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Non-kinetic phenomena in thermal analysis data;

Computational fluid dynamics reactor studies

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Abstract

Computational fluid dynamics (CFD) has been used to develop a characterisation method for the transport phenomena occurring within thermal analysis reactors. This method allows the comparison of different equipment configurations to identify which are most suitable for obtaining intrinsic data. In this work, four equipment configurations are compared from two broad categories; pan-style and tubular reactors. In general, it was concluded that there are both heat and mass transport issues within pan-style and non-uniform diameter tubular reactor configurations and that these should be avoided if extraction of kinetic parameters is the goal. Uniform diameter tubular reactors are suitable for kinetic experimentation, but checks should be made using the dimensionless analysis discussed in this work.

Key Words:

Thermal analysis; computational fluid dynamics; pan-style reactor; tubular reactor; heat and mass transport

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Nomenclature

Symbol	Definition	Units
Letters		
С	Concentration	mol m ⁻³
c _p	Heat capacity	J K ⁻¹
D ^{eff}	Molecular diffusivity	m ² s ⁻¹
d_i	Inner diameter	mm
d _o	Outer diameter	mm
d _p	Particle diameter	m
h	Specific enthalpy	J kg ⁻¹
k	Thermal conductivity	J kg ⁻¹ K ⁻¹
K	Permeability	-
L	Length	m
m	Mass	g
Mr	Molar mass	g mol ⁻¹
n	Moles	mol
n' _R	Reactor mass transfer rate	mol s ⁻¹
$\dot{n_S}$	Sample mass transfer rate	mol s ⁻¹
Р	Pressure	Ра
r_k	Kinetic rate	mol s ⁻¹
R	Universal gas constant	J mol ⁻¹ K ⁻¹
t	Time	S
t_{av}	Average time of experiment	S
t_m	Mean residence time, reactor	S
t_{mp}	Mean residence time, sample	S

Т	Temperature	К
u	Gas Velocity	m s ⁻¹
V _{bed}	Volume of sample	m ³
Greek Letters		
β	Temperature ramp rate	K s ⁻¹
δ_T	Error tolerance on temperature	К
З	voidage	-
μ	Viscosity of fluid	kg m ⁻¹ s ⁻¹
ρ	Density	kg m ⁻³
σ	Variance	S ²

1. Introduction

Within the thermal analysis literature, experimental conditions are often referred to as factors which can influence the kinetic analysis of reactions. These conditions, whether it be sample weight, pressure, gas flow rate or temperature ramp rate [1], [2], all impact the heat and mass transfer occurring within the thermal analysis reactor and sample. Understanding their impact on the internal and external transport phenomena is key to obtaining intrinsic data, hence enabling kinetic analysis.

The terminology of kinetic analysis has a broad interpretation, from complex mathematical modelling, which extracts kinetic parameters, to qualitative evaluation, such as judging 'by-eye' whether a peak has shifted in temperature. Often thermal analysis results are analysed simply: by looking at peak position/shape, onset temperature and peak temperature. Frequently these are only roughly estimated. Even simple qualitative 'by-eye' kinetic analysis will be flawed if transport limitations are present within the experimental data, thus understanding these phenomena is key for thermal analysis.

Gibson et al. [3] presented three thermal analysis case studies, all modelled using the modified Sestak-Berggren equation [4], [5]. Whilst confidence in the model has been established with *in silico* and experimental case studies [3], [4], for some datasets residual trends with temperature ramp rate were present and nonsensical kinetic mechanisms were estimated. These poor fits and anomalous predicted mechanisms imply possible heat and/or mass transport effects were present within the data [3]. Although the Sestak-Berggren method gives some indication that behaviour which is not due to the intrinsic kinetics is present, it cannot currently identify or quantify it. It is worth noting that this is an improvement on isoconversion modelling, where deviations from kinetically limited behaviour may be difficult or impossible to detect.

In this paper, suspected transport limitations present during thermal analysis experiments and their influence on the experimental data are investigated using Computational Fluid Dynamics (CFD). CFD has been used previously to study transport phenomena within thermogravimetric analysis (TGA) reactors [6]– [9]. Comesaña et al. [7] reported using CFD to improve the lag between FTIR measurements and sample weight loss profiles using a top loaded TG-DSC unit. In the same model TG-DSC unit the indium phase change process was simulated [8]. Good agreement between model predicted and experimentally obtained TG curves was observed, with discrepancies noted between theoretical and observed DSC curves. Buczynski et al. [6] used CFD with coupled kinetics to model the decomposition of coal in a suspended TGA. Heat transfer appeared a focus of this work, and it was concluded that discrepancies between measured sample temperatures and CFD modelled temperatures created errors in the activation energy prediction. Benedetti et al. [9] studied the external transport limitations in a horizontal TGA reactor [10] for the decomposition of calcium carbonate, they concluded that the external mass transport issues could have a big effect on the TGA profile obtained for the experiment.

The work presented in this paper investigates the differences in transport phenomena (both heat and mass transport) between four equipment configurations. This will include pan-style TGA reactors and flow through tubular reactors used for other temperature programmed experimentation. A method to characterise and compare these reactors will be discussed, and recommendations for kinetic experimentation made.

2. Modelling Methodology

2.1 The model geometries and meshing

Thermal analysis is a broad class of experimentation and not all types of experiments can be carried out in a single piece of equipment. This has led to varying equipment designs from different manufacturers. This study will investigate four pieces of thermal analysis equipment; generically, there are two classes of equipment design:

(i) where the sample is supported on a "pan". The mass of the samples is thus tracked during the experimental temperature ramp run. The gas flow is around rather than

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directed through the sample. This may be equipped also with exit gas phase analysis, ranging from simple Flame Ionisation Detector (FID) through to Mass Spectrometry (MS). Reactors A and B represent this design class, shown in Figure 1.



Figure 1:Sketch of reactor A (left), reactor B (centre) and sample pan for reactor B (right)

(ii) where the sample is packed into a tube and supported using a plug of quartz wool, with the gas flow forced through the permeable powder sample. This class is not able to track the sample mass, eliminating the possibility of TGA experiments. Calorimetry, thermo-conductivity detector (TCD) or mass spectrometry (MS) are common ways to monitor the progress of a reaction. Reactors C and D represent this through-flow class, shown in Figure 2.



Figure 2: Sketch of rector C (left) and reactor D (right).

All dimensions of the units have been measured with a ruler/callipers, and the 3D drawings were generated using SolidWorks. Meshing has been carried out in snappyHexMesh (OpenFOAM Ltd). A full mesh independence was carried out study was carried out and the resulting number of cells used in the fluid domain for each unit are shown in Table 1.

Table 1: Cell Numbers Used for Meshing

Reactor A Reactor B Reactor C Reactor						
Number of Cells in Fluid Region						
1,567,437	3,703,353	621,652	1,485,645			

Each sample was added as porous zone in the fluid region. The properties of this porous zone are given in Table 6. For the pan-style reactors, a cone has been used to represent the pile of powder (the sample), whereas for the flow-through reactors, the sample is represented by cylinder with a diameter equal to the inside diameter of the reactor tube. For all sample regions, the volume has been calculated based on the mass of calcium carbonate selected for each unit (Table 2).

For the flow through equipment (reactors C and D) quartz wool is required to hold the sample in place. This quartz wool has been added as an additional region and is also represented by a cylinder of equal diameter.



Figures 3 shows an example image of the resulting mesh, for reactor C.

Figure 3: Example of mesh, reactor C

2.2 CFD simulations

These simulations were solved in SmartFOAM[©] version 5.0.0, a user-friendly GUI based on OpenFOAM[©] version 4.2, using a finite volume methodology.

Figure 4 outlines the workflow for these simulations. The aim of these simulations is to investigate the mass and heat transport within the thermal analysis reactors, using simple simulations. To make the following results as general as possible, no specific reaction terms have been applied.



Figure 4: Workflow for CFD Simulations

The conditions shown in Table 2 represent the sample mass and carrier gas flow rates used within the CFD simulations. These are based on standard operating methodology for the equipment studied, or plausible experimental conditions in thermal analysis.

Reactor	Sample Mass (mg)	Carrier Gas Flow Rate (mL min ⁻¹)
A	20	20
A	20	100
В	30	110
С	70	20
С	70	50
D	100	40
D	100	100

Table 2: Sample mass and carrier gas flow rate conditions

2.2.1 Flow Simulations

Steady state incompressible flow fields were solved for all four geometries. The equipment is assumed to be operating at a constant temperature under atmospheric backpressure. These assumptions enable the simplification of the model. Gas properties have been assumed constant as estimated for a temperature in the middle of the ramp, in this case 793 K. Laminar flow was simulated based on Reynolds number calculations; values between 0.4 and 19.3 were obtained for the equipment discussed in this work. The gas was modelled as an incompressible fluid, as the relative pressure drop is sufficiently low that the change in density is negligible, and the problem is treated as isothermal. This approach enabled the rapid generation of representative flow fields for each of the equipment types in the middle of a ramped temperature experiment.

Equations 1 and 2 show the continuity and momentum equations respectively.

$$\nabla \cdot \boldsymbol{u} = 0 \tag{1}$$

$$\rho(\boldsymbol{u}\cdot\nabla\boldsymbol{u}) = -\nabla\boldsymbol{P} + \nabla\,\boldsymbol{\tau} + \boldsymbol{S} \tag{2}$$

In this case, as the gas was assumed to be Newtonian, the viscous stress tensor ($\nabla \tau$) is equal to $\mu \nabla^2 u$, where μ is the fluid viscosity. The source term, S, was set to zero, except in the sample porous region, where Darcy's law was used (equation 6).

$$S = -\frac{\mu}{\kappa} u \tag{3}$$

The inlet boundary condition was set to a uniform velocity profile (normal to the boundary) of the selected flow rate for the simulation. A no-slip wall boundary condition was used for all solid surfaces. The outlet was set to a gauge pressure of 0.0 Pa. Initial conditions for the fluid zone were set to the velocity of the inlet(s), and a gauge pressure of 0.0 Pa.

Additional simulations at different temperatures (298 K and 1000 K) have been performed using the same method outlined in this section. The gas properties at these temperatures are given in Table 4.

2.2.2 Tracer Simulations

The converged flow fields calculated in the previous simulations were fixed and do not require recalculation. A homogeneous species tracer (passive scalar) was introduced into the voids of the sample and released instantaneously. The tracer species were matched to the gas properties used for the bulk flow simulations. This simulation was transient, with the concentration of the tracer monitored for convergence.

In these simulations, the diffusion and convection of the tracer has been accounted for using equation 4. The diffusion properties of the gas and tracer are given in Table 4.

$$\frac{\partial C}{\partial t} + \nabla \cdot (\boldsymbol{u} \, C) - D^{eff} \nabla \cdot (\nabla C) = 0 \tag{4}$$

Monitors were placed on the surface of sample regions to calculate the volume weighted average for the tracer, and the reactor outlet to calculate the mass weighted average for the tracer. The results from these monitors were used to calculate the residence time distributions for the sample and the reactor respectively, during post-processing.

2.2.3 Heat Step Simulation

In this heat step simulation, a small temperature difference between the sample and the reactor wall/inlet was imposed. A difference of 5K was selected, and it was calculated that the change in gas properties with this temperature increase would be negligible (< 1%), hence this simulation was treated as incompressible.

The tube wall and inlet had constant temperature (Dirichlet) boundary condition set to 798 K. The sample and continuum zones were given an initial temperature value of 793 K.

This was a transient simulation solving the energy equation 5, while the flow field was assumed constant. All conditions were the same as the standard flow simulations with the addition of the temperature values. Temperature monitors were placed on the surface of the sample and the outlet.

$$\frac{\partial(\rho h)}{\partial t} + \nabla(\rho \boldsymbol{u} h) = \nabla\left(\frac{k}{c_p}\nabla T\right) + \frac{dP}{dt}$$
(5)

2.2.4 Heat Ramp Simulation

This simulation aimed to simulate heat transfer over a typical ramped temperature experiment. These experiments feature an initial room temperature (298 K) hold for 1000 s, followed by a steady ramp at a rate of 10 K min⁻¹ to a final temperature of 1000 K, finishing with a final temperature hold for another 1000s. The initial hold helps establish flow in the reactor and any baseline signal. The final hold allows time for any ongoing reactions to reach completion and to establish any baseline drift.

The flow fields for a wall temperature boundary condition of 298 K were solved using the methodology discussed for the standard steady-state flow simulation, up to 1000 seconds. This simulates the initial isothermal temperature hold which is common for non-isothermal

thermal analysis experiments. The compressible transient simulation was then started from 1000 seconds.

The properties of the gas change with temperature over this range (298 K to 1000 K) and can thus no longer be assumed constant. This simulation used the same boundary conditions as the standard flow simulations, except for the energy boundary condition for the wall. In this case, a temperature specification was used to incorporate a transient piecewise linear condition show in Table 3.

 Table 3: Boundary Conditions for Heat Ramp Simulation

Point	Time (s)	Temperature (K)
1	1000	298
2	5212	1000
3	5512	1000

This boundary condition simulates the common 10 K min⁻¹ temperature ramp rate experiment used in thermal analysis experiments.

During this transient simulation equations 1-3 and equation 5 are solved. Monitors for the temperature were added to the inlet(s), outlet, reactor wall. A volume averaged temperature was used for the sample. And a point monitor was added at the approximate location for a thermocouple.

2.3 Physical properties of the gas and sample

Temperature	Property	Value Used	Units
	Density [11]	1.204	kg m ⁻³
298 K	Viscosity [12]	1.813×10^{-5}	kg m ⁻¹ s ⁻¹
	Mass Diffusivity	2.2×10^{-5}	m ² s ⁻¹
	Molar Mass	28.97	mol g ⁻¹
	Density [11]	0.48	kg m ⁻³
	Viscosity [12]	3.46×10^{-5}	kg m ⁻¹ s ⁻¹
	Mass Diffusivity	1.0×10^{-4}	m ² s ⁻¹
798 K	Molar Mass	28.97	mol g ⁻¹
	Specific Heat Capacity [13]	31.83	J kg ⁻¹ .K ⁻¹
	Thermal Conductivity [14]	0.05579	J kg ⁻¹ .K ⁻¹
	Density [11]	0.2773	kg m ⁻³
4000 1/	Viscosity [12]	4.788×10^{-5}	kg m ⁻¹ s ⁻¹
	Mass Diffusivity	2.14×10^{-4}	m ² s ⁻¹
	Molar Mass	28.97	mol g ⁻¹

Table 4: Gas properties for constant temperature simulations

The carrier gas used in these simulations was representative of air. The gas properties in Table 4 were used in the constant temperature simulations. For the heat ramp simulations, correlations are used to calculate the properties at each point in the temperature ramp. All correlations take the form of equation 6.

$$\Phi = \Phi_0(a_0 + a_1T + a_2T^2 + a_3T^3)$$
(6)

Table 5 shows the parameters used for the temperature based variations. Density was set to an incompressible ideal gas (equation 7).

$$\rho_g = \frac{m_w P}{RT} \tag{7}$$

|--|

Property	Φ ₀	<i>a</i> ₀	<i>a</i> ₁	<i>a</i> ₂	<i>a</i> ₃	Unit
Viscosity	1.84 × 10 ⁻⁵	9.47 × 10 ²	2.18 × 10 ⁰	-5.44×10^{-4}	0.0	kg m ⁻¹ s ⁻¹

Conductivity	5.58 × 10 ⁻²	4.32×10^{-1}	1.25×10^{-3}	-3.58×10^{-7}	0.0	W m ⁻¹ K ⁻¹
Specific Heat	1.08×10^{3}	8.69×10^{-4}	-1.86×10^{-7}	-3.72×10^{-11}	0.0	J kg⁻¹ K⁻¹

The properties of the solid sample and quartz wool support material are given in Table 6. The sample properties were based on calcium carbonate, to ensure values are realistic.

Table 6: Solid properties

Property	Sample [15] [16]	Quartz Wool [17] [18]	Units
Density	2710	2200	kg m ⁻³
Specific Heat Capacity	837	720	J kg ⁻¹ K ⁻¹
Thermal Conductivity	0.454543	1.4	W m ⁻¹ K ⁻¹
Voidage	0.4	0.488	-
Viscous Resistance	4.05×10^{11}	1.17×10^{7}	-

2.4 Analysis of CFD Results

From the outlet concentration profiles in the tracer simulations, described in Section 2.2.2, a residence time distribution (RTD) curve can be constructed. These tracer experiments simulate a 'pulse' experiment, so the E curve is represented by equation 8 [19], which was solved using the trapezium rule.

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt}$$
(8)

The mean residence time and variance for the reactor can be calculated using equations 9-10 respectively [19]. These moments are extracted directly from the RTD curve [19].

$$t_m = \int_0^\infty t E(t) \, dt \tag{9}$$

$$\sigma^{2} = \int_{0}^{\infty} (t - t_{m})^{2} E(t) dt$$
 (10)

From the concentration profile taken from the surface of the sample in the tracer simulations, described in Section 2.2.2, a residence time can be estimated. As the time for the tracer

leaving the sample is fast, the residence time (t_{mp}) was taken to be the time for 99.5% of the tracer to leave the sample.

The number of CSTRs in series can be used as an indication of the flow pattern occurring within the reactor. This model is also known as Tanks-in-Series (TIS) [20], shown in equation 11. Whilst this model does have limitations [19], in this work it is used as an analytical tool, rather than a model of the RTD.

$$TIS = \frac{t_m^2}{\sigma^2} \tag{11}$$

An infinite TIS equates to plug flow. The RTD of 5 TIS is usually taken as an adequate approximation of plug flow [20]. Less than 1 TIS implies back mixing is occurring within the reactor. When attempting to extract kinetics, plug flow is desired, hence > 5 TIS.

The estimation of the kinetic rate is a simple approximation, using the typical time for a 10 K min⁻¹. Calcium carbonate has been selected as the material of choice, as this would produce a single thermal event [1], [21]. In this case the kinetic reaction rate was taken to be 7.97×10^{-9} mol.s⁻¹. This simplification allows a comparison of a representative rate of reaction compared to the rate at which material moves inside the reactor, without solving a fully defined reaction model. In the real system, the rates will vary above and below the average rate, but the comparison will be order-of-magnitude correct.

$$r_k = \frac{\frac{m}{Mr_{solid}}}{t_{av}}$$
(12)

The amount of tracer present in the CFD simulation can be calculated from the total pore volume of the sample pile.

$$n_{tracer} = \frac{V_{bed} \cdot \varepsilon \cdot \rho_{air}}{M r_{air}}$$
(13)

From the residence time distribution, the mean residence time was calculated, this is used to calculate the reactor mass transfer rate in mol/s.

$$\dot{n_R} = \frac{n_{tracer}}{t_m} \tag{14}$$

Similarly, the moles of tracer calculated in equation (13) is used to calculate the sample mass transfer rate in mol/s.

$$\dot{n_S} = \frac{n_{tracer}}{t_{mp}} \tag{15}$$

Using these rates, variations of the dimensionless Damköhler numbers can be calculated. The Damköhler numbers are the ratio of reaction to transport timescales. Advective and diffusive mass transport are represented in Damköhler numbers I and II respectively [22]. The dimensionless numbers calculated in this work combine the advective and diffusive transport for each case. While these values are not strictly Damköhler numbers as normally defined [22], they illustrate similar properties, and are thus sufficiently analogous that they shall be referred to in this paper as Da(R) and Da(S) for the reactor and sample respectively.

Da(R) uses the reactor mass transport rate so shows the bulk transport, whilst Da(S) uses the sample mass transport rate, so shows the mass transport inside the porous sample pile.

$$Da(R) = \frac{r_k}{n_R} \tag{16}$$

$$Da(S) = \frac{r_k}{n_S} \tag{17}$$

These Damköhler numbers indicate if the system is mass transport limited. For both of these numbers if Da > 1 then the system can be considered to be mass transport limited [22]. These Damköhler-like numbers contain both advective and diffusive contributions.

If Da < 1 then the system is kinetically limited [22]. This means that the mass transport rate is faster than the reaction rate allowing the reaction to be monitored directly. For pure, or intrinsic kinetics a Da << 1 would be desired.

To resolve the relative impact of the advection and diffusion effects, the Bodenstein number (a mass transfer analogue of the Peclet number) can be used, as described in equation 18.

This is defined as the ratio of the amount of substance introduced by advection to the amount introduced by diffusion [20].

$$Bo = Re \cdot Sc = \frac{d_p \cdot u \cdot \rho_{gas}}{\mu} \times \frac{\mu}{\rho_{gas} \cdot D^{eff}}$$
(18)

In this case, if Bo> 1 then the system is convection controlled. If Bo<1 then the system is diffusion controlled [20]. This can be used in a similar way to the TIS model, to indicate whether conditions match plug flow. For the Bodenstein number a high value indicates plug flow, hence a high value of the Bodenstein number is required for kinetic studies.

2.5 Interpreting the Analysis

Thermal analysis reactors are designed on the basis that they are dominated by bulk flow; hence the evolved gas leaving the reactor is representative of the gas evolved from the sample. This is the assumption which allows for kinetic analysis.

For a reactor to be considered as a point source (equation 19), there either needs to be no possible reverse reaction or the removal of evolved gas must be considerably faster than the generation of evolved gas, such that any reverse reaction may be neglected. Many reactions studied by thermal analysis have reverse reactions, a good example of this is the decomposition of calcium carbonate, so it is not desirable to restrict kinetic study to only unidirectional reactions.

$$\frac{dC_a}{dt} = r_a \tag{19}$$

A plug flow reactor (PFR) assumes there are thin 'plugs' of gas which have uniform composition (in the radial direction) flowing through the reactor. In this case, axial mixing (mixing between plugs) is negligible, this means that the gas exiting the reactor is representative of the gas evolved from the sample. Radial mixing by contrast is "fast", ensuring uniformity of the plug in the direction normal to flow. There is a geometry- and flow-specific offset between the time the gas is released, and the time the gas is detected. This is a simple offset which can be accounted for with suitable models, equations 20 and 21. Note that most solid-state kinetic equations are in dimensionless form, so an appropriate scale factor would be needed to incorporate these into equation 20.

$$\frac{dC_a}{dt} = -u\frac{dCa}{dz} - Ca\frac{du}{dz} + r_a(\alpha, C_a, T) \text{ in sample region}$$
(20)

$$\frac{dC_a}{dt} = -u\frac{dC_a}{dz} - C_a\frac{du}{dz}$$
 elsewhere (21)

Modifications would be required for the traditional thermokinetic models, to account for the inhomogeneity within the sample and the variation in residence time during the experiment. Similarly, if a reverse reaction is possible it must be accounted for in the thermokinetic model.

A CSTR assumes perfect back mixing within the reactor; the concentration is uniform and equal to the exit concentration, shown in equation 22. This means that once evolved gas is released it is instantaneously mixed throughout the reactor.

$$\frac{dC_a}{dt} = u(C_a - C_{a,out}) + r_a \tag{22}$$

For thermal analysis the amount of volatiles released at a specific temperature is the observed variable. Having the concentration uniformly mixed throughout the reactor would distort this. Although this flow pattern is amenable to analytical mathematical analysis, as the RTD for a temperature ramp rate experiment is dynamic, there is no guarantee that this ideal distribution will be present for the whole experiment. Most likely at some point during the temperature ramp, the RTD will become non-ideal/complex. Hence, this flow profile is not desired for kinetic analysis.

In these dynamic experiments, mixing within the reactor is the same as mixing in time, which is the same as mixing across temperatures. This mixing can be simple (like a PFR, where there is a simple time lag) or complex (CSTR or other). Having a complex RTD means that it is no longer possible to simply fit kinetics, because there is no simple relationship between when a gas is measured and the temperature (or time) at which it was released. If the aim of the experiment is to perform kinetic analysis, a simple well understood flow pattern or residence time distribution is desired, such as a point source or PFR.

If a complex RTD is present for example $1 \le TIS < 5$, this equipment may be suitable for kinetic studies however different conditions would be required. A higher flow rate may be possible, which could produce more PFR like behaviour. These conditions should be re-tested to confirm the new flow regime and considerations for pressure drop should also be made before experiments are carried out.

Figure 5 shows the workflow when analysing the dimensionless numbers calculated in this work. This shows the scenarios in which kinetic analysis would be possible (even if traditional models may require some modification), and some scenarios which would not be desired for kinetic analysis.



Figure 5: Interpreting Dimensionless Analysis

The following scenarios are undesirable: stagnant zones/back mixing, CSTR, complex RTD (between CSTR and PFR). Each of these will be complex and changing throughout the temperature ramp experiment, making kinetic modelling infeasible. These scenarios arise in numerous ways, but the root cause is diffusion dominating the mass transport (which is evaluated using the Bo number). Diagnosis of these scenarios using CFD may suggest alternate experimental protocols to improve the flow characteristics of the equipment.

Predictable well defined PFR or point source conditions are desirable for kinetic analysis. PFR behaviour is established using the TIS model and the Bodenstein numbers. Whether a reactor can be treated as a point source (the ideal case assumed by traditional thermokinetic models) will depend on the error tolerance for the temperature within the reactor, and the temperature ramp rate. This relationship is shown in equation (23).

$$e = \frac{\beta \cdot t_m}{\delta_T} \tag{23}$$

If e < 1 then the reactor can be treated as a point source, as the temperature measured will match the temperature at which the gas evolved within error tolerances, as is intended for thermal analysis. However, if e > 1 this indicates the temperature discrepancy will be larger than the tolerable levels, hence the reactor must be treated as a PFR to account for this difference.

Once the reactor mass transport has been considered, and PFR behaviour established, the sample should also be considered. The gas phase within the sample can encounter two conditions: homogeneity and inhomogeneity. If the gas phase within the sample is homogeneous, this would result in a Da(S) << 1, meaning the reaction can be treated as a point source (providing the reactor is also point source). Physically, this means each part of the sample behaves identically.

If the sample has a Da(S) > 1, this implies gas phase inhomogeneity. In this case the sample can be treated as under PFR conditions, providing the reactor is either point source or PFR.

This would require modifications to traditional thermokinetic models (as these assume point source conditions).

3 Results and Discussion

For simplicity, a single example of experimental conditions for each reactor configuration will be presented in this results section, with final dimensionless numbers presented for all conditions tested in Section 3.3.

3.1 Hanging-pan geometries



Figure 6: Tracer simulation results. Top: reactor A, 20 mL min⁻¹. Bottom: reactor B, 110 mL min⁻¹

In reactor A, the walls of the sample pan create a region of low bulk gas velocity, which inhibited the released tracer from mixing with the bulk gas. Back mixing was also observed around the sample pan, as tracer mixes with the bulk flow around the sample stand (3.35 seconds after tracer release). A significant fraction of the tracer remained within the sample pan 7 seconds after release.

Back mixing is also observed in reactor B; the tracer left the sample but travelled upwards and to the right, against the flow of gas. After 2.84 s, a significant portion of the gas remains in the sample pan with only small concentrations leaving the reactor.

These images indicate mass transport issues within the reactor, which were quantified using the reactor residence time distributions shown in Figure 7.



Figure 7: Residence time distributions. Left: reactor A, 20 mL min⁻¹ Right: reactor B, 110 mL min⁻¹

Both residence time distributions in Figure 7 show very skewed curves with long tails. For reactor A this was quantified with a mean residence time of 24.9 s and a variance of 269 s². This is equivalent to a TIS value of 0.09. From the dimensionless analysis, the following values were calculated: Da (R) = 4006, Da (S) = 6021, Bo = 0.6.

For reactor B, the mean residence time was 2.35 s and the variance 5.2 s², equivalent to a TIS value of 0.5. From dimensionless analysis the Damköhler numbers for the reactor and the sample were calculated to be 377 and 321 respectively. The Bodenstein number was calculated as 0.6.

A value of TIS below 1 (i.e. worse than a CSTR) implies either multiple stagnant zones or significant back mixing, which was also observed in Figure 6 (highlighted with green circle). Large Damköhler numbers and low Bodenstein numbers imply there are significant mass transport issues within these pan-style reactors, both in the bulk gas and sample. This is a clear case of a stagnant zone dominated by diffusion. Material is well-mixed within this zone but must diffuse into the gas jet to leave the reactor. The fact that bulk advection away from the sample also appears poor explains why the TIS model is worse than 1 CSTR.

With the current experimental conditions and these reactor geometries, it would be unlikely that a kinetically limited condition could be reached. This means that this pan-style equipment should not be used for kinetic studies.

3.1.1 Influence of Temperature on Residence Time Distribution

The simulations in section 3.1.1 were completed for a mid-ramp temperature value of 793 K. In thermal analysis, large temperature variations within the reactor are expected. To investigate the impact of temperature on the residence time distribution for this reactor, additional flow and tracer simulations were carried out. The temperature for these were taken to be at the start (298 K) and the end of a conventional temperature ramp (1000 K). The same inlet flow rate of 20 mL min⁻¹ was used. Figure 8 shows the variation in the residence time distribution curves.



Figure 8: Influence of Temperature on Residence Time Distribution, reactor A

The variation in these curves is expected because of the dependency of the gas density and other gas properties on temperature. The gas feed to the reactor is a constant standard volume, effectively a constant molar flow. As the gas warms, its density falls and so the actual volume flow of gas and actual velocities in the reactor increase. This leads to a small improvement in mixing and shorter mean residence times at higher temperature.

One implication of this is that because reactor RTD is a function of temperature and gas flow, building an RTD model to resolve the impact of the mass transport within the reactor would be complex, and ultimately not practicable.

3.1.2 Temperature Step Simulation

The objective of this simulation was to evaluate the time required following a thermal disturbance for the equipment to relax to the new temperature. Such thermal lag is common where the flowing heat capacity is insufficient relative to the stasis thermal mass of the equipment. In this case, no enthalpy of transformation (positive or negative) from the sample has been included, so this can be viewed as a least stressing scenario. With an endothermic reaction, the temperature lag in the sample would be worse than the example shown below.

For an exothermic reaction, the temperature of the sample would no longer be related to the wall temperature hence it is possible to get falsification of the sample temperature and even runaway reactions.

Figure 9 shows the lag between the sample and the bulk gas temperature. This is caused by the static heat capacity of the sample and the limited rate of heat transfer from the bulk gas.



Figure 9: Temperature step experiment, reactor B

Ideally a rapid convergence between gas and sample temperatures would be observed. However, the lag time for the sample to approach 0.5 K of the wall temperature for this simulation was calculated to be 70 s; this is 3.9 K min⁻¹, compared to a typical thermal ramp rate of 10 K min⁻¹.

The thermal conductivity and heat capacity value of the solid and gas will impact the shape of the curve in Figure 8. However, as reasonable values (taken for calcium carbonate and air) have been used in this study, it is not expected that this lag issue would be eliminated when using most materials. In reality the size of the lag will depend on at least the heat capacity of the material under study, the rate and energetics of any reaction or phase change which occurs, and the efficiency of heat transfer, which will itself depend on gas flow and

temperature. Most of these factors are either difficult to observe or are the object of study. This makes it exceptionally challenging to calibrate for or model.

3.1.3 Temperature Ramp Simulation

This simulation is the closest approximation to the linear temperature ramp rate experiments which are common in thermal analysis. As above, no enthalpy of transformation was assigned to the sample. This is the most computationally expensive of the simulations and was prompted by the observation that the relaxation time found in the heat step simulation is of a similar order to the imposed ramp rate in a typical experiment, making extrapolation challenging.

It was found that the gas temperature, as measured by the equipment thermocouple, is very close to the wall temperature throughout the ramp experiment. Figure 10 shows the difference between the set wall temperature and the sample throughout the temperature ramp rate simulation.





Figure 10 shows that the difference between the sample and the set wall temperature is dynamic during the experiment. A maximum difference of ~5.5 K occurs early within the temperature ramp. The temperature ramp rate stops after 4221 s, and the difference quickly

reduces to zero. The dynamic nature of this offset is likely due to the varying heat transfer coefficient of the bulk gas- this value increases with temperature, decreasing the offset between the sample and bulk gas.

This dynamic change in sample lag means that calibration is not sufficient to account for the temperature difference between the sample and the wall. Conventionally calibrations are carried out based on the onset temperature for known thermal events. This is carried out at multiple ramp rates and compared to known values. This methodology would not be sufficient to account for the changes shown in this simulation because the temperature lags within the simulation are material and quantity specific, as well as dynamic.

3.2 Flow-through geometries

The tracer simulation results for reactors C and D at 50 mL min⁻¹ and 100 mL min⁻¹ respectively, are shown in Figure 11.



Figure 11: Tracer simulation results. Left: reactor C, 50 mL min⁻¹. Right: reactor D, 100 mL min⁻¹

Figure 11 shows a front of tracer moving through the sample bed (0.64 seconds after tracer release) of reactor C. Due the constriction in the u-tube just after the sample, there also appears significant axial mixing, which is elongated in the thinner leg of the u-tube. Whereas the tube of uniform diameter (reactor D) shows very little axial mixing and the tracer quickly

leaves the sample region. The residence time distributions for these reactors are shown in Figure 12.



Figure 12: Residence time distribution. Left: reactor C, 50 mL min⁻¹ Right: reactor D, 100 mL min⁻¹¹

For reactor C, the mean residence time was calculated to be 1.9 s with a variance of 0.42 s^2 . Although the TIS of 8.3 implies a good approximation of plug flow and the Bodenstein number is higher than 1 (at 4.12), the Da (R) and Da (S) values of 302 and 838 respectively, show that there are still mass transfer issues within this reactor. A higher value for Da (S) than Da (R) indicates that there is an issue with removing the tracer/produced gas from the sample region. In this equipment design, the sample is located just prior to a constriction of the tube. This constriction is causing the high Da (S) value as the gas released from the sample cannot leave the region in a timely manner.

The mean residence time calculated for reactor D was 1.03 s with a variance of 0.01 s². This curve could be represented by 89 CSTR reactors in series, giving a good approximation for plug flow. From dimensionless analysis the following values were calculated: Da(R) = 165, Da(S) = 15, Bo = 20.2. Again, both Damköhler numbers indicate mass transport is still an issue within this reactor, under these conditions, but that it could be plausible to adjust the space

velocity used to achieve a kinetically limited regime within the sample. As the TIS model and Bodenstein number show a good approximation for plug flow, the mass transport in the bulk is most likely to manifest as a small time delay. This time delay would also result in a temperature offset (due to the convolved nature of time and temperature in thermal analysis experiments), which could be calculated. This means that this equipment configuration could be suitable for kinetic studies, depending on the conditions chosen. As a standard kinetic rate has been used here, experimentalists should check expected kinetic rates. For slower expected kinetic rates, this flow rate could be free from limitations. For faster expected kinetic rates, a higher flow rate would be required to be free from bulk flow transport limitations.

3.2.1 Temperature Step Simulation

The heat step simulation for reactor D produced the graph shown in Figure 13. This shows an almost ideal curve, with the sample temperature increasing to match the specified wall temperature very quickly, in less than 0.05 seconds. This fast temperature change is likely due to the sample's contact with the reactor wall; this means that conductance will be the primary mode of heat transfer, rather than via convection (as is the case for the pan-style reactors).



Figure 13: Temperature step simulation results, reactor D.

3.2.2 Temperature Ramp Simulation

Figure 14 shows the temperature lag between the sample and the carrier gas for a dynamic simulation representing a 10 K min⁻¹ temperature ramp rate.





The lag between the sample and the wall temperature is very small for this simulation, again due to the improved heat transfer caused by the contact between the sample and the reactor wall. The magnitude of this lag is consistently less than 0.5 K, which is likely to be tolerable for this type of experiment.

3.2 Comparison of Geometries

The results from the tracer simulations for all equipment configurations and carrier gas flow rates have been collated in Table 7.

Equipmont	Elow Poto	Reactor	Sample	
Equipment	FIOW Rale	Da (R)	Da (S)	Во
Reactor A	20mL min ⁻¹	4006	6022	0.6
Reactor A	100mL min ⁻¹	726	482	3.1
Reactor B	110mL min ⁻¹	378	321	0.6
Reactor C	20mL min ⁻¹	3139	9161	1.7
Reactor C	50mL min⁻¹	302	838	4.1
Reactor D	40mL min ⁻¹	418	78	8.1

Table 7: Comparison of dimensionless analysis results

Reactor D	100mL min ⁻¹	165	16	20.2
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As a standard kinetic rate has been assumed for this dimensionless analysis (as shown in Section 2.4) it is advised that if kinetic interpretation is the goal of experimentation, then an estimate for the expected kinetic rate should be used to re-calculate these Damköhler numbers to determine the suitable equipment and conditions to carry out the experimentation.

3.3 Retrospective look at previous cases

Previous studies using uniform diameter tubular reactors have been successfully analysed using the kinetically limited Sestak-Berggren equation such as the temperature programmed reduction on an FT catalyst [4]. In this study, plausible kinetic mechanisms were estimated along with sensible kinetic parameters such as activation energy for each thermal event.

Gibson et al. [3] discussed a case study of a zinc nitrate catalyst precursor decomposition. This reaction was studied using a pan-style TGA coupled with MS, as a consequence, the TGA and MS data could be modelled separately using the modified Sestak-Berggren methodology [4], [5]. From the parameters estimated, it was possible to predict the extent of reaction for each methodology. For the TGA data set, this used a standard Sestak-Berggren method, however for the MS data the water and NOx signals were analysed separately. In order to construct the composite MS extent of reaction curve, the contribution term estimated for the water peak in the TGA data was used to weight the water and NOx data, allowing both to be plotted on the same axis. This extent of reaction curve for MS data could not have been constructed without the use of the Sestak-Berggren equation and the prediction of the curve contributions. The extent of reaction curves are shown in Figure 15.



Figure 15: Comparison of thermogravimetric analysis extent of reaction and mass spectrometry extent of reaction

The TGA curve in Figure 15 shows the extent of reaction at the sample. However, this is affected by mass transport issues in the solid phase, so does not give a kinetically limited extent of reaction. As the signal has flatlined for a significant time, it can be assumed that all thermal events have gone to completion.

The MS curve in Figure 15 shows a delay from the TGA curve, this is reflecting the residence time distribution within the reactor. The change in curve shape, the delay in the start of the thermal events and the elongated nature of the events, reflects the bulk mass transport / back mixing occurring within this unit.

As the MS curve does not reach 1.0, at least one thermal event has not finished. This emphasises the need for an isothermal hold period at the end of these experiments, to allow all thermal events to reach completion. The possibility of unfinished thermal events should also be considered when baseline correcting such data. In the original study [3] a baseline correction was applied to this data; this may not have been necessary and may have removed relevant data. This highlights the difficulties in trying to analyse transport limited data.

This explains the difference in estimated parameter values from these datasets. They are describing the system at different points in space. The mass spectrometry data are convolved with the reactor RTD; this is reflected in the Da(R) value. From the Damköhler numbers it is observed that neither the TGA nor the MS data are free from transport effects, hence the nonsensical nature of the parameters estimated using the modified Sestak-Berggren model which assumes the data are kinetically limited.

4 Conclusions and Recommendations

4.1 Pan-Style Reactors (Reactors A and B)

Pan style equipment cannot be used for kinetic analysis, including comparing peak temperatures, onset temperatures or shapes of peaks. The only valid information which can be extracted from pan style thermal analysis equipment (most TGA units) is:

- A final residual mass (providing steady state has been observed for a sufficient period of time to be confident that no further reaction will occur)
- Species identification, when coupled with evolved gas analysis (EGA).
- A rough temperature range for a thermal event can be estimated.
- If thermal events are sufficiently separated, species and mass changes can be identified with a relevant event.

Due to the mass transport issues in these reactors, evolved gas is not removed sufficiently rapidly from the sample. For reversible reactions, this means that the reverse reaction could have a significant impact on the results obtained. These pan style arrangements cannot be used to compare different materials, as differing amounts of gas released, and the type of gas released will alter the residence time profiles shown in this report.

The pan style reactors show a significant temperature lag between the sample and the specified wall temperature. This lag is dynamic throughout a linear temperature ramp rate experiment, and worse at lower temperatures. Traditional calibration is insufficient to account

for this temperature lag in the sample. As an accurate measurement for the temperature of the sample is required for kinetic experiments, it is not advised to use these pan-style reactors to extract intrinsic data.

Thermogravimetric analysis experimentation carried out on pan-style reactors could be heavily mass and heat transport limited and these experiments should be analysed carefully, to avoid kinetic parameters which appear dependent on temperature ramp rate [23]. Other reactor configurations are available for TGA and this methodology should be applied when selecting equipment. Novel designs for these thermal analysis reactors could also be considered.

4.2 Tubular reactors (Reactors C and D)

Tubular reactors can be suitable for kinetic experiments, depending on the shape of the tube and flow rates chosen. Specific care should be taken when using reactor tubes with constrictions after the sample bed, as these may not produce intrinsic data.

Tubular reactors with uniform diameters can produce intrinsic data, however these units do not have the capability to carry out thermogravimetric analysis. It is advised that if carrying out kinetic studies, experimenters should either check the expected reaction rate from literature or generate a rough estimate after initial experiments.

Tubular reactors show a fast temperature change when perturbed and a minimal lag between the specified wall temperature and the sample temperature for a simulated linear temperature ramp. The contact between the sample and the walls of the reactor aids in conductance, resulting in good heat transfer. It is expected that these good heat transfer properties would be retained in any tubular arrangement where the sample is in contact with the reactor walls. This tendency for good heat transfer reinforces that these tubular reactor types would be the most suitable for kinetic experimentation.

4.3 Other Learning

This dimensionless analysis has confirmed the uniform diameter tube style reactors operate in a plug flow regime, which means a reaction may not be treated as a point source. Currently models for solid-state reactions, including the modified Sestak-Berggren model, assume a point source. These kinetic models would require adaptation for plug flow behaviour.

Trivially comparing results between equipment types should be avoided. Comparison between reactors is only valid if it can be shown that the properties of the sample are measured, rather than the properties of the reactor. Each reactor type in this report has differing degrees of mass transport issues; these would need to be accounted for, which is not always trivial, prior to any comparisons being made. It is important to be aware of the transport limitations possible within the equipment chosen for a given experiment.

The authors make the following recommendations for the interpretation of thermal analysis data:

- For kinetic studies, uniform diameter tubular flow through reactors should be used.
- When preforming kinetic analysis on any thermal analysis data, residual trends with ramp rate should be analysed, as these can indicate the presence of heat/mass transport effects.
- Pan style or non-uniform tubular reactors should not be used for kinetic studies.
- Pan style or non-uniform tubular reactors should not be used to compare different materials.
- Thermal analysis results obtained using different equipment should not be directly or trivially compared. Comparison may be possible but requires careful analysis and a full understanding of the mass transport occurring within the reactors in question.

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