centre to see if thermal run-away occurs within 30 minutes at that temperature. This is repeated over a range of temperatures to determine the minimum ignition temperature.

The correlation between the diffusion cell result and the basket temperatures for the simulated materials can be exploited to more efficiently locate the critical temperature for the 25 mm basket test. This can be seen in Figure 8 where roughly 96 % of the variability in the basket temperature could be explained by the diffusion cell result.

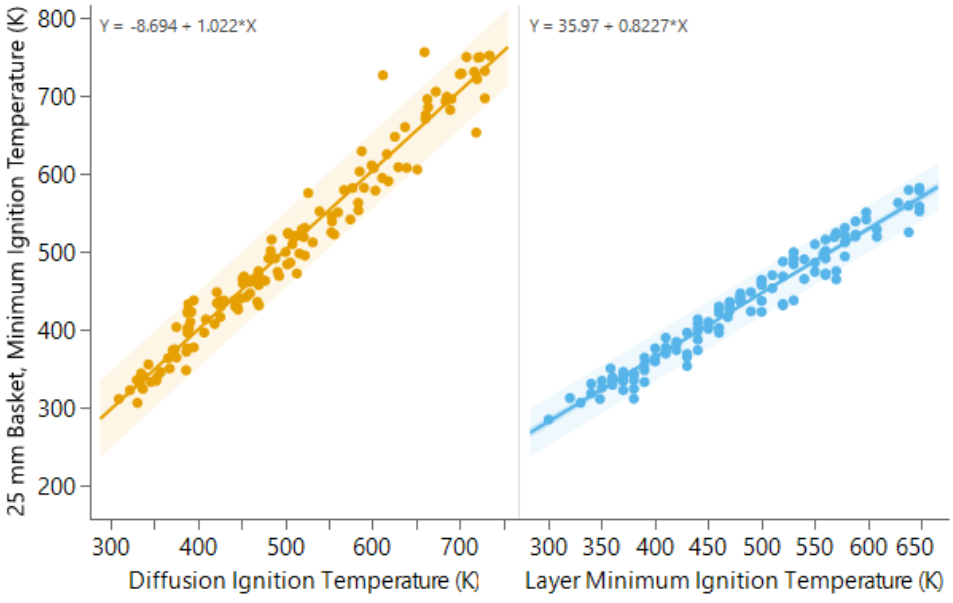

Figure 8: There is a strong correlation between diffusion cell result, thin layer minimum ignition temperature and the basket data.

Prediction Process for New Materials

A new material is first tested by calorimetry to determine the melting point and energy of decomposition. Provided the material is not too energetic and melts above 100 °C it can then be screened by the diffusion cell test.

What follows is a worked example for Carbon Black. The sample temperature exceeded the oven temperature in the diffusion cell test at 434 K. Using a TanH(3) neural network model [built from the 175 simulated materials] we can use the diffusion test result to predict the result for a 25 mm basket test.

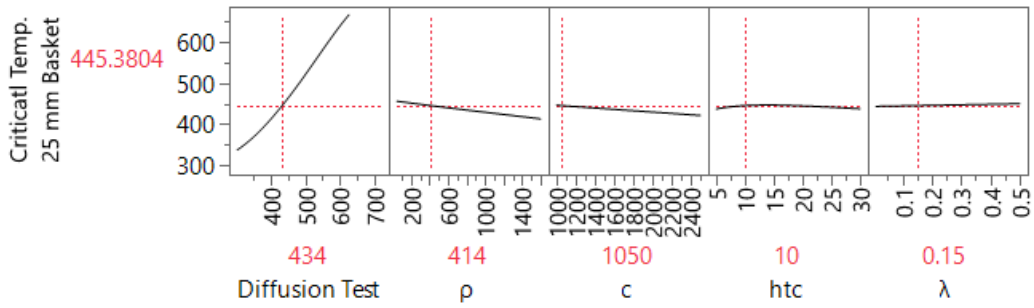

Figure 9: Predicted result for a 25 mm equi-cylinder of Carbon Black. Diffusion Test and ρ are measured experimentally; c and htc are taken from the literature; and λ was estimated from the heat-up curve [see appendix for details]. Note the actual tests were carried out in ~25 mm cubes. Variability in the exact dimensions of the cubic baskets means that predictions for an equi-cylinder are close enough to be useful.

The maximum non-ignition temperature for a 25 mm cubic basket was found experimentally to be 446 K. This information can be combined with the diffusion cell result to make a prediction for a 50 mm basket [using a TanH(3) neural network model built from the data for the 175 simulated materials].

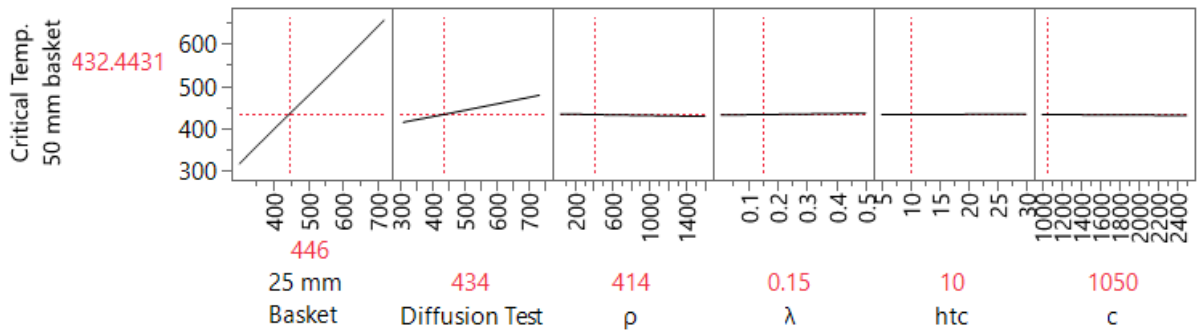

Figure 10: Predicted result for a 50 mm equi-cylinder of Carbon Black. d0.025, Diffusion Test and ρ are measured experimentally; c and htc are taken from the literature; and λ was estimated from the heat-up curve [see appendix for details]. Once a basket result is known this is a much stronger predictor than the diffusion cell test. This is because the physics of self-heating requires the result for a bigger basket to be at a lower temperature. How much lower depends on the relative basket sizes but is typically 10-30 K lower.

The maximum non-ignition temperature for a 50 mm cubic basket was found experimentally to be 419 K. This is lower than predicted but the model still gave a useful starting point for the search. Examining the traces for tests which are super-critical or just sub-critical can be informative about how far from the critical temperature the test is.

At this point we now have at least 4 data points bounding the critical temperature. Using equations 2 and 3 it is possible to estimate the activation energy of the oxidation process. Lines are drawn between

the maximum non-ignition for one basket and the minimum ignition at the other basket size [and vice-versa], Figure 11.

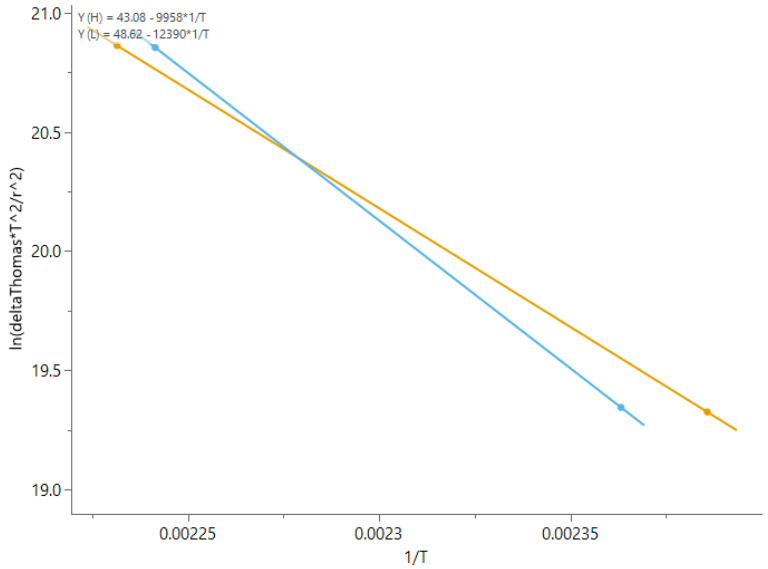

Figure 11: Using the Thomas model to estimate plausible activation energies. The slope of the lines of fit are E/R. This gives a predicted activation for the oxidation of the carbon black to be 83-103 kJ/mol.

Analysing the data in this way gives the most extreme plausible lines of best fit from which the activation energy can be obtained [83-103 kJ/mol]. Traditional linear regression is not helpful in this case as we have prior knowledge that the slope is typically in the range -7216 to -19244 for self-heating solids [60 to 160 kJ/mol]. Values higher then 160 kJ/mol would likely be screened out as potential explosives and not subject to a basket line test.

The objective of any further testing is to narrow the estimate of the activation energy as much as possible. The empirical Lueschke plot [1/T versus ln(V/S)] is a helpful tool to do this. Using the same approach as in Figure 11 we obtain two lines which can be extrapolated to the basket size of interest.

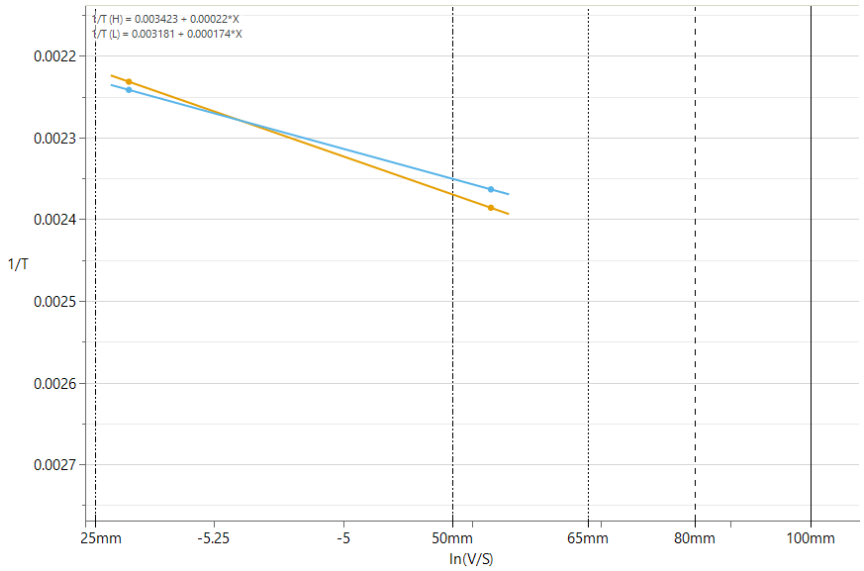

Figure 12: Extrapolation over small scales to identify test temperatures for further testing. Note the data points don't line up with the nominal basket sizes. The volume of the basket is measured, which is used to determine the actual radius and thus ln(volume/surface area).

Testing the mid-point temperature at 65 mm will halve the prediction window for 80 mm & 100 mm. This should reduce the uncertainty in the activation energy to 10-15 kJ/mol which is as accurate as one might expect given the experimental set-up.

If the result is just sub-critical it is particularly informative about the location of critical temperature. Whatever the result at 65 mm, the opposite result is targeted at 80 or 100 mm by testing at the upper [if 65 mm is sub-critical] or lower [if 65 mm is critical] end of the prediction range.

Basket Size / mm	Temperature Range / K
65	413-418
85	404-412
100	396-407

Table 2: Predicted temperature ranges containing the critical temperature.

The maximum non-ignition temperature for a 65 mm cubic basket was found experimentally to be 415 K. This revises the estimate of the activation of oxidation to 92-98 kJ/mol. This understanding was confirmed by obtaining a thermal run-away at 407 K for a 100 mm basket as expected.

Conclusion

The empirical approach to the problem of self-heating solids is largely a result of the historic origins of the field (Bowes and Cameron, 1971). Advances in physics simulation software allow us to reframe it as problem in a bounded 7-dimensional parameter space.

Previously such a study would have required too many manhours to be feasible. However, using JMP we can generate space filling designs with constraints and control the simulation software. This enables efficient exploring of the parameter space with minimal human intervention. The resulting data can then be appropriately modelled, and in conjunction with the prediction profiler used to guide experimental work on real-world materials.

The experimentalists have been able to change their approach from trying to hunt for the maximum non-ignition temperature at a range of basket sizes to a more targeted approach. The data from each thermal stability test helps to refine the estimates of the key material properties.

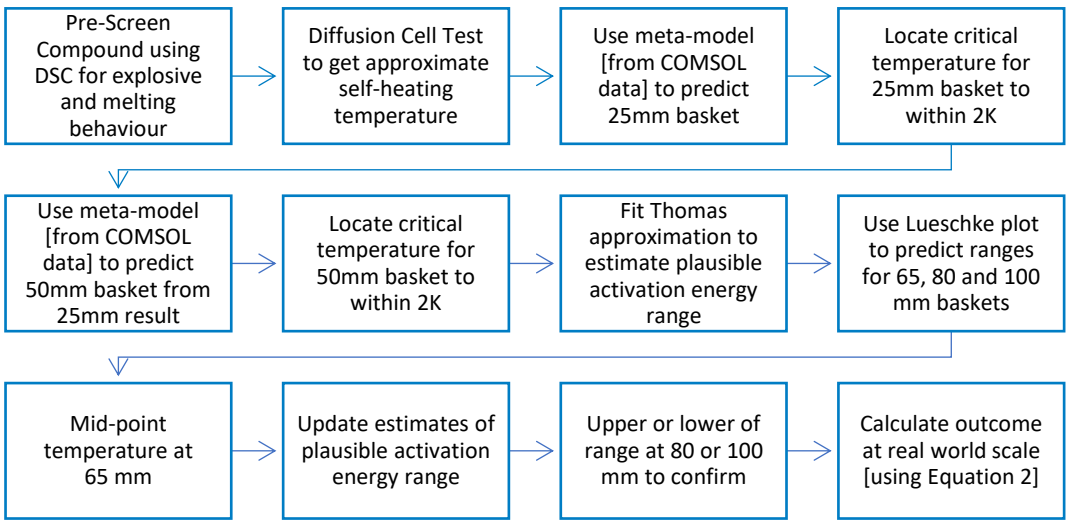

Figure 13: Steps taken by experimentalists to determine if a new material is safe to store or transport for a given pack size or geometry. The focus is on getting the best estimates of the material properties rather than extrapolation from laboratory to real world scales.

Appendix

During the heat up from room temperature, the heat generation term is close to zero. The thermal diffusivity [α] can be estimated from the heat up curve via a Fourier series (Kimpel, 2010). This information can help refine where in the bounded chemical space the current material under test is located.

$$\frac{thetaC}{theta0} = \frac{OvenTemp - CurrentSampleTemp}{OvenTemp - StartingSampleTemp}$$

$$\frac{thetaC}{theta0} = 2\left(\frac{\sin t}{t}\right) \times e^{-\left(t^2 \times \frac{\alpha \times time}{half\ edge\ length^2}\right)} + \ \ldots,\ t = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \frac{7\pi}{2}, \ldots, \frac{19\pi}{2}$$

$$\alpha\ (thermal\ diffusivity) = \frac{\lambda}{c \times \rho}$$

Equation 4: Obtaining the thermal diffusivity from the sample warming to oven temperature. Density is measured and the heat capacity can be measured or obtained from related materials allowing the internal heat transfer term to be obtained.

The non-linear platform can be used to solve the Fourier series over the first 3600 seconds of each test. Using the JMP Scripting Language [JSL] the process of altering the active data, updating the half edge length [HEL], running the fit and saving the estimate can be automated [~100 lines of code].

```
//Launch Platform
obj = dt << Nonlinear(
Y( :Name( "thetaC/theta0" ) ),
X( :Fourier ), Newton);
robj = obj << report;
robj[CheckBoxBox( 1 )] << Set( 2 ); //Lock the Half-Edge Length value

//Set Initial Values and Fit
robj[Number Col Edit Box( 2 )] << Set Values( Matrix( List(seedAlpha, HELList[i]) ) );
obj << Go;

//Get Estimates
estimate = robj[Number Col Edit Box( 2 )] << Get As Matrix;
```

Equation 4 was solved for 3086 simulation results across the different basket sizes. The results indicate this method doesn't work for 0.2 m baskets. The predicted value of λ for smaller basket sizes has a systematic bias of -0.09 W/m/K from the true value. It is not clear if this is a limitation of the theory or an artefact of how the simulations are configured.

References

2004. *Rapport Silobrand Härnösand* [Online]. Räddningstjänsten Höga Kusten-Ådalen. Available: https://rib.msb.se/Filer/pdf/20155.pdf [Accessed 02/12/2019].

2015. COMSOL Multiphysics v. 5.3. COMSOL AB, Stockholm, Sweden.

2017. JMP Pro. 14.0.0 ed.: Cary, NC: SAS Institute.

AZHAR, T. & ARBAEE, T. N. 2018. *Experimental study and numerical modelling of self-heating behaviour of torrefied and non-torrefied biomass fuels.* University of Sheffield.

BABYAK, M. A. 2004. What You See May Not Be What You Get: A Brief, Nontechnical Introduction to Overfitting in Regression-Type Models. *Psychosomatic Medicine,* 66**,** 411-421.

BLOMQVIST, P., PERSSON, H., VAN HEES, P., HOLMSTEDT, G., GÖRANSSON, U., WADSÖ, L., SANATI, M. & RUPAR-GADD, K. 2007. An experimental study of spontaneous ignition in storages of wood pellets. *10th International Conference-Fire and Materials 2007*.

BODDINGTON, T., GRAY, P. & HARVEY, D. I. 1971. Thermal Theory of Spontaneous Ignition: Criticality in Bodies of Arbitrary Shape. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences,* 270**,** 467-506.

BOWES, P. & CAMERON, A. 1971. Self‐heating and ignition of chemically activated carbon. *Journal of Applied Chemistry and Biotechnology,* 21**,** 244-250.

COCCHI, G. 2014. Estimating the activation energy of exothermic reactions in substances that undergo self heating processes with the Heat Release method: Use of sub critical data. *Fuel,* 125**,** 152-154.

EVERARD, C. D., SCHMIDT, M., MCDONNELL, K. P. & FINNAN, J. 2014. Heating processes during storage of Miscanthus chip piles and numerical simulations to predict self-ignition. *Journal of Loss Prevention in the Process Industries,* 30**,** 188-196.

FRANK-KAMENETSKII, D. A. 1946. On non-stationary theory of thermal explosion. *J. Phys. Chem.,* 20.

FROST, K., LÜTH, P., SCHMIDT, M., SIMON, K. & UHLIG, S. 2016. Evaluation of the interlaboratory test 2015-2016 on the method DIN EN 15188: 2007 “Determination of the spontaneous ignition behaviour of dust accumulations”.

GROSS, D. & ROBERTSON, A. 1958. Self-ignition temperatures of materials from kinetic-reaction data. *Journal of Research of the National Bureau of Standards,* 61**,** 413-417.

HEDLUND, F. H. 2018. Carbon dioxide not suitable for extinguishment of smouldering silo fires: Static electricity may cause silo explosion. *Biomass and Bioenergy,* 108**,** 113-119.

JANES, A., CARSON, D., ACCORSI, A., CHAINEAUX, J., TRIBOUILLOY, B. & MORAINVILLERS, D. 2008. Correlation between self-ignition of a dust layer on a hot surface and in baskets in an oven. *Journal of Hazardous Materials,* 159**,** 528-535.

JONES, J. C. 1998. A means of obtaining a full kinetic rate expression for the oxidation of a solid substrate from a single criticality data point. *Fuel,* 77**,** 1677-1678.

KIMPEL, S. 2010. Bestimmung der Selbstentzündungstemperatur von Schüttungen aus adiabatischen Warmlagerversuchen. Hochschule Darmstadt Fachbereich Chemie- und Biotechnologie.

LEKIVETZ, R. & JONES, B. 2015. Fast flexible space‐filling designs for nonrectangular regions. *Quality and Reliability Engineering International,* 31**,** 829-837.

NATIONS, U. 2003. UN Recommendations on the Transport of Dangerous Goods.

THOMAS, P. H. 1960. Some approximations in the theory of self-heating and thermal explosion. *Transactions of the Faraday Society,* 56**,** 833-839.

WORDEN, J. T. 2011. *Spontaneous Ignition of Linseed Oil Soaked Cotton using the Oven Basket and Crossing Point Methods,* Maryland, University of Maryland.