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Prediction of Self-Heating in Detergent Powders for Applications to Spray Dryer Wall Accumulations

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Abstract:

During the spray drying of detergent formulations, powder can accumulate on the inner walls of the spray drying tower. Under certain conditions, when the accumulations are large enough self-heating can occur, leading to unwanted charring and in severe cases to thermal runaway. In this study, basket heating methods, namely the steady-state approach and cross-point temperature method, were used to estimate the zero-order kinetics of the self-heating reaction of a typical detergent formulation. It was found that the resulting kinetics of these two methods were not in agreement, with this being attributed to the Cross-Point Temperature method's sensitivity to errors. The estimated kinetics were used in a 2D-axismmetric transient model of heat transfer within an oven heated basket of detergent powder. Temperature-time profiles, and critical ambient temperatures, predicted by the model agreed well with experimental measurements. The model was also used to explore the value of using n^{th} order kinetics estimated using a thermogravimetric measurement technique. Theses kinetic showed no benefit versus the zero order kinetics and introduced unnecessary complexity. Future work will see this model and the insights gained applied to the problem of modelling self-heating in spray dryer wall accumulations.

Keywords: detergent powder, self-heating, thermal runaway, spray drying, cross-point

Introduction

Self-heating is the process by which some materials can increase in temperature without the application of an external energy source. An exothermic reaction within the material causes the temperature to rise and the stability of these systems is a balance between the internal heat generation and heat loss from the system boundaries. Many materials exhibit self-heating behaviour including milk powder [1], coal [2], and biomass [3], and this behaviour can cause problems in the processing and storage of these materials. During the spray drying of detergent formulations, layers of powder can build-up on the hot internal walls of the spray drying tower. If this build-up is of sufficient thickness and the local temperature high enough, the powder in these layers can self-heat. This can cause the powder to char which compromises the final product quality or. In the worst cases thermal runaway can occur, whereby an uncontrollable exothermic reaction leads to a rapid and often dangerous increase in temperature. Being able to understand this behaviour and predict the self-heating of these materials aids in product quality assurance and the minimising of risks in the process.

The self-heating behaviour of similar materials have previously been explored using a number of methods. The long established method is the steady-state method based on Frank-Kamenetskii's theory of thermal explosions [4]. This is a basket heating method which was originally used to estimate self-heating kinetics for activated carbons [5]. The steady-state method is an effective approach based on determining the critical ambient temperatures, the temperature above which thermal runaway will occur, for different basket sizes of material. This is a slow method requiring several experiments to yield a single data point. Developed as a faster alternative, the cross-point temperature (CPT) method is another basket heating method, first proposed by Chong *et al.* [1], and originally used to estimate the self-heating kinetics of skimmed and whole milk powders. Since then, Sujanti *et al.* [2] has used this approach to study coal, and has shown that the steady-state method and the cross-point temperature method estimate similar kinetics. Malow and Krause [6] has also compared these two methods, along with the differential scanning calorimetry (DSC) based Ozawa-Flynn-Wall method to estimate the kinetics of coal dust, cork dust, riboflavin and a detergent powder. This is also one of the few studies that addresses self-heating in detergent powders. Little details were given with regards the detergent powder formulation, but it was shown that the steady-state and CPT methods estimated similar kinetics, giving activation energies of 102(±30)x10^3 J mol^{-1} and 112(±24)x10^3 J mol^{-1} respectively. These errors are relatively large but this is possible due to only 4 and 5 points being determined for the steady-state and CPT methods respectively.

This study draws on this previous work and seeks to determine the best means of estimating the self-heating reaction kinetics of a typical detergent powder, such that the estimated kinetics can be used in a newly developed numerical model and applied to the study of self-heating in detergent powder accumulations. The reaction kinetics have been estimated using three different methods. Two of these are the previously outlined steady-state and cross-point temperature (CPT) methods, which are used to estimate zero-order reaction kinetics. The third method is a thermogravimetric fitting method, adapted from that of Yang *et al.* [7]. This method is used to fit n^{th} order kinetics to mass loss data from Thermogravimetric Analysis (TGA). The kinetics estimated using these methods are compared and the advantages and disadvantages of each method explored.

These kinetics are applied in a newly developed 2D-axistmmetric model of transient heat and mass transfer in a cylindrical basket of detergent powder. This model is adapted from the models of Chen [8] and Chong and Chen [9], which were used to model self-heating in milk powders and explore aspects of the cross-point temperature method. Heat and mass transfer properties of the detergent powder system are measured and the comparison of this model to experimental temperature profiles explored. The properties measured were the self-heating reaction kinetics, the powder drying kinetics, and the effective heat transfer coefficient of the oven. Both the numerical model and the two basket heating methods are based on the same energy balance for a self-heating body, given by:

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

Here, ρ (kg m^{-3}) is the bulk density of the powder, C_p (J kg^{-1} K^{-1}) is the specific heat capacity, k (W m^{-1} K^{-1}) is the thermal conductivity, Q (J kg^{-1}) is the heat of reaction, A (s^{-1}) is the pre-exponential factor of the zero-order Arrhenius reaction, E (J mol^{-1}) is the activation energy, R (J mol^{-1} K^{-1}) the universal gas constant, t (s) the time, and T (K) the temperature. In this energy balance the left hand term denotes the local rate of enthalpy change in the solid, the first right hand side term denotes the conductive heat transfer in the solid, and the final term denotes the heat generation of the zero-order exothermic reaction.

This model is then used to predict temperature-time profiles in these baskets of detergent powder across a range of ambient temperatures. Critical ambient temperatures for baskets of varying size are also predicted. These predictions are then compared with experimental data. The influence of the specific heat capacity, and the differences in predicted temperature profiles from using zero-order and *n*th order reaction models are also explored. In future work, the knowledge acquired here will be applied to predicting self-heating in spray dryer wall build-up.

Materials and Methods

Detergent Powder Composition

This investigation explores the self-heating properties of a model detergent powder. The detergent powder used in this investigation was produced by Procter and Gamble, consisting of surfactant/s, polymer/s, and inorganic salts. This sample was designed as a model compositions that is representative of the spray-dried powder present in a commercial laundry detergent product. The surfactant used is linear alkylbenzene sulphonate, present at levels of approximately 17%, and it is thought to cause the majority of the observed self-heating behaviour in this formulation. A finer grade of inorganic salt was used to reduce the composition variability that can be seen between particles and between different sizes of particles [10]. The particle size distribution of the detergent powder was measured by sieving. The median particle diameter, the diameter for which 50% of the particles are smaller (D_{50}), was measured as 328µm. This has implications in the spacing of the thermocouples used in the Cross-Point Temperature method experiments.

Steady-State Approach

The steady-state approach, sometimes referred to as the F-K method, initially developed by Bowes and Cameron [5], is based on the steady-state dimensionless form of the energy conservation equation (1). It is widely used for determining the zero-order reaction kinetics of self-heating powders and is the basis of the British Standard BS EN 15118:2007. The dimensionless form is obtained by defining the dimensionless temperature, θ, the dimensionless length, ξ, the dimensionless exponent, α, and the dimensionless parameter, δ:

$$\theta = \frac{E}{RT_\infty^2}(T - T_\infty) \qquad \xi = \frac{x}{L}$$
$$\delta = \frac{E}{RT_\infty^2}\frac{\rho QAL^2}{k}e^{-\frac{E}{RT_\infty}} \qquad \alpha = \frac{E}{RT_\infty} \tag{2}$$

Where x (m) is the position, L (m) is a characteristic length, and T_∞ (K) the ambient temperature. The steady-state energy conservation equation can then be expressed as:

$$\nabla_\xi^2\theta = -\delta e^{\frac{\theta}{1+\frac{\theta}{\alpha}}} \tag{3}$$

The Frank-Kamenetskii parameter, δ, is a dimensionless term that encompasses all the quantities required to describe the problem of self-heating, with a value above the critical value, δ_{cr}, leading to thermal runaway. The value of δ_{cr} is a function of geometry, the dimensionless exponent α in equation (2), and the Biot number, Bi, used in defining the dimensionless boundary conditions of this problem. Rearranging δ in equation (2) gives:

$$\ln\left(\frac{\delta_{cr}T_{\infty,cr}^{2}}{L^{2}}\right)=\ln\left(\frac{\rho QA}{k}\frac{E}{R}\right)-\frac{E}{RT_{\infty,cr}} \quad (4)$$

The steady-state approach is based on this equation. A stainless steel equi-cylindrical (cylinder of equal height and diameter) mesh basket was filled with detergent powder and placed in a Memmert UF75 forced convection oven. A type K thermocouple was inserted into the centre of this basket to measure the core temperature. The oven temperature is set and an additional thermocouple was placed near to the basket to measure the true ambient temperature close to the basket. The temperature is measured over a number of hours to determine if the powder undergoes thermal runaway at the oven set ambient temperature. The test is repeated at different ambient temperatures, in 0.5°C increments, to find the critical ambient temperature, above which the basket of powder undergoes thermal runaway, for the size of basket used. Repeating this for baskets of different sizes and plotting according to equation (4) allows the zero-order activation energy and pre-exponential factor for the self-heating reaction to be estimated. In this investigation three equi-cylindrical baskets were used, with diameters of 50mm, 60mm, and 70mm.

δ_{cr} has previously been calculated for common geometries under the conditions of $\alpha=\infty$ and $Bi=\infty$ [11]. In reality, δ_{cr} is influenced by the finite values of α and Bi, and can be found by numerically solving equation (3), in a similar way to Parks [12]. δ_{cr} was found for different geometries and a range of values of α and Bi by finding the greatest value of δ for which a steady state solution exists. A 1D implicit finite difference model was used to calculate δ_{cr} for the infinite slab, infinite cylinder, and sphere, whereas a 2D implicit finite difference model was used to calculate δ_{cr} for the equi-cylinder. This value of δ_{cr} as a function of α and Bi for an equi-cylindrical basket is illustrated in Figure 1. Interpolating this data allows the δ_{cr} value to be found for the α and Bi values used in this study as shown in Table 1. This value is then used when experimentally determining the kinetics of the detergent using equation (4).

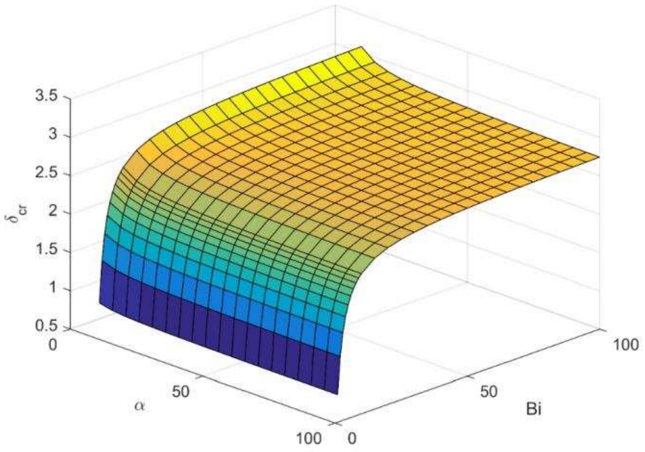

Figure 1. δ_{cr} as a function of α and Bi for an equi-cylindrical basket.

Table 1. δ_{cr} values for common geometries at ideal conditions (left) and at the conditions used in this investigation (right).

	$\alpha = \infty, Bi = \infty$	$\alpha = 32.64, Bi = 7.025$
Infinite Slab	0.878	0.720
Infinite Cylinder	2	1.587
Sphere	3.32	2.621
Equi-Cylinder (height=diameter)	2.844	2.218

Cross-Point Temperature (Transient) Method

The Cross-Point Temperature method is a transient means of determining zero-order self-heating reaction kinetics developed by Chong et *al.* [1]. As a basket of powder is heated in an oven the peripheral regions of the basket reach the oven temperature first. Heat conducts slowly into the centre of the basket and as self-heating begins the core temperature rises above that of the periphery, such that at some time the basket centre and an offset point are at the same temperature. At this time the conduction between these two points is assumed to be zero. The temperature at which this occurs is known as the cross-point temperature (CPT) and at this point equation (1) reduces to:

$$\ln\left(\frac{dT}{dt}\right)\bigg|_{T=T_{CPT}} = \ln\left(\frac{QA}{C_p}\right) - \frac{E}{RT_{CPT}} \quad (5)$$

In this method a basket of powder with a number of type K thermocouples embedded in the powder is heated in a Memmert UF75 forced convection oven. Of these thermocouples one is placed at the geometric centre, and at least one more thermocouple is radially offset from this. For a set ambient temperature the basket is heated and the temperature is recorded at the centre and offset point for the duration of the experiment. From this the cross-point temperature and heating rate at basket centre, dT/dt, is noted. Repeating this for a range of ambient temperatures and plotting the cross-point temperature and dT/dt values for each test in accordance with equation (5) allows the zero-order kinetics to be estimated. Unlike the steady-state approach, every test performed using this method yields a data point. In this investigation, two equi-cylindrical baskets of diameter 50mm and 60mm were used with an array of three thermocouples spaced at distances of 0mm, 6mm, and 12mm from the basket centre, and at basket half-height, as shown in Figure 2. These thermocouples are connected to a Pico Technology USB TC-08 data logger and sampled at a rate of 1 measurement per second. These baskets were heated at temperatures ranging from 222°to 235°C.

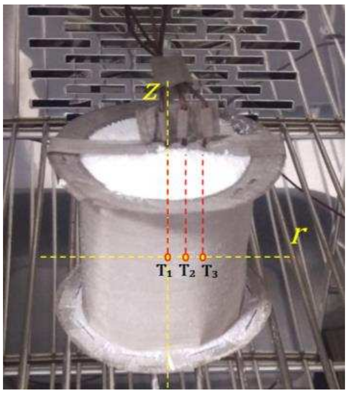

Figure 2. Basket of detergent powder and thermocouple setup.

Thermogravimetric Method

A method adapted from the DTG (differential thermogravimetry) method of Yang et al. [7] was used to fit n^{th} order kinetics to the mass loss curves of detergent powder samples measured using thermogravimetric analysis (TGA) under ramped heating conditions. A sample of powder was sieved into a number of size ranges such that the reactivity of each size range could be compared. A sample of detergent powder, approximately 11mg in mass, was placed into an aluminium pan and loaded into the TA Instruments Discovery TGA. These samples were heated at 5°C min^{-1} from 50 to 500°C in air, with data sampled at a rate of 1 measurement every 0.5 seconds. Mass loss due to initial water evaporation and mass loss which occurs after the reaction were removed from the curves and the data normalised. To this curve the following equation for conversion, α, was fitted.

$$\frac{d\alpha}{dt} = (1-\alpha)^n A e^{-\frac{E}{RT}} \tag{6}$$

The curve fitting toolbox built into MATLAB was used to fit this equation to the experimental data. This tool uses the method of least squares to fit to this data. The best fitting values for the activation energy, E, the pre-exponential factor, A, and the order of the reaction, n, were determined for each TGA experiment.

Numerical Model

This system was modelled using a set of 2D-axisymmetric partial differential equations in the radial direction, r, and axial direction, z, describing the heat transfer and mass transport in a cylindrical basket of powder. The transient energy conservation equation for this system across a basket of radius R (m) and height Z (m) in 2D cylindrical coordinates, adapted from that of Chen [8] and Chong and Chen [9], is given by:

$$\rho C_p \frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2}\right) + \rho Q A e^{\frac{-E}{RT}} + \rho_{sd} H_v \frac{\partial X}{\partial t} \tag{7}$$

ρ_{sd} (kg m^{-3}) is the solid density of the powder particles, H_v (J kg^{-1}) is the heat of vaporisation of the liquid water in the particles, and X (kg kg^{-1}) is the moisture content of the particles on a dry basis. This form of the energy conservation equation makes use of zero-order kinetics.

If the higher order kinetics determined using TGA are to be used then the reaction term is adjusted accordingly to account for the reaction's dependency on the concentration of reactive component, c_{rc} (kg m^{-3}), its initial concentration, $c_{rc,0}$ (kg m^{-3}), and the reaction order, n. The reaction term in equation (7) is replaced with $\left[c_{rc,0}\left(\frac{c_{rc}}{c_{rc,0}}\right)^{n} QAe^{-\frac{E}{RT}}\right]$, and the depletion in reactive component with time is expressed as:

$$\frac{\partial c_{rc}}{\partial t} = -c_{rc,0}\left(\frac{c_{rc}}{c_{rc,0}}\right)^{n} Ae^{-\frac{E}{RT}} \tag{8}$$

The moisture in the system is modelled in two states, firstly as liquid moisture in the particles and secondly as vapour in the voids between the particles. The transport of water vapour through the voids in the basket of particles is described by:

$$\frac{\partial Y}{\partial t} = \varepsilon D_{vap}\left(\frac{\partial^2 Y}{\partial r^2} + \frac{1}{r}\frac{\partial Y}{\partial r} + \frac{\partial^2 Y}{\partial z^2}\right) - \rho_{sd}\frac{\partial X}{\partial t} \tag{9}$$

Y (kg m^{-3}) is the water vapour concentration, ε is the void fraction or porosity, and D_{vap} (m^{2} s^{-1}) is the diffusion coefficient of vapour through the powder voids. X (kg kg^{-1}), the moisture content on a dry basis, can be expressed as:

$$-\rho\frac{dX}{dt} = h_{m,in}A_p n_p(RH_s Y_{sat} - Y) \tag{10}$$

Here, $h_{m,in}$ (m s^{-1}) is the internal mass transfer coefficient, A_p (m^{2}) is the average particle surface area, n_p (m^{-3}) is the number of particle per unit volume, Y_{sat} (kg m^{-3}) is the saturated vapour concentration, and RH_s is the surface relative humidity. Drying of the powder was modelled using the Reaction Engineering Approach (REA). The REA was first proposed by Chen and Xie [13] and is a means of modelling drying kinetics by applying chemical reaction engineering principles. This approach assumes that evaporation is a first order activation process with an energy barrier to overcome, taking the form of an activation energy, while condensation is a zero order process without such a barrier. The REA is a simple and robust approach capable of describing drying behaviour with minimal experiments required to yield the necessary model parameters. The relationship between the REA and other drying theory is unclear, but for this self-heating model where drying is not of critical importance this approach is sufficient. This approach has been used extensively to model the drying of droplets but has also been used to model the drying of layer materials such as silica gel particle layers [13], thin layers of pulped kiwifruit [14], and layers of mango and apple tissues with thicknesses of a few centimetres [15]. In this model, the following Arrhenius equation is used to express the relative humidity at the particle surface:

$$RH_s = \exp\left[-\frac{\Delta E_v}{RT_s}\right] \tag{11}$$

ΔE_v is a correction factor in the apparent activation energy accounting for the added difficulty in drying at low moisture contents. When water covers the entire surface of the solid this correction term reduces to zero, with relative humidity increasing to unity and drying reducing to evaporation from a pure water surface. Drying is not a critical element of this model as it does not impact on the observed self-heating behaviour in these powders, and as such only preliminary testing has been carried out. Using an approach based on that of Chen [16] this REA model was fit to sorption isotherm data, and it was found that for the detergent powder used in this investigation, the correction factor can be expressed as:

$$\Delta E_v = 8.36x10^7 \exp[-13.65(X^{0.09928})] \tag{12}$$

It was found that the choice of values for parameters such as the internal mass transfer coefficient, $h_{m,in}$, and the vapour diffusion coefficient, D_{vap}, have as much of an influence on the predicted drying behaviour as the drying model and correction factor used. Further work is required to properly understand the drying behaviour in these systems. Despite this, the drying model has been included to allow the self-heating model to be more easily compared with experimental results.

Symmetrical boundary conditions are used along the central axes of the cylinder. In the radial direction these are expressed as:

$$\begin{gathered} \left.\frac{dT}{dr}\right|_{r=0} = 0 \\ \left.\frac{dY}{dr}\right|_{r=0} = 0 \end{gathered} \tag{13}$$

Similar gradients in the axial direction apply at $z = 0$. At the exposed boundaries heat transfer is dependent on the external effective heat transfer coefficient, h (W m^{-2} K^{-1}), and mass transfer is dependent on the mass transfer coefficient, h_m (m s^{-1}), such that in the radial direction:

$$\begin{gathered} -k\left.\frac{dT}{dr}\right|_{r=R} = h(T|_{r=R} - T_\infty) \\ -\varepsilon D_{vap}\left.\frac{dY}{dr}\right|_{r=R} = h_m\left(\left.\frac{Y}{\varepsilon}\right|_{r=R} - Y_\infty\right) \end{gathered} \tag{14}$$

Again, similar gradients apply in the axial direction at $z = Z$. The heat transfer coefficient for the oven was determined by using the transient temperature measurement method used by Carson *et al.* [17], where the average effective heat transfer coefficient is back calculated from the transient temperature measured at the core of a black aluminium cylinder. For this oven, the convective heat transfer coefficient was correlated as: $h_{con} \approx -1.93x10^{-4}T_\infty^2 + 0.102T_\infty + 13.71$ (W m^{-2} K^{-1}). The effective heat transfer coefficient is calculated by summing this with the radiative component for the powder basket.

This model was made in gPROMS ModelBuilder and uses in-built solvers to solve this set of 2D model equations. The basket radius and half height were each discretised into 31 points. Having solved this model with discretisations of 62 and 124 points, it was found that 31 points was sufficient to achieve grid independence. The differential equations in this model were solved using central finite difference methods, and a variable time step and variable order implicit Backward Differentiation Formulae (BDF) based solver. The time step in this solver is varied so that the following is satisfied:

$$\sqrt{\frac{1}{n_d}\sum_{i=1}^{n_d}\left(\frac{\epsilon_i}{a + r|x_i|}\right)^2} \leq 1 \tag{15}$$

Here, n_d is the number of differential variables, ϵ_i is the solver's estimate for the local error in the i^{th} variable, x_i is the current value of the i^{th} variable, a is the absolute error tolerance, and r is the relative error tolerance. This means that error, ϵ_i, in the variable x_i is not allowed to exceed $a + r|x_i|$ over a single time step, where the default value for a and r of $1x10^{-5}$ was used.

This model verified against analytical solutions for heat transfer in an infinite cylinder documented by Carslaw and Jaeger [18]. This was done by using a large ratio of axial to radial length such that this model can be assumed to be for an infinite cylinder. The heat of reaction and drying terms were removed for this verification. The model solution agreed with the analytical solution for the discretisation in space and time used. The heat generation aspect is validated later by comparing model predicted and experimentally measured critical ambient temperatures.

Results and discussion

Basket Heating Methods Results

The steady-state approach and cross-point temperature method were carried out as outlined previously with the results shown in Figure 3 and 4. The estimated kinetics, accompanying confidence intervals, and critical ambient temperatures for a 60mm equi-cylinder as calculated from these kinetics are given in Table 2. The steady-state approach is often seen as the standard method for determining the self-heating reaction kinetics for powder systems and has been used extensively to determine such kinetics for powdered materials such as coal, sawdust, and milk powder. Using this approach an activation energy of $125.3x10^3$ J mol^{-1}, and a $\ln(QA/k)$ value of 34.63 were estimated, and these kinetics can be used in the equation for δ in equation (2) to predict critical ambient temperatures for simple geometries of any size. This simple approach is often used when dealing with the problem of the storage of large quantities of self-heating materials.

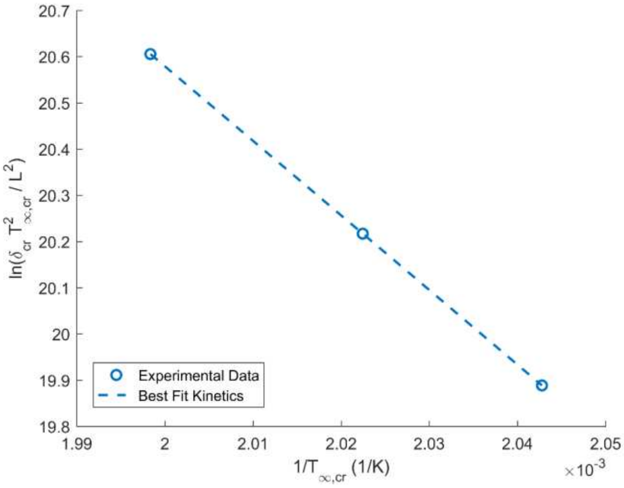

Figure 3. Steady-state approach results using a 50mm, 60mm, and 70mm equi-cylindrical baskets.

The cross-point tTemperature method was developed by Chong et *al.* [1] as an alternative to the steady-state approach, with each test taking far less time and yielding a result. In this investigation an array of three radially spaced thermocouples were used. These thermocouples, as labelled in Figure 2, are T_1 at 0mm, T_2 at 6mm, and T_3 at 12mm from the centre. By having an array of three thermocouple it is possible to evaluate three different cross-point temperatures, as shown in equation (16).

$$Case\ 1: T_1 = T_2; \quad Case\ 2: T_1 = T_3; \quad Case\ 3: \frac{-15T_1 + 16T_2 - T_3}{6\Delta r^2} = 0 \qquad (16)$$

Case 1 and 2 come from a symmetrical three-point finite difference approximation for the second order radial temperature derivative term in equation (1). Case 3 comes from a symmetrical five point approximation for the second order radial temperature derivative term. In a perfect system a five point stencil reduces the order of the error in approximating the second order derivative term from an order of $O(\Delta r^2)$ to $O(\Delta r^4)$. It is worth noting that a similar three thermocouple setup has been used in previous investigations [19], but in each case a three-point second order finite difference approximation was applied to the three thermocouples. In doing this the cross-point was measured at the position of T_2, whereas in this approach, using symmetry, case 3 measures the cross-point temperature at the position of T_1 (i.e. the basket centre).

The results for each case are shown in Figure 4, along with the best fit linear regression to the data from which the reaction kinetics are determined. Experiments run at oven temperatures below 222°C exhibited little self-heating, making the cross-point temperatures difficult to measure at these temperatures and more sensitive to errors in thermocouple readings.

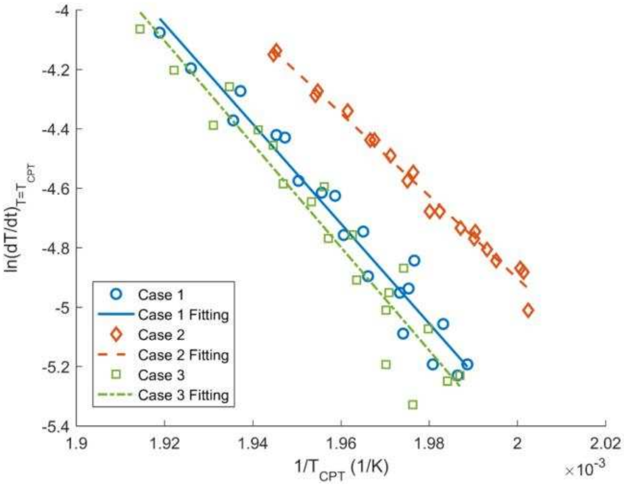

Figure 4. Cross-point temperature (CPT) method results for three cases using a 50mm and 60mm equi-cylindrical baskets.

Table 2. Summary of estimated kinetics for the two basket heating methods and the corresponding critical ambient temperature for a 60mm equi-cylindrical basket.

	$\boldsymbol{E}$ (J mol^{-1})	$\boldsymbol{ln\left[\frac{QA}{k}\right]}$	$\boldsymbol{ln\left[\frac{QA}{C_p}\right]}$	60mm $\boldsymbol{T_{crit}}$ (K)
Steady-State Approach	125.3 (±1.0) x10^3	34.63 (±0.25)	-	221.3
CPT Case 1	139.7 (±14.9) x10^3	-	28.21 (±3.51)	229.1
CPT Case 2	115.5 (±6.4) x10^3	-	22.88 (±1.53)	223.9
CPT Case 3	144.4 (±21.2) x10^3	-	29.24 (±4.99)	229.9

It can be seen that each case gives different results. The activation energies of case 1 and 3, 139.7x10^3 and 144.4x10^3 J mol^{-1} respectively, are very different to the activation energy estimated using the steady-state approach, 125.3x10^3 J mol^{-1}. The kinetics of case 2, with an activation energy of 115.5x10^3 J mol^{-1} and $\ln(QA/C_p)$ value of 22.88, are much more similar to the steady-state approach kinetics. They also predict a much closer critical ambient temperature (223.9°C) to that observed experimentally for a 60mm equi-cylindrical basket (221.3°C). Case 1 and 3 over predict this with values of 229.1°C and 229.9°C respectively. Other work [2] [6] has shown that the steady-state approach and CPT method yield comparable results for coal, cork dust, riboflavin, and a detergent powder. The activation energies for this detergent formulation are greater than those of Malow and Krause [6], although the difference in formulation is unknown. The associated error for the steady-state and case 2 results in particular are considerably smaller than those of Mallow and Krause.

It can also be seen in Figure 4 that the data points for case 2 are much less scattered than the other two cases. This is echoed in the confidence intervals for case 2 which are considerably smaller than those of case 1 and 3, with the confidence intervals of case 3 found to be particularly large. These experiments were simulated using the numerical model and the cross-point temperatures determined for the same three cases. The results of this analysis are shown in Figure 5 and suggest that there shouldn't be such a large discrepancy between the results of these three cases. It does, however, show that a small difference should exists between the cases. This difference is found to increase with an increase in thermocouple spacing. The approximation associated with the cross-point temperature assumption and the finite difference approximations used in equation (16) are thought to be the reason for this difference.

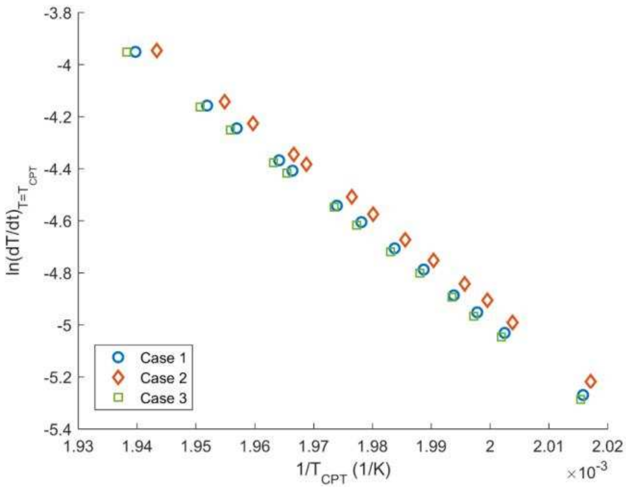

Figure 5. Model simulated cross-point temperature method experiments simulating the same three thermocouple pairing cases as measured experimentally.

Uncertainty Analysis

The errors in this approach can be attributed to a combination of the error in thermocouple readings (±0.25°C) and error in thermocouple placement (±1mm). In the cross-point region, the difference in temperatures across the three thermocouples is quite small, and thus any error in the measured temperatures, be it due to error in thermocouple readings or errors in placement, will have a significant impact on the measured cross-points. Looking across all the 50mm basket experiments, an increase in oven temperature of 1°C corresponds to an average increase in the case 2 cross-point temperature of 1.32°C. With such small differences in cross-point temperatures it is evident that an error in thermocouple readings of ±0.25°C will have a significant impact. Errors in thermocouple placement are difficult to quantify. It is difficult to verify their position because the thermocouples are inserted into the powder after the basket is filled, and thus the approximated error in placement of ±1mm could have a significant impact on the measured cross-points.

These issues account for the errors in measurements, but do not explain the differences observed between the results of the three cases. This difference may be because of the small number of particle diameters which fit into the 6mm gap between thermocouples T_1 and T_2. The median particle diameter is 328µm, such that as few as 19 particles of median diameter could fall within this space, which would heavily influence the case 1 results. This would explain why the confidence intervals associated with the case 2 results are much smaller than those of case 1. A finer grade of inorganic salt was used in this detergent formulation to reduce composition variability and help alleviate this issue. Similar experiments conducted using other detergent formulations, not shown here, without reduced composition variability have had much more pronounced issues when using the same thermocouple spacing of 6mm, and in some cases this variability made it impossible to fit kinetics to the results.

It can been seen from the equation for case 3 in equation (16) that the thermocouple T_2 has a much greater influence than T_3 on the five point finite difference approximation for the second order temperature derivative. This explains why the case 3 results are more similar to the case 1 results, with case 3 also being affected by composition variability and the problem of the small number of particle diameters that fit between T_1 and T_2.

Thermogravimetric Method Results

The best fit of the n^{th} order conversion equation (6) to the normalised experimental conversion curves are illustrated in Figure 6. Samples of different particle size ranges were tested as mentioned previously. All samples reacted similarly showing no significant difference in kinetics across the size ranges measured. This means that the effects of the size distribution of the powder from a reactivity point of view can be considered negligible. A representative fit is shown in Figure 6 and the kinetics given in Table 3. These kinetics were used in the numerical model, making use of the reactive component dependent equation (8). Very little self-heating behaviour was exhibited when using these kinetics at temperatures where notable self-heating would be expected.

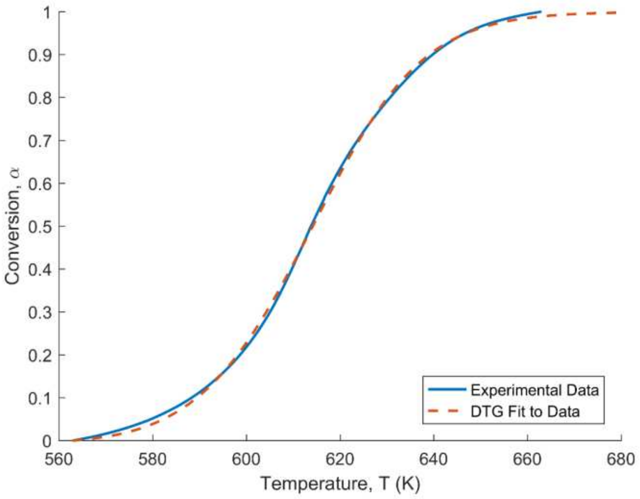

Figure 6. n^{th} order reaction model fitting to the entire TGA measured conversion profile of detergent powder particles of size >212µm and <300µm at a heating rate of 5°C min^{-1}.

In reality, multiple reactions may be occuring within this sample and fitting to the entire thermal degredation, as has been done here, may not be a suitable approach. The oven heated baskets of powder at sub-critical temperatures reached a maximum core temperature of 541K, which is below the reaction onset temperature seen in the TGA experiments. For this reason it is thought that the self-heating seen to occur in the baskets is largely caused by the initial portion of the reaction observed using TGA. Because of this, the fitting approach was applied only to the initial portion of the normalised conversion curve, for $0 \geq \alpha \geq 0.4$, as can be seen in Figure 7, with the kinetics given in Table 3.

These kinetics are more similar to those found using the basket heating methods shown in Table 2. Critical ambient temperatures for the *nth* order kinetics were not determined because thermal runaway is difficult to pinpoint when using an *nth* order numerical model as the reaction is always curtailed by reactive component depletion.

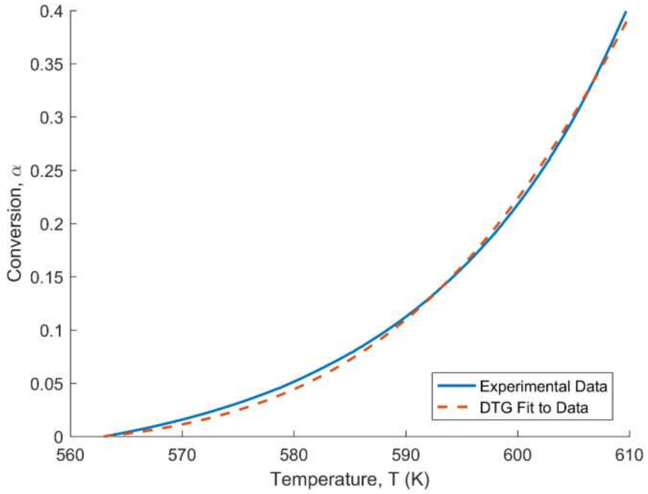

Figure 7. n^{th} order reaction model fitting to the entire TGA measured conversion profile of detergent powder particles of size >212μm and <300μm at a heating rate of 5°C min^{-1}.

Table 3. Summary of estimated kinetics using the Thermogravimetric Fitting Method.

	$\boldsymbol{E}$ (J mol^{-1})	$\boldsymbol{A}$ (s^{-1})	$\boldsymbol{n}$
TGA Fitting (Full Curve)	168.9x10^{3}	3.14x10^{11}	1.531
TGA Fitting (Initial)	136.2x10^{3}	4.10x10^{8}	1.01

Numerical Modelling of Self-Heating Basket Systems

The developed model predicts temperature, moisture content, and vapour concentration profiles in the radial and axial directions of a quarter portion of a cylindrical basket. The predicted temperature profiles are of most interest in this investigation, with the drying behaviour included to allow for a better comparison with experimental data. The evolution of these temperature profiles with time can be seen in Figure 8, showing the capabilities of the model and illustrating how the core of the basket increases in temperature due to self-heating in a typical basket heating experiment.

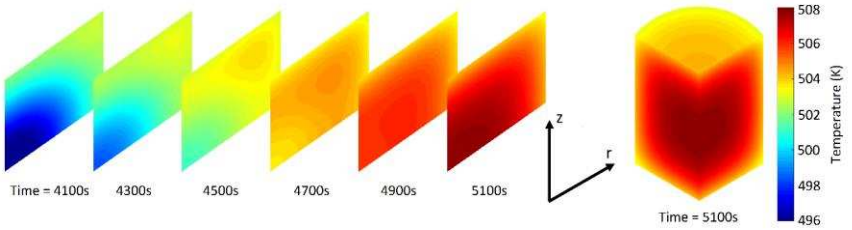

Figure 8. 2D model calculated temperature evolution in 50mm equi-cylindrical basket at and ambient temperature of 502.5K as self-heating causes the core temperature to rise.

The internal mass transfer coefficient, $h_{m,in}$, and the vapour diffusion coefficient, D_{vap}, were unknown and were estimated for this study. Drying is not of critical importance to this study, and as such these values were adjusted to provide reasonable agreement with the drying period of the experimentally measured temperature profiles. The model predicted core temperature and how this compares to the experimental data can be seen in Figure 9. The ambient temperature profile in the model is imported from the experimental data. The increase in temperature of the powder above the oven temperature is of most interest as this is an indication of the self-heating occurring. The kinetics determined using the steady-state method were applied in this model and the good agreement seen in this region suggests that these self-heating kinetics are correct.

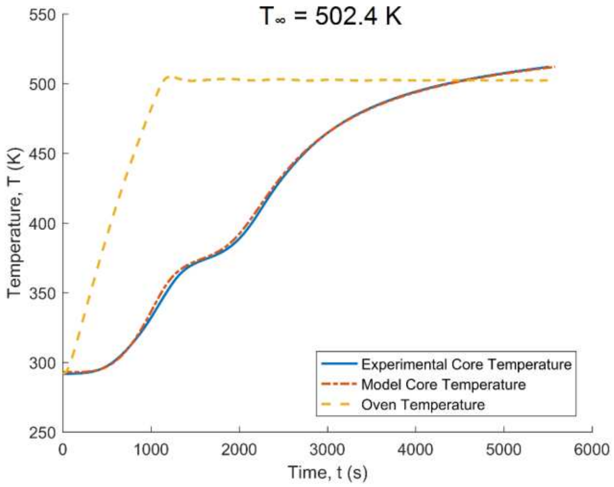

Figure 9. Comparison of model predicted basket core temperature profile and experimental data at an oven temperature of 502.5 K. Kinetics for this model were estimated using the steady-state method.

In this study, the specific heat capacity, C_p, of the powder was unknown, and a known value for similar detergent powders was used as a first estimate. The specific heat capacity does not feature in the equation for the Frank-Kamentskii parameter, δ, in equation (2) and therefore does not influence the critical ambient temperature of these self-heating systems, merely the thermal response time. The effect of varying the specific heat capacity is shown in Figure 10. This figure shows the model predicted core temperature profile of the basket using varying values of C_p and how this compares to the experimentally measured temperature. The temperature profile using a C_p value of 1200 J kg^{-1} K^{-1} is seen to compare best with the experimental data, with lower values than this giving a faster thermal response.

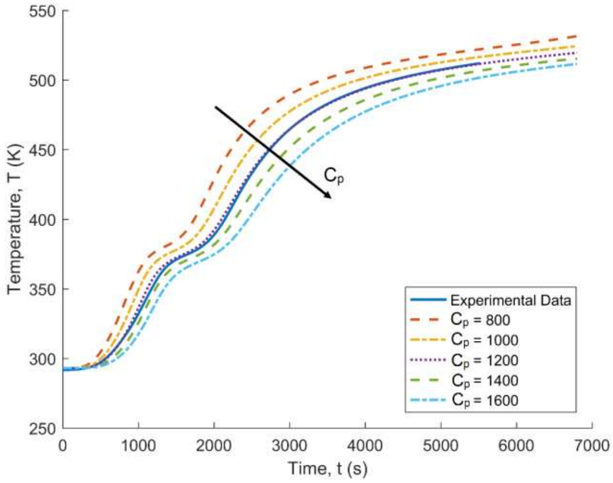

Figure 10. Comparison of model predicted basket core temperature profiles to experimental data using different specific heat capacity values.

The comparison of the model predicted temperature profiles for a range of different ambient temperatures is shown in Figure 11. This figure shows the comparison for the three thermocouples at radial distances of 0mm, 6mm, and 12mm. These plots are for four experiments run at oven controlled ambient temperatures from 498.5K to 504.4K. Again good agreement is seen across these experiments, suggesting that this model is very capable of predicting these temperature profiles.

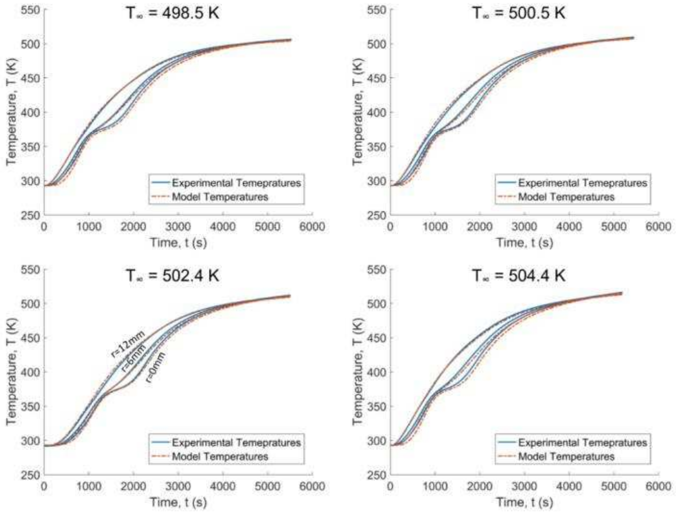

Figure 11. Comparison of model predicted temperature profiles to experimental data from an array of three thermocouples at radial distances of 0mm, 6mm, and 12mm, and at oven temperatures from 498.5 K to 504.4 K. Kinetics for this model were estimated using the steady-state method.

Two different sets of kinetics and their accompanying models were used in this investigation, these being zero-order kinetics as estimated using the steady-state approach, and n^{th} order kinetics as estimated using the Thermogravimetric approach. The steady-state approach kinetics are essentially fit to the experimentally determined critical ambient temperatures. This means that thermal runaway as predicted by the model occurs at the same temperatures as in the experiments. This can be seen in the plot of the basket core temperature profile at a sub-critical ambient temperature in Figure 12 and at a super-critical ambient temperature in Figure 13. This also serves as a validation of the heat generation aspect of the model. Despite this, the same peak temperature is not reached because in reality this is influenced by the depletion of reactive component which is not accounted for in the zero-order kinetics model.

As mentioned previously, the kinetics from fitting to the entire TGA conversion curve were used in the model with little self-heating exhibited. Because of this the kinetics from the initial portion of the reaction were used instead, with this model yielding better results. Despite this, the model predicted temperature profiles are still significantly different to the experimental profiles as can be seen in Figure 12 and Figure 13. The system is seen to react quickly, but as the reactive component depletes the reaction slows and the temperature falls towards the oven temperature. In reality, the oxygen dependency of the reaction and the slow diffusion of oxygen into the basket core may inhibit the rapid increase in temperature generated by the reaction, as seen in this model. Additionally, this model is highly dependent on the value used for the initial concentration of reactive component, $c_{rc,0}$, and this is difficult to quantify. Only the initial portion of the reaction was accounted for when fitting these kinetics, and if it is assumed that further reactions occur at higher temperatures then characterising these reactions and including them in the model may help in replicating the observed behaviour. The added complexity of the n^{th} order model, and the difficulty in getting the model to replicate the observed behaviour makes the zero-order model the preferred choice for modelling these systems. When modelling self-heating in oven heated baskets or in spray dryer wall accumulations such complexity is not required and the zero-order models provide sufficient results.

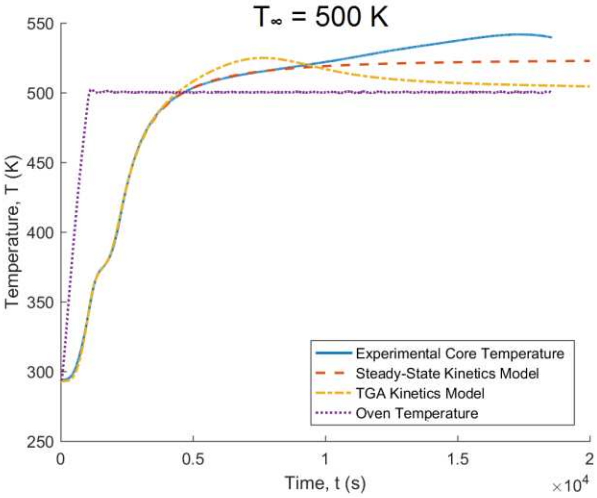

Figure 12. Comparison of model temperature profiles using zero-order (estimated using the steady-state method) and n^{th} order (estimated using TGA fitting to the initial degredation profile) kinetics to experimental data for a 50mm equi-cylindrical basket at a sub-critical temperature of 500K.

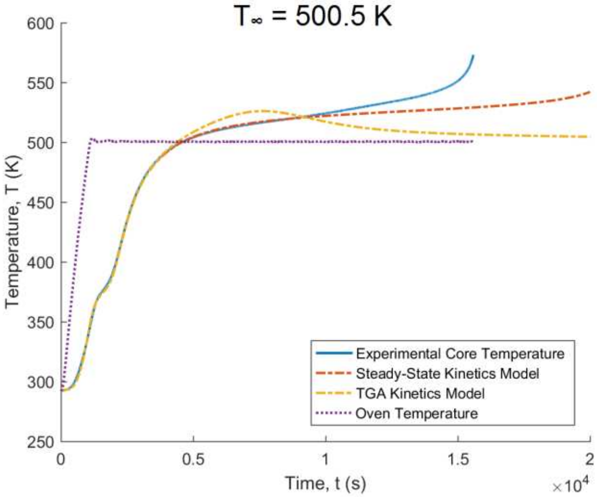

Figure 13. Comparison of model temperature profiles using zero-order (estimated using the steady-state method) and nth order (estimated using TGA fitting to the initial degradation profile) kinetics to experimental data for a 50mm equi-cylindrical basket at a super-critical temperature of 500.5K.

Conclusions

This study sought to determine the best means of estimating the self-heating reaction kinetics of detergent powders. The kinetics determined from the steady-state approach allow a model fit to the experimentally observed critical ambient temperatures to be produced, fitting very well with observed temperature profiles at the early stages of the reaction. The method however is slow with each test taking between 4 and 8 hours, and a number of tests required to obtain a single data point.

The Cross-Point Temperature method is a faster alternative, but this approach is more susceptible to errors. The estimated kinetics using this approach varied depending on the spacing of the thermocouples used. A relatively large spacing of 12mm helps to alleviate issues of composition variability. The kinetics estimated using this spacing predicted thermal runaway for a 60mm equi-cylindrical basket at 223.9°C, only 2.6°C greater than the experimentally measured critical ambient temperature of 221.3°C. A smaller spacing of 6mm produced more variability and kinetics that significantly over-predicted this temperature at 229.0°C. A slight discrepancy in estimated kinetics is expected, as shown using model simulated experiments, but the large discrepancy observed experimentally could be due to a combination of errors in thermocouple placement (±1mm), thermocouple readings (±0.25°C), and the variability caused by the small number of particle diameters that fits in the smaller thermocouple spacing of 6mm.

A numerical model was developed to allow predictions in temperature profiles and critical ambient temperatures to be made. Having estimated a number of parameters, and using a zero-order reaction model with the kinetics estimated using the steady-state method, the predictions of this model were found to agree well with the experimentally measured temperature profiles. This agreement was shown for baskets at a range of ambient temperatures.

The n^{th} order kinetics found by fitting to the entire TGA profile exhibited little self-heating behaviour when used in the model, while fitting to the initial portion of the profile gave kinetics which exhibit more of the expected behaviour. This model can be improved in a number of ways but it is thought that this may merely an over-complication. The much simpler zero-order model compared considerably better to experimental data and such a model is usually sufficient to describe self-heating in these systems.

Future work will see the approaches explored here, and the developed self-heating model used to explore the problem of self-heating in spray dryer wall accumulations.

Acknowledgments

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