Speaker Bio

Stephen Pearson is a Specialist Data Scientist at Syngenta. He provides support to scientists at the Grangemouth, Huddersfield and Jealotts Hill sites. The role is cross-disciplinary and involves identifying areas of need, building tools to enhance working practises and teaching new techniques.

Stephen is experienced in building systems to automate the collection, processing, analysis and reporting of experimental and manufacturing data. This often involves writing code in multiple languages to use the most appropriate tool for each step. He holds a PhD in chemistry from the University of Edinburgh.

Abstract

Many materials slowly oxidise with time which generates heat. If the material is in a bulk form (such as during storage or transport) then heat generation can exceed heat loss which leads to ignition of the material.

Laboratory tests are well established but are time consuming and can require large volumes of test material which are not always available. The physics of the process is well described and 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?

JMP was used to generate an experimental design, control the simulation software, fit the results, build meta-models and simulate the outcome for new materials.

Keywords: thermal stability; Thomas approximation; JMP; COMSOL Multiphysics; space filling; meta-model;

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Modelling self-heating solids

JMP UK User Forum 18th July 2019

Dr Stephen Pearson
Specialist Data Scientist
Huddersfield and Grangemouth Manufacturing Centres

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Acknowledgments

Some of the work was done in collaboration with Dr John Paul Gosling of the University of Leeds

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

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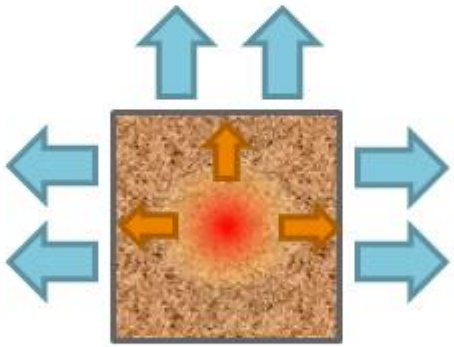
The Situation

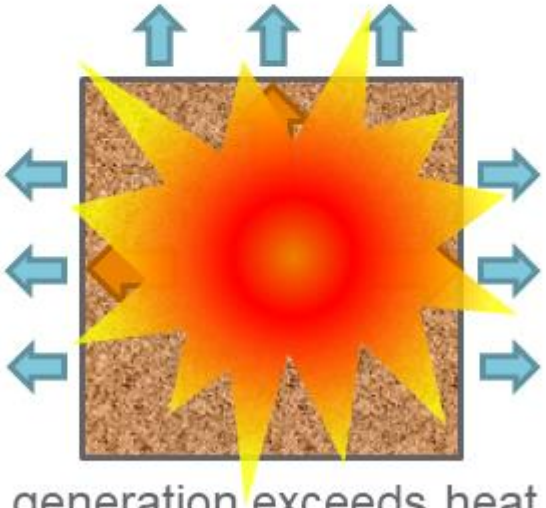
Many materials (raw materials, final active ingredients, granular formulations & seeds) have the potential to slowly oxidise which generates heat.

No Go



Heat loss exceeds heat generation

Go



Heat generation exceeds heat loss

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Consequences

Silobrand Härnösand (8-13 Sept 2004)

Hallingdal Trepellets (10 July 2010)

https://rib.msb.se/Filer/pdf/20155.pdf
https://www.msb.se/Upload/Insats_och_beredskap/Brand_raddning/Brand%20i%20silo/Pellets%202010.pdf

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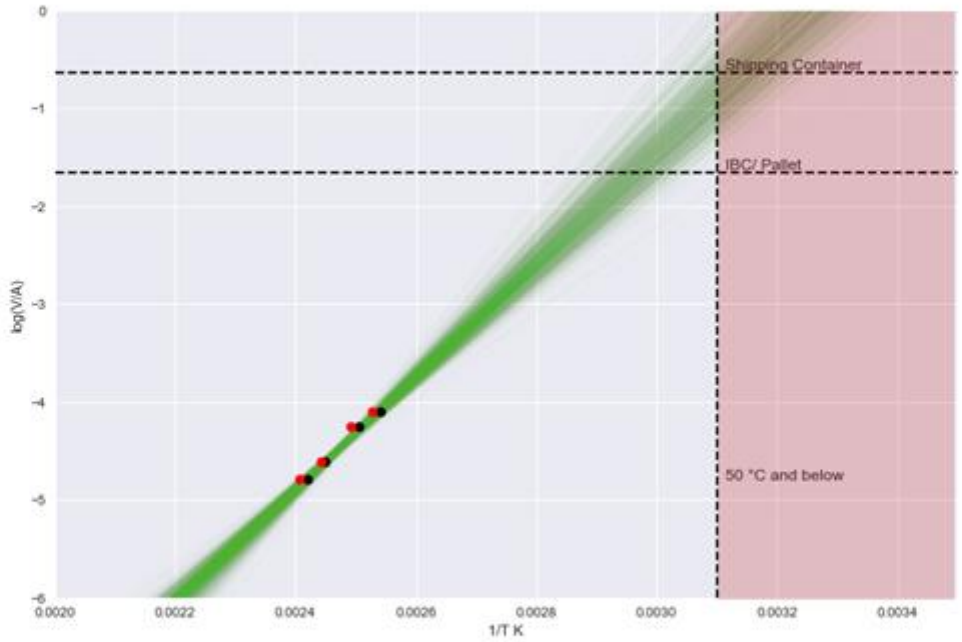
Basket Line Example

The milk powder tested here is considered safe to ship in $1m^3$ container but not at $27m^3$.



This is empirically scaled from the laboratory results based on the volume/area ratio.

Frost, K., et al., *Evaluation of the interlaboratory test 2015-2016 on the method DIN EN 15188: 2007*

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Thermal Equations

Heat Equation:

$$\rho c \cdot \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \rho Q A e^{-\frac{E}{RT}} \qquad (1)$$

Frank-Kamenetskii:

$$\delta = r^2 \cdot \frac{\rho Q A}{\lambda T_o} \cdot \frac{E}{R T_o} \cdot e^{-\frac{E}{R T_o}} \qquad (2)$$

Thomas Approximation:

$$\delta_{crit} = \frac{0.8047}{0.2830 + \frac{0.7292}{Bi}}, Bi = \frac{htc}{\lambda} \cdot r \qquad (3)$$

Frank-Kamenetskii, D.A., *On non-stationary theory of thermal explosion*. J. Phys. Chem., 1946. **20**(2).
Thomas, P.H., *Some approximations in the theory of self-heating and thermal explosion*. Transactions of the Faraday Society, 1960. **56**: p. 833-839.

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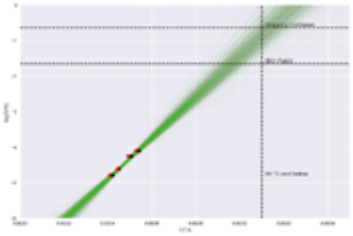
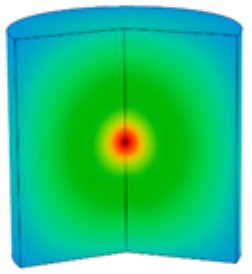
Approaches to a Numerical Solution

1. Analytically solve the heat equation for a given geometry (possible for simple shapes).
2. Empirical correlations



3. Solve Equation 1 with time by numerical simulation (time consuming).



4. Solve Equation 2 & 3 via hunting technique to locate transition from 'No Go' to 'Go'.

How could this be generalised over chemical space?

Can it be practically applied in the laboratory?

Boddington, T., P. Gray, and D.I. Harvey, *Thermal Theory of Spontaneous Ignition: Criticality in Bodies of Arbitrary Shape.* Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 1971. **270**(1207): p. 467-506.

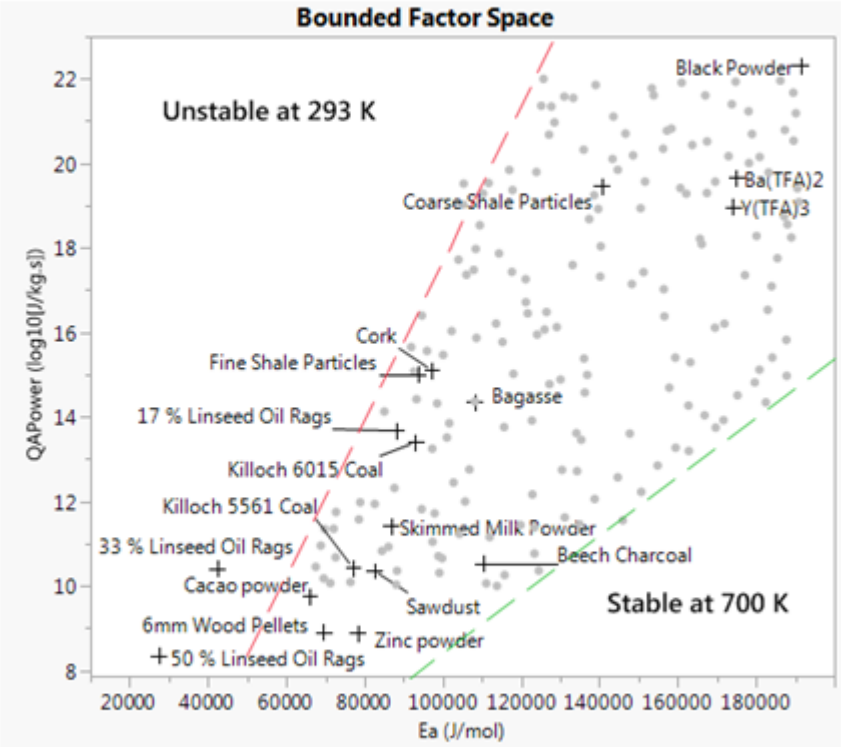
Chemical Space

Based on the Thomas approximation, capability of laboratory equipment and published material properties a bounded chemical space was defined:

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
d	Diameter of equicylinder (d=h)*	0.025	0.2	m
htc	Heat Transfer between Surroundings and Body	5	30	$W/m^2/K$
T	Ambient Temperature	293.15	673.15	K

 Engineering ToolBox. 2001; Available from: https://www.engineeringtoolbox.com

Chemical Space in Context



The self heating behaviour of a number of materials has been determined:

Linseed Oil Rags, Gross & Robertson (1958)
Killoch Coal, Jones (1998)
Sawdust, Wood Pellets, Van Hees (2006)
Bagasse, Mitchell (2007)
Cork, Corrion (2008)
Cacao, Zinc powder, Janes (2008)
Linseed Oil/Cotton Rags, Worden (2011)
Charcoal, Cocchi (2014)
Micanthus Chips, Everard (2014)
Skimmed Milk Powder, Lueth (2016)

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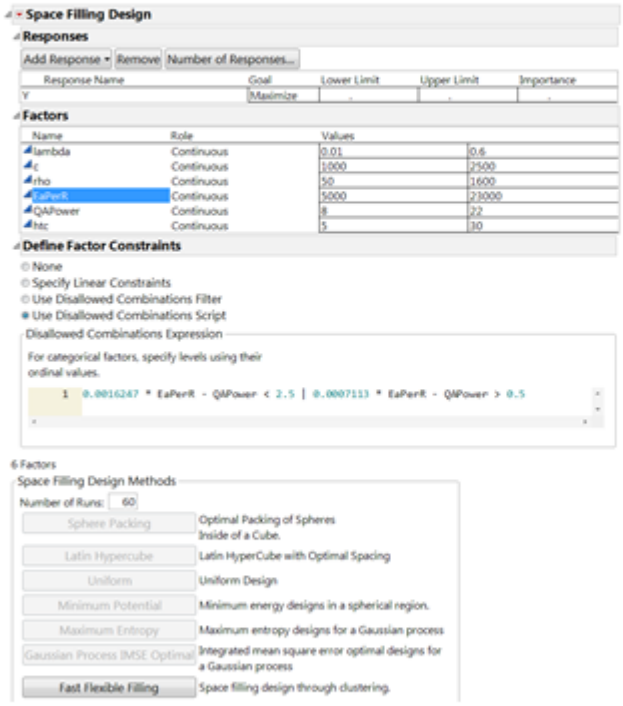
Space Filling Design with disallowed combinations



To be able to create a meta-model of a digital simulation the minimum number of runs is 10x number of factors.

For 7 factors, this would be 70 but it was increased by 2.5x to give a better chance of fitting a model.

It is possible to define a region where certain combinations of factors are disallowed.

The Fast Flexible Filling algorithm generates many 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 in multidimensional space.

Lekivetz, R. and B. Jones, *Fast flexible space-filling designs for nonrectangular regions.* Quality and Reliability Engineering International, 2015. **31**(5): p. 829-837.

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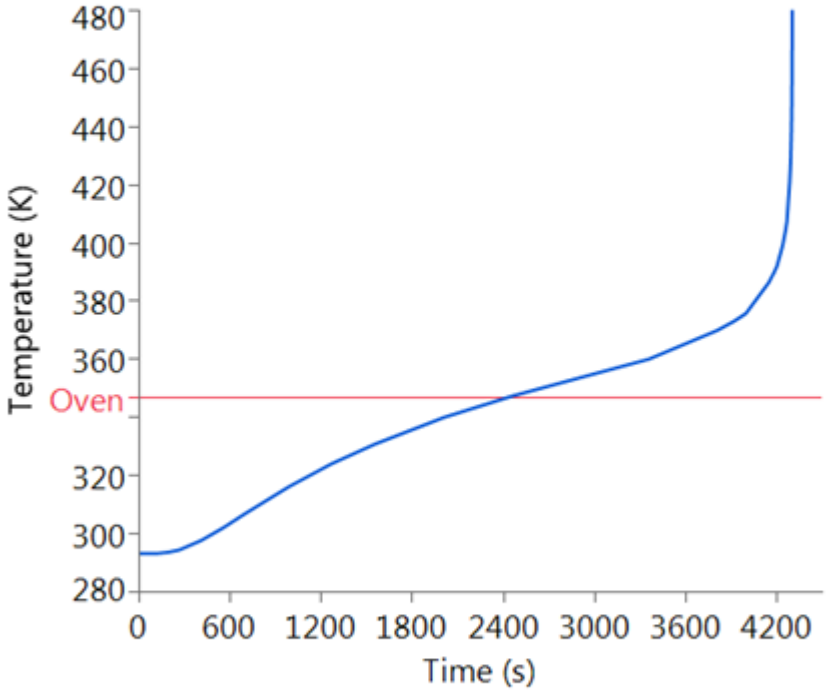
Simulation Approach

The heat equation, geometry and heat transfer from the oven were programmed in COMSOL Multiphysics®.

Starting from the result of the Thomas approximation, simulations were carried out for 25, 50, 75, 100 & 200 mm baskets.

Locating the maximum 'No Go' temperature for all 5 sizes took 15-20 simulations per material .



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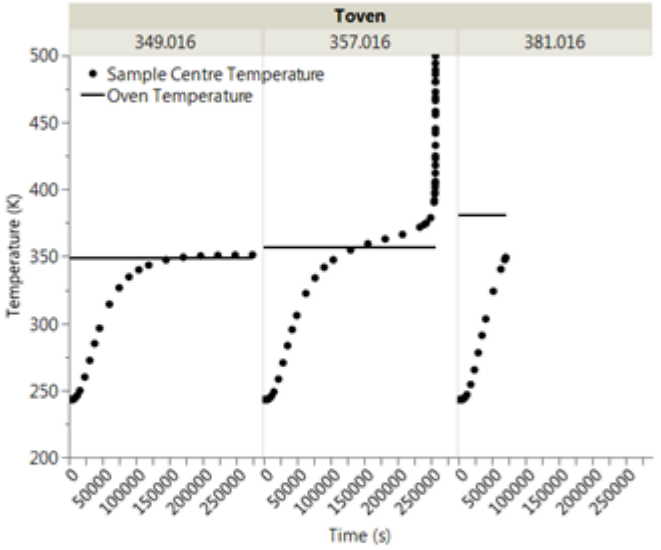
Controlling COMSOL Multiphysics via JMP

```
// Load Parameters From File
dtParam = Open( “SpaceFillingDesign.jmp" );
parameterList = dtParam << Get As Matrix;
Close( dtParam, NoSave );
...

// 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" ));
```

Data Analysis

1. Each simulation result ‘Go’ or ‘No Go’.
2. Difference between minimum ‘Go’ and maximum ‘No Go’ <= 2K at each size.
3. Tabulate maximum ‘No Go’ by material and basket size.
4. Join material properties to results
5. Fit model to predict maximum ‘No Go’ based on material properties



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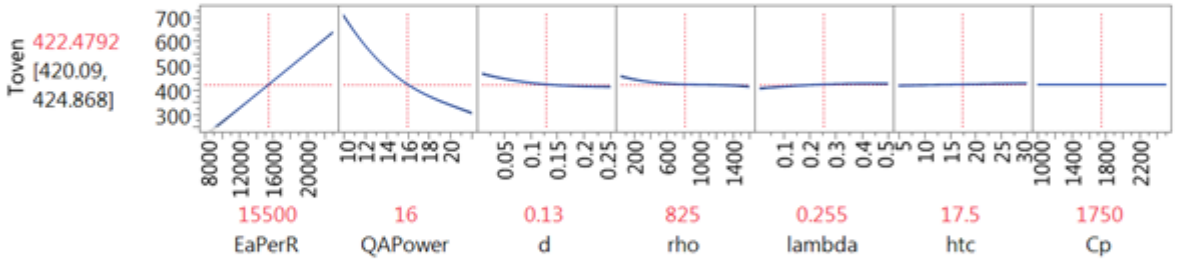
Gaussian Model

Simulation models have no error terms (same input = same output)

Gaussian models use spatial correlation to interpolate between data points. The model effectively contains a copy of your data set.



Column	Main Effect	Total Effect
EaPerR	0.521	0.568
QAPower	0.411	0.46
d	0.005	0.011
rho	0.003	0.006
lambda	0.001	0.003
htc	4e-4	0.001
Cp	1e-10	2e-10

The response surface is quite smooth and can also be modelled using a Neural Network.

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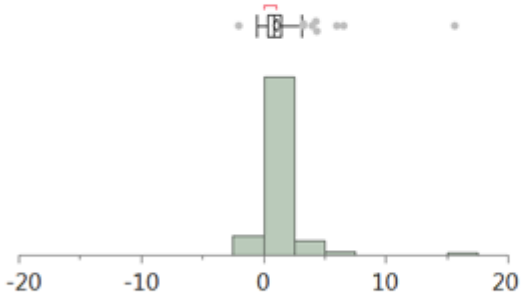
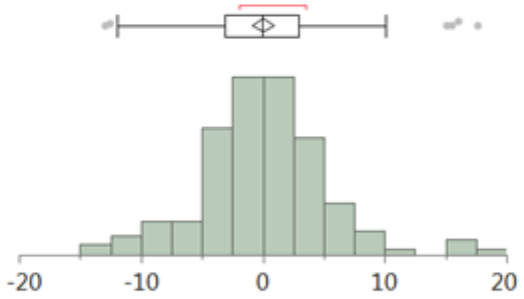
COMSOL and Thomas, Gaussian, Neural Models

The Thomas model is a better fit to the simulations than can be achieved by either the Gaussian or Neural models.

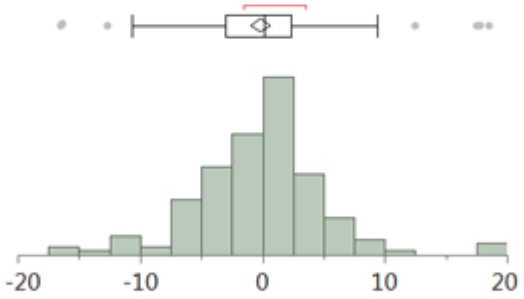
T_{COMSOL}-T_{Thomas}



T_{COMSOL}-$T_{Gaussian}$



T_{COMSOL}-T_{Neural}



Note: The extreme value for T_{Thomas} is where COMSOL found 647 K, but 631 K was predicted.

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Obtaining equation parameters λ, c and ρ

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

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:

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

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

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

Density (ρ) is measured and the heat capacity (λ) can be measured or obtained from related materials.

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

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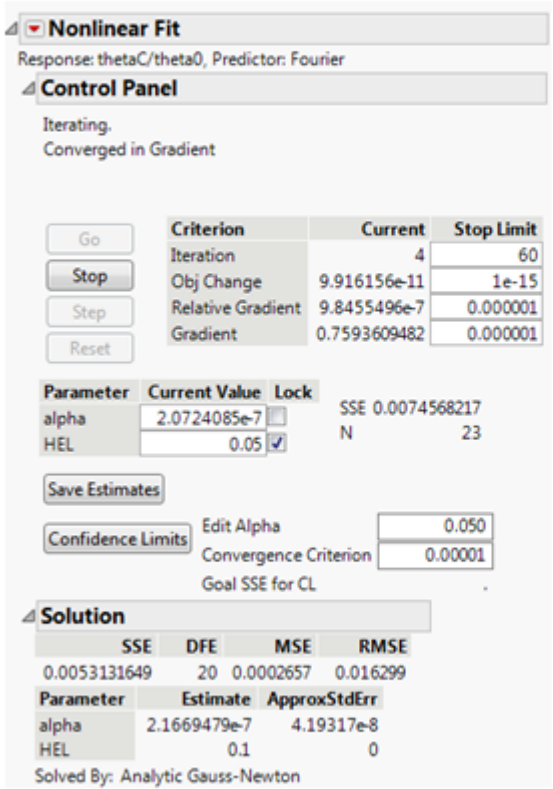
Non-linear fitting in JMP



The non-linear platform in JMP 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).

The heat-up profiles of 3086 simulations were solved covering the parameter space.

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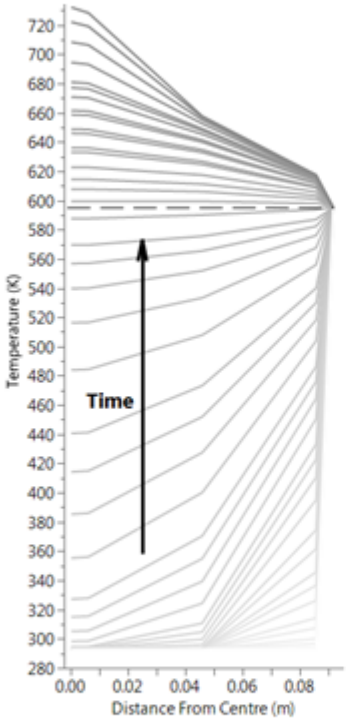
Non-linear fitting in JMP

```
//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( {seedAlpha, HELList[i]} ) );
obj << Go;

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

Crossing Temperature Theory



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

T_{centre} versus $T_{centre+mm}$ – Transition Method, Chen (1995)

T_{centre} versus T_{oven} – Heat Release, Jones (1996)

Potentially better:

- Use less material (25 mm basket only)
- Faster since only need to run tests to crossing point

Chong, L.V., I.R. Shaw, and X.D. Chen, *Thermal ignition kinetics of wood sawdust ....* Process Safety Progress, 1995. **14**(4): p. 266-270.
Jones, J.C., *A single-point estimation of the combustion rate expression....* Journal of Fire Sciences, 1996. **14**(4): p. 325-330.

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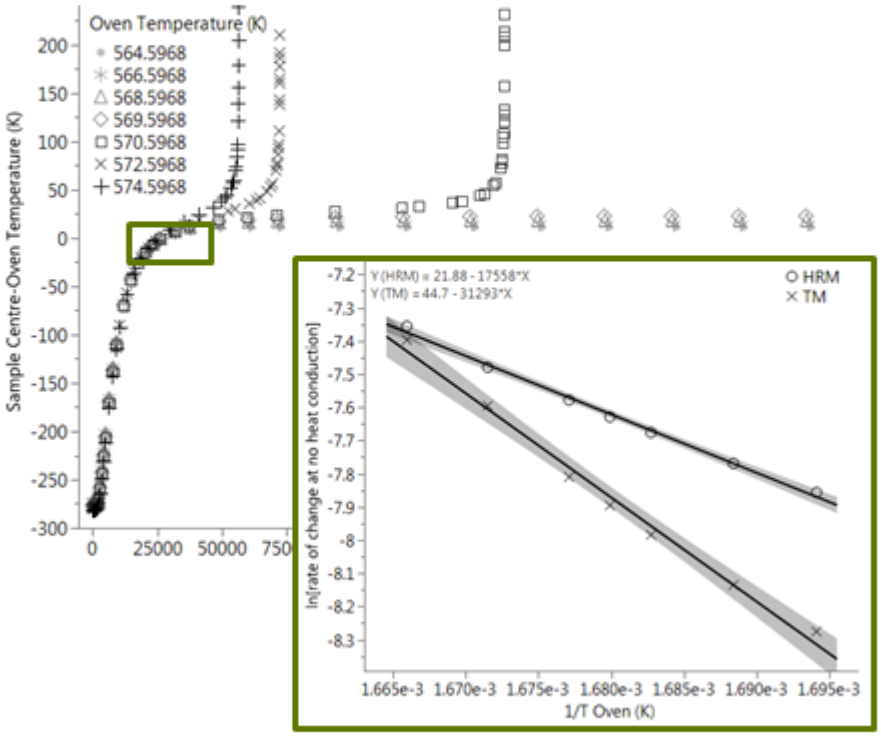
Crossing Temperature Methods



1. For a fixed size (25 mm), carry out simulations for 7+ temperatures close to the maximum 'No Go' temperature.
2. Fit a spline to each result.
3. Locate the time $T_{centre} = T_{oven}$.
4. Calculate the rate of change in T_{centre} for this time ± 30 seconds.
5. Fit-Y-by-X ln[dT/dt] versus 1/T by material.
6. Compare predicted E and QA versus actual.

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Spline Fitting in JMP

For a smooth response spline function can be used to interpolate.

Original data 0.013 GB

Interpolated 1.3 GB

As well as converting unevenly spaced data can also map different time stamps onto same common time.

1. Fit-Y-By-X with By clauses
2. Fit Spline and save formula
3. Tabulate By
4. Generate Time Base
5. Cartesian Join of 3 & 4
6. Copy formula from 2
7. Fit-Y-By-X with By clauses
8. Fit line to obtain dt/dT

Conclusions

Space filling designs are an efficient & flexible way to explore a parameter space.

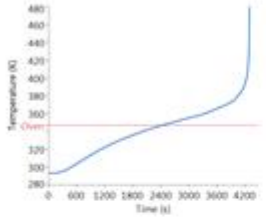
Control of other software via JMP can enable studies that would otherwise be impractical (10,000 simulations in a month with minimal oversight).

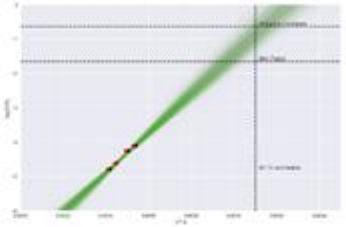
Gaussian modelling and Neural Networks can be used to produce meta-models.

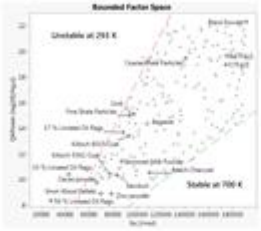
The fit non-linear can be scripted to solve the same equation for many different experiments.

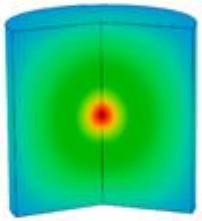
Splines (Fit-Y-By-X platform) can be used to convert uneven data or different time stamps onto same common time.

Questions?

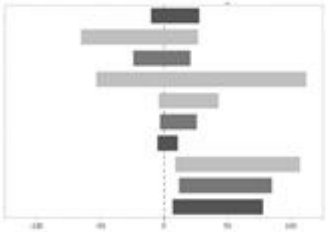


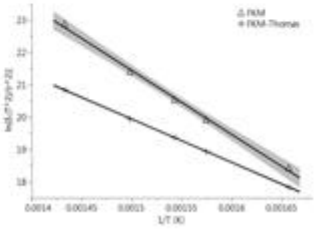


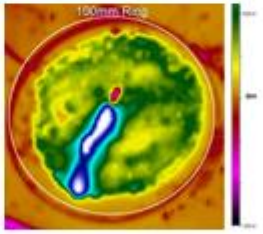




$$\rho c \cdot \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \rho Q A e^{-\frac{E}{RT}}$$







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