

Cranfield University

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Material Chemistry Control for the Additive
Manufacture of Composite Propellants

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ABSTRACT

This thesis has sought to aid the additive manufacture of propellants using a novel dry powder printing system developed at Cranfield. The energetic performance and hazard safety of crystalline energetic materials is intrinsically linked to crystal properties such as size, morphology, and crystalline phase. By optimisation of cooling, antisolvent, sonocrystallisation, spray drying and microencapsulation, the properties of cyclotrimethylenetrinitramine (RDX) and ammonium perchlorate (AP) have been engineered towards better performance within our printing system.

Crystallisation of AP from solution in water has been assessed as a means of producing particles with a controllable particle size and morphology. Slow cooling processes ($-7.5\text{ }^{\circ}\text{C hr}^{-1}$) failed to produce material suited for use in propellant formulations. However, by significantly increasing the nucleation rate using rapid cooling crystallisation processes ($\sim -5\text{ }^{\circ}\text{C min}^{-1}$) the size of generated crystals was greatly reduced, with a d50 range of 79.1 - 152.3 μm , compared to $\sim 500 - 2000\text{ }\mu\text{m}$. The application of ultrasonic radiation via a horn to the rapid cooling crystallisation gave promising results – leading to particle size reduction (d50 range: 33.5 – 43.4 μm) and a reduced frequency of secondary nucleation. Moreover, the average particle size distribution width was reduced from 245 μm to 75 μm by the application of sonication. Flow character, as assessed by angle of repose measurements, was good for these sonicated materials (31.0° to 34.1°).

Spray drying and micro encapsulation was assessed as a means of RDX particle size reduction. Initial studies using paracetamol as an inert simulant demonstrated that modifications to spray drying process parameters (flow, atomisation pressure, nozzle diameter and feed concentration) produced measurable changes in particle size and size distribution. However, attempts to rationalise these effects using a multifactorial design of experiment were inhibited with the significant errors retrieved from the model. Attempts to understand how particle properties impact the flow character of a powder led to the observation that increased particle size gave decreased angle of repose.

However, the magnitude of change was negligible when compared to the effect of reformulation in the presence of known glidant nanomaterials.

Microencapsulation of RDX with cellulose acetate butyrate (CAB) was conducted at a range of operating temperatures between 55 and 100 °C. Both particle morphology and impact Figure of insensitiveness were demonstrably affected by drying temperature, and both were minimised by the use of lower drying temperatures ($d_{50} = 2.60 \mu\text{m}$, $F_{ol} = 102.0$). F_{ol} values for RDX/CAB microparticles correlated negatively with drying temperature, suggesting that the strain imparted by this rapid crystallisation process may be retained in the material thereby acting to influence its hazardous nature.

Crystallisation of RDX by antisolvent precipitation and spray drying was assessed with the inclusion of five different tailor-made additives (TMAs). Of the assessed TMAs, 2,4-dimethyl-1-nitrobenzene and 1,2-dimethyl-3-nitrobenzene were noteworthy for causing significant particle size reduction of antisolvent precipitated RDX. Crystal size enlargement and aspect ratio elongation was most pronounced when 1,3,5-triazine-2,4-diamine impurity was present. A novel application of the Scherrer equation was employed, to study the effect of TMA inclusion on the constituent crystallites within spray dried microparticles. The investigation revealed reduced coherence length of the (002) plane and extension of the (210) plane when RDX was spray dried in the presence of TMAs.

Keywords:

Cyclotrimethylenetrinitramine, ammonium perchlorate, paracetamol, RDX, AP, sensitiveness, powder flow, microstrain, spray drying, microencapsulation, sonocrystallisation, tailor-made additive, habit modification, Kissinger, Williamson-Hall, Scherrer equation.

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1 Introduction

Propellants are materials that, when initiated or burnt, undergo a rapid exothermic reaction in which stored chemical potential is converted into vast quantities of hot pressurised gas. Motion of the kinetic energy rich gaseous decomposition products is confined, along a gun barrel or through a rocket motor central port and nozzle, to generate the thrust required to achieve propulsion of a projectile or rocket.

Conventional manufacturing of propellants is generally effective, safe, and reliable. However, as with most conventional manufacturing technologies, it is not as versatile as additive manufacture. Versatility is used here in a broad sense. Additive manufacture can allow for the production of propellant grains with geometries and formulations that are inaccessible by conventional means. This research has sought to control the solid feed material for a novel form of additive manufacturing developed by researchers at Cranfield. The properties focused on include:

1: Safety: Aside from reformulation of the binding system, to improve the elastomeric properties, significant improvements to the safety of energetic materials can and have been attained through control of energetic crystal morphology, size and quality. Since our additive manufacture system involves handling large quantities of sensitive dry crystalline energetic materials, it is crucial the safety characteristics are optimised. Herein, spray drying and microencapsulation have been used to desensitise powders with respect to initiation due to impact.

2: Flowability: Since our printing system relies on direct deposition of dry powder, with flow mediated by hopper vibration, it is critical that the flow character of feed stock is known since disruption to the powder flow can result in failed prints. Moreover, confidence that powder will flow reliably allows the manufacturer to produce parts with minimal direct intervention from a safe standoff position. Flowability of materials depends on particle size, morphology,

and surface interactions - through process and formulation control the flow character of fine to coarse powders have been assessed and optimised.

3: Storability: Storage of powders over long periods can result in caking. This is especially prevalent in materials with hygroscopic properties, such as ammonium perchlorate - a principal component of composite propellants. Caking of materials can be caused and prevented by a variety of factors. The most common causes being either incorrect storage, which is beyond the scope of this research, and the slow release of occluded solvents. As with flowability modification, the prevention of caking can be achieved by postproduction modification, regularly using the same materials as flow modification. However, the reduction of occluded solvent by optimisation of the production process is highly effective and allows for elimination of a postproduction step.

4: Binding: The current system has a robust powder dispensing mechanism but is perhaps limited in the binding functionality, it is hoped that application of binder coatings, through microencapsulation may improve the mechanical properties of our additively manufactured parts whilst also improving the handling safety of these materials.

5: Energetic performance: The burn pressure and burn rate of composite propellants is a complex subject, that can loosely be attributed to the quality of material mixing, particle size and various other inherent material properties such as porosity and polymorphism. Predictions of the energetic performance of AP has been conducted for a range of particle types using kinetic thermal analysis.

This thesis is presented in the following structure: Initially a background on propellants, additive manufacture and crystalline materials is given. Recent literature is then critically reviewed in a separate chapter. This is followed by a materials and methodology chapter which contains details of the raw materials, crystallisation kit, general crystallisation processes, and analytical techniques used throughout this work. Results and discussion are presented in a single, subdivided, chapter followed by my conclusions and expected future research areas.

2 Background, context and theory

2.1 Composite propellants

2.1.1 Overview

Energetic materials which functionalise the conversion of chemical potential to kinetic energy are referred to as propellants. During the exothermic decomposition of a propellant, oxidation of fuels releases gaseous products at high temperature and under great pressure. The gasses are then expelled from the propellant grain with a gas mass flow rate q and an exhaust velocity V_e . The product of these two properties is thrust, a reactive force that acts in the opposite direction to the exhaust velocity, Equation 1.

$$F = q \cdot V_e \quad (1)$$

Like all energetic materials, propellants must contain both fuel and oxidising components which may be in solid, liquid or gaseous states. This research shall focus exclusively on solid state propellants. Solid propellants can be split into two categories: double base derived or composite. Double base propellants conventionally consist of nitrocellulose plasticised with nitro-glycerine that may be either cast (CDB) or extruded (EDB) into propellant grains [1]. Unlike double base propellants which combine fuel and oxidising functions at the molecular level, composite propellants are a heterogenous mixture of solid oxidiser and metallic fuel particles suspended in a continuous polymer matrix [2]. Figure 1 shows a chronology of development for the two propellant systems.

Within the two classes of propellant there exists a wide variety of subtypes, as is illustrated by Figure 1. The relative value of each type is strongly dependant on the purpose for which the propellant is required, which will constrain factors such as the desired burn rate or operating temperatures. Heavy propellant grains, such as those found in strategic missiles or space boosters are typically case bonded composite propellant. Whereas the lighter free standing grains used in tactical missiles tend to be made of either double base or smokeless CMDDB propellant [2].

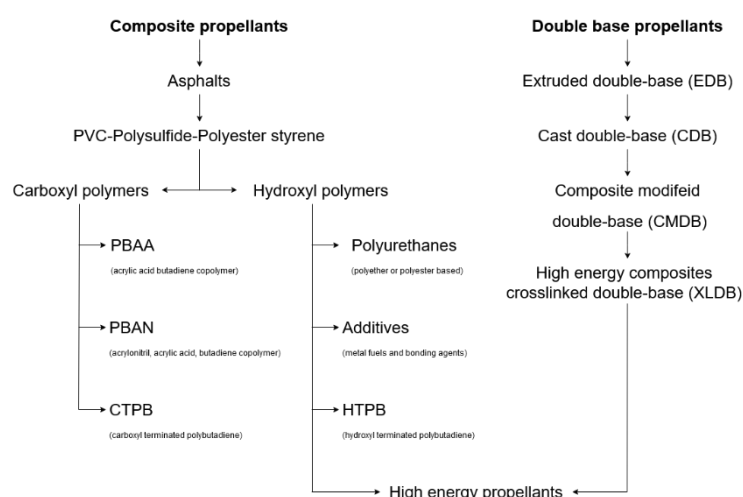


Figure 1: Chronological development of composite and double base propellants [2]

2.1.2 Composite Propellant Formulations

2.1.2.1 Fuel, Oxidiser and Binder

Across composite propellants, the most common combination of oxidiser, fuel and binder is ammonium perchlorate (AP), aluminium (Al) and hydroxyl-terminated poly-butadiene (HTPB) [3]. Ammonium perchlorate possesses features such as high density, thermal stability and exclusively gaseous decomposition products that are very amenable to generating propulsive energy [3–5]. The combination of these properties with ease of processing and storage have led to its widespread use as an oxidiser for tactical missiles and civil space exploration. Decomposition of AP composite propellants has been extensively studied, and models exist that link formulation, processing and performance [6,7].

Desirable fuels for composite propellants are those which form stable oxidation production and thus yield considerable energy when burnt. Carbon and hydrogen in the polymer binder are readily oxidised to yield stable gaseous products. However, the energetic yield of decomposition can be improved by inclusion of polarising metal powders such as magnesium and aluminium, or metalloids such as boron. Due to its high density (compared to organic polymers), commercial availability in the form of spherical powders and ease of handling due to the inert oxide coating, aluminium is most prevalent metal fuel

[4]. Use of aluminium nanomaterials has been shown to further increase the energy output [8,9]. Application of coatings to micronized aluminium has been shown to enhance their performance by the prevention of agglomeration and reduction of the inert oxide layer thickness [10,11]. Although less common due to respective lack of energy and high toxicity, magnesium and boron are occasionally used in propellant formulations; acting both as fuels and burn rate modifiers via condensed phase heat release mechanisms [12].

One of the major drawbacks of AP as an oxidiser is the decomposition product hydrogen chloride (HCl). From a practical sense, this corrosive waste material is damaging to both the launch apparatus and the environment. From a tactical standpoint, the extremely hygroscopic nature of HCl fumes is undesirable as it causes nucleation of atmospheric moisture to form a clearly visible smoke trail, as shown in Figure 2 [13,14]. To combat the issue of smoke trails, research into ammonium nitrate (AN) as a replacement oxidiser has been gaining traction. Issues posed by AN such as low burn rate, lack of energy and multiple solid-solid transitions within the range of munition operating temperatures inhibited widespread use. Though such issues are now being reconciled through the use of catalysis, inclusion of metallic fuels and energetic binders, and phase stabilisation respectively [15,16].



Figure 2: Burn trails of smokeless (left) and perchlorate (right) propellants [17]

Increasing demand for a smokeless high energy propellant system, led to the substitution of the AP/Al composition with nitramine energetic materials, primarily RDX and HMX, Figure 3. These organic materials, while traditionally used as brisant explosives due to their high detonation velocity, are rich in potential energy because of their endothermic enthalpy of formation, and thus give increased specific impulse when burnt [4]. Unlike the traditional fuel and oxidiser combinations previously mentioned, employing nitramines as a source of energy offers little scope for tailoring the stoichiometry of a formulation due to their fixed oxygen balance. Both RDX and HMX have negative oxygen balance (OB%) values – both equal to 21.61 % [18]. To maximise the energy density of nitramine based formulations, high energy propellants substitute the carbon rich HTPB binder for energetic polymers such as GAP or NC [19,20].

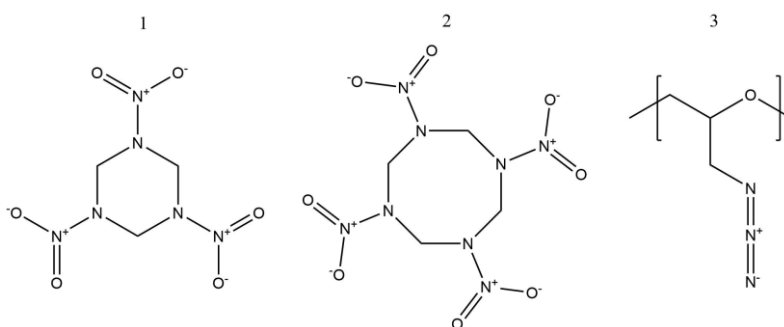


Figure 3: Chemical structures of (1) RDX, (2) HMX and (3) GAP

2.1.2.2 Additives

Regardless of the main components in the formulation, additives are always present in low quantities (<5 wt.%) to moderate various properties of the propellant. A number of reviews exist, and critical additives are summarised below [6,21]:

- Curing agents catalyse chain extension and crosslinking reactions of binder, modification of chain extension to crosslink rates has a significant impact on the mechanical properties of a propellant grain.
- Plasticisers such as iso decyl pelargonate (IDP), dioctyl adipate (DOA), dioctyl azelate (DOZ), dioctyl sebacate (DOS), and diethyl phthalate (DEP) are commonly used in composite propellant formulations to modify the temperature dependence of elastomeric binders [20]. This is especially important for binders with glass transitions temperatures above room temperature, such as GAP and CAB [22].
- Bonding agents increase the adhesive forces active at the interface between discrete solid and continuous binder phases, preventing dewetting [23].
- Surfactants reduce the viscosity of uncured propellant formulations, resulting in improved mixing, reduced liquid migration and better handling of the uncured slurry. Inclusion of sodium lauryl sulphate at concentrations as low as 0.005 wt% relative to HTPB has been shown to reduce the viscosity by 30% [24].
- Burn rate modifiers catalyse various decomposition routes, offering acceleration or deceleration of burn rate, thus allowing for control over the thrust generated by a propellant, the decomposition of AP is particularly sensitive to metal oxide catalysis [25].

2.1.3 Conventional Manufacture of Propellants

2.1.3.1 Process

Conventional manufacture of composite propellants occurs with four distinct stages: mixing, casting, curing and finishing.

A liquid prepolymer, wetting agents, binding agents and plasticiser are combined and mixed typically with a twin blade mixer, although recent studies demonstrate some significant benefits of using resonant acoustic mixers (RAM) [26,27]. Solids are then added in sequential mixing steps that are chosen to minimize the impact on slurry viscosity. Crosslinking agents and polymerisation catalysts are added last so as to provide the longest time possible to process the uncured formulation into the desired propellant grains [28].

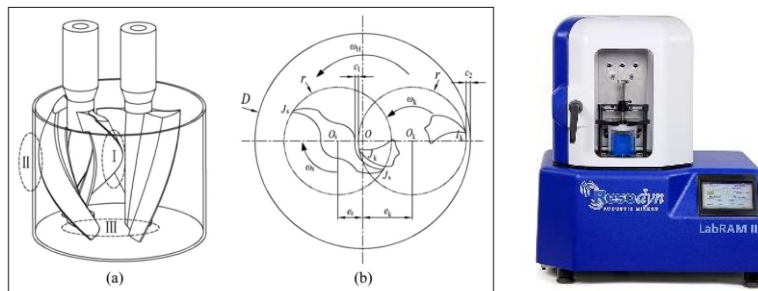


Figure 4: Planetary twin blade and resonant acoustic mixers [29,30]

In the vacuum casting process, the mixture is poured into the mould from above and falls, under gravity, through a slit plate that slices the viscous fluid into ribbons to aid degassing. This process is used for large propellant grains and is not applicable to high performance motors with complex central port designs and narrow grain diameters. Such cases require die-casting, where the propellant formulation is made to flow under application of pneumatic, hydraulic, or mechanical pressure. Critically, mixing and casting steps are always conducted under vacuum to ensure degassing since the formation of a bubble in the grain would have severe effects on both mechanical and energetic performance [4].

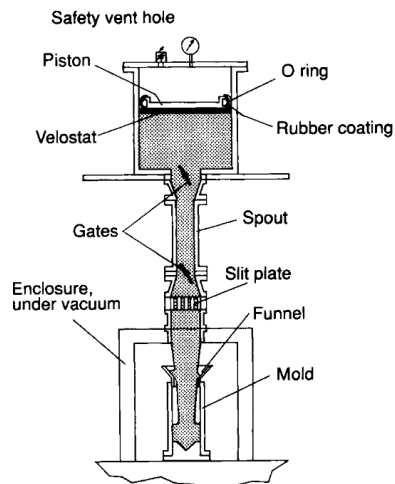


FIG. 10.14. Casting.

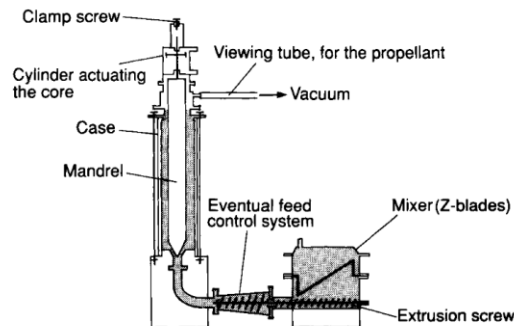


FIG. 10.17. Direct transfer through mixer/extruder.

Figure 5: Gravity and die casting schematics [4]

Curing is a vital stage responsible for ensuring homogeneous polymerisation throughout. Chain extension of butadiene is typically performed prior to the mix, thus curing usually refers to crosslinking of the polyol (HTPB) by the isocyanate (IPDI) to form a solid polyurethane. Polyols are preferred over polyesters as this prevents the undesirable elimination of water into the cast propellant grain. Curing is regularly conducted at elevated temperatures to accelerate polymerisation reactions by aiding any diffusion limited reaction steps via the abating of viscosity increases as the polymerisation runs to completion [28].

Upon completion of the curing step, the part is “finished” – a generic term for any final steps required to transform the part into a usable state. Finishing generally involves removal of the central port mandril and surface preparation. Since this step involves subjecting the energetic material to various frictional forces, it is perhaps the most high risk stage of this manufacturing process [31].

2.1.3.2 Limitations

Composite propellants require high levels of solid content to attain the desired propellant density and specific impulse. The level of solids that may be added is primarily constrained by the impact that their inclusion has on the viscosity of the uncured mix. Through calculations based on solid spherical particles, Farris showed that impact of solid loading on viscosity and how this effect can be negated somewhat by changing the modality of the solids in the formulation, as

illustrated in Figure 6 [32]. Typical composite formulations contain bimodal distributions of AP to achieve 86% solid loading [33]. Trimodal distributions that attain solid loadings of 89% are used in very high performing formulations [34].

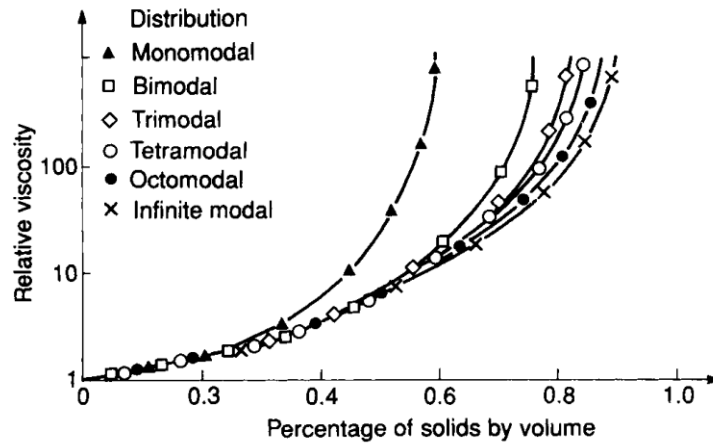


Figure 6: The effect of modality on high solid content composite blends [32]

The impact of high solid loading on the mechanical behaviour of the binder is significant, involving a transition from isotropic elastomeric behaviour into non-linear viscoelastic behaviour due to the presence of solids in the crosslinked binder [35]. Since the solid loading is a fixed requirement, careful formulation of the polymeric binder is required to prevent unwanted responses by the propellant to applied external stresses and strains. Since the 1970s, hydroxyl-terminated poly-butadiene has been the favoured binder: offering higher specific impulse than other non-energetic binders, versatile compatibility with different diisocyanate curing agents and excellent mechanical properties at high solid loading [36]. Cast based manufacturing processes afford limited ability to modify the composition of the propellant grain across a given part. Since the formulation that is cast is by necessity homogenous, any modification to the formulation in each part is achieved either by stepwise casting of separate formulation mixes or, more commonly, by manufacturing separate parts that are then joined in a post processing step. The introduction of phase boundaries between regions of homogenous formulation present a disruption to the otherwise homogenous viscoelastic behaviour of the part, often providing a nucleus for vacuole growth and subsequent failure [37].

2.2 Additive manufacture of composite propellants

2.2.1 Fundamentals of Additive Manufacture

Additive manufacture, abbreviated to AM, is the formal term used to describe the range of manufacturing processes that were once referred to as rapid prototyping or 3D printing [38]. Rapid expansion in both research and application of additive manufacture has affected most industries, prompting some regard as a “disruptive technology” that is driving a new industrial revolution [39].

AM technologies share the commonality of a part being created by stepwise addition of two-dimensional layers known as slices. The part is designed and analysed using three-dimensional computer aided design software (3D CAD, CAD), then converted to an .stl file that represents the various slices that when compiled would represent the original part. Conventional subtractive manufacture such as CNC milling, on the other hand, involves the production of a part by sequential steps in which material is removed from the bulk.

2.2.2 Additive Manufacture of Energetics

A breadth of different processes are enclosed within the general term that is additive manufacturing, details on their mode of operation, advantages and limitations are reviewed elsewhere [39]. Techniques such as selective laser sintering, powder bed fusion or directed energy deposition are not applicable to use with energetic formulations and would pose a significant risk of inadvertent initiation due to the high energies involved. Vat photopolymerization, material jetting and material extrusion appear to be the preferred methods. Some examples are given below as illustrations. More can be found in a review Muravyev *et al* [40].

Vat photopolymerization methods selectively trigger photopolymerization of liquid photopolymer/solid slurry to build a part layer wise. Straathof *et al*, report successful production and testing of a gun propellant grains, shown in Figure 7, composed of RDX, acrylate binder and energetic plasticiser (50:25:25 ratio) by vat photopolymerization [41].

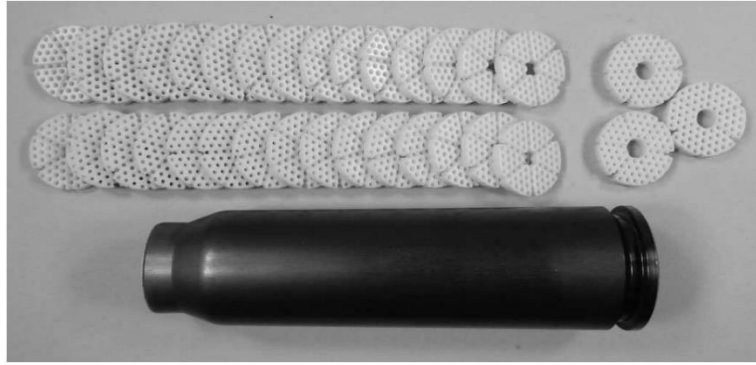


Figure 7: Porous LOVA propellant disks prepared by vat polymerisation of acrylate resin [41]

Additive manufacture by material extrusion involves forcing a paste or slurry through a nozzle. The part assumes form due to the relative movements of the nozzle and the build plate. Paste/slurries contain the solid particles suspended in either a molten thermoplastic as is the case for fused deposition modelling (FDM) printing, or in a rapidly curable prepolymer. Filament preparation for FMD printing can result in severe limitations on the maximum workable solids content, as was demonstrated by print consisting of 20wt.% Al in polyvinylidene fluoride (PVDF) [42]. Extrusion of high viscosity paste, containing >80wt% Al was achieved by application of high amplitude ultrasonic (US) radiation to reduce friction and flow stress [43]. This approach was then successfully applied to production of burn strands with varied porosity, containing AP, HTPB and a photocurable binder, Figure 8 [44]. The resolution of these prints, however, was significantly worse than the printed parts prepared by Straathof *et al.*

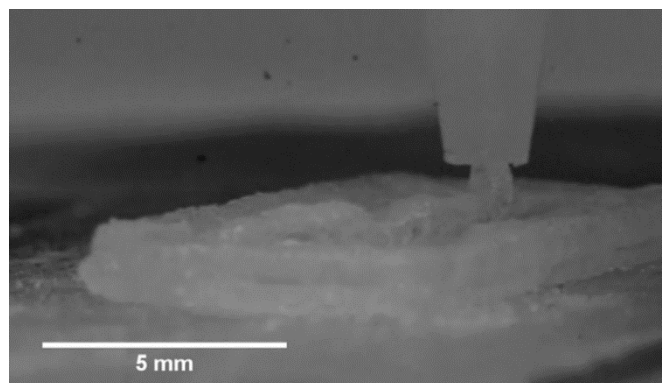


Figure 8: High AP content burn strands prepared by US assisted paste extrusion [44]

Although not strictly relevant, material jetting has been used to additively manufacture nanothermite pyrotechnic structures by *in situ* mixing of fuel and oxidiser suspensions, Figure 9 [45]. The inks used in this print contained <10 vol% solids.

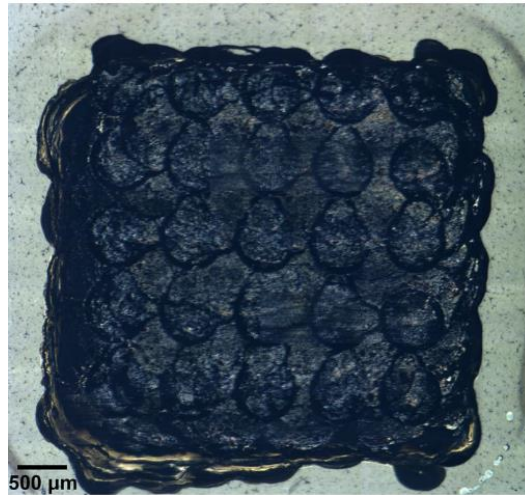


Figure 9: Nanothermite device prepared by material jetting [45]

2.2.3 A novel AM method

The above section has shown several recent examples of successful additive manufacture of propellants, explosive, and pyrotechnics by modifying pre-existing technologies. Ignoring any reported issues of delamination, porosity, or phase separation - all of which will be resolved with time and optimisation - these systems lacked the capacity to process formulations containing the high solid loading levels that are conventionally used in energetic devices. Evidently, McClain *et al*, were an exception, however there is a noticeable reduction of print quality when compared to low solid content formulations [44].

Members of our group have developed a novel mode of additive manufacture [46,47]. The printing system, referred to as powder deposition, was designed and built to circumvent many of the issues posed by additive manufacturing of energetics. As yet unpublished work has demonstrated the capability of this process for the manufacture of explosive charges, composite propellant grains, pyrotechnics and pharmaceuticals. The novel design also allows for continuous modification of composition throughout a given print, a facility that has very significant implications for both the Defence and Pharmaceutical sectors. Propellant grains manufactured using this system are shown below alongside a representation of how the formulation can be modified throughout the print, in Figure 10.



Figure 10: Propellant grains manufactured using the selective powder deposition system at Cranfield, showing complex port geometries and deliberate composition variation [47]

The key behind this success is deviation from the reliance on premixed composite slurry in favour of *in situ* solid-binder mixing on the print bed. While

this system closely resembles the pre-established binder jetting technology, it is distinguishable due to the application of selective solid deposition. The print is prepared by depositing successive layers of solid then binder from a print head with x-y mobility. As the part is formed, the baseplate recedes along the z axis to maintain a constant separation between the surface of the part and the print head. The print head consists of vibrationally mediated solid and solenoid/pressure mediated binder nozzles.

The system may well circumvent the viscosity limitations associated with material extrusion and vat polymerisation, but as with every manufacturing process, the system has its limitations, the majority of which originate from the solid and binder dispensing nozzles. Detailed discussions of the various issues encountered are discussed in the doctoral theses of McGee (2021) and Bonifacio (2022) [46,47].

Crucial to the safe operation of this printer is reliable powder flow characteristics. Predictability of flow character can further aid the process by reduction of the time spent optimising print conditions. Theoretically, the print speed is a function of layer deposition rate and curing time. Improved flowability of powders enables faster print head movement while producing the same layer height.

Safety is a major concern in all energetic manufacturing processes and two key characteristics of the feedstock can be controlled to reduce risk while printing. Firstly, assurance that powder flow will proceed without issue allows for printing from a standoff location thus reducing the severity of unwanted events. Secondly, minimising the sensitiveness of materials towards unwanted initiation reduces the likelihood of an unwanted event.

2.3 Crystalline Solid Materials

With 86-90% of a typical propellant formulation being material in the solid state, appreciation of the material chemistry of solid materials is vital. Matter in the solid state can be characterised as being either amorphous or crystalline. Crystals are defined as homogeneous solid-state bodies with constituent atoms, ions or molecules arranged in a periodically regular arrangement in three dimensions known as a crystal structure. Amorphous materials on the other hand are not constrained by regularity or homogeneity.

When studying amorphous materials, the bulk behaviour of every randomly orientated constituent domain is observed and so these materials are typically isotropic – physical properties are independent of the direction of measurement. Crystals are typically anisotropic and will display differences in properties such as hardness or elasticity, electric or thermal conductivity, electric polarizability and magnetisation depending on the direction of measurement. As such, crystalline materials can often be distinguished from amorphous materials when observed under polarised light due to anisotropy of their refractive index. Exceptions to this generalisation do exist, particularly for highly symmetric materials, for example some cubic system crystals display optical isotropy.

2.3.1 Unit cells, crystal systems, lattices and motifs

A unit cell is an entity from which an entire crystal structure can be derived through repeated geometric transformations. Unit cells are characterised by a metric requiring six lattice parameters: the lengths of each edge (a , b and c), and the angle between the edges (α , β and γ). Conventionally, the coordinate system that describes positions within a unit cell not in orthogonal cartesian axes. Instead, the x , y , and z axes are aligned with unit cell edges a , b and c respectively. The angles α , β and γ represent the interaxial angles between $b:c$, $a:c$ and $a:b$ respectively. The minimum size a unit cell is constrained such that it must represent the point group (every symmetry element possible) for the unit cell whilst also containing the same stoichiometry as the base compound. Every possible unit cell is classified as one of seven crystal systems following these constraints.

The structure of a crystal can be described using the concepts of a lattice and motif. Where the lattice is an infinite arrangement of points in space that have identical local environments and result from translation by the lattice vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$. Each lattice point represents a motif, which details the arrangement of unit cell constituents. When a lattice contains no points besides those located at the vertices it is termed primitive, however, inclusion of lattice points within the unit cell centred at one of the faces (*A/B/C*), within the body (*I*) or on all faces (*F*) produces distinct lattice types. By geometric reasoning Bravais identified the cases in which this centring was valid, yielding seven more lattices to give a total of 14 Bravais lattices, shown in Figure 11.

Table 1: Crystal systems and defining unit cell constraints [48]

System	Interaxial angles	Axial lengths
Cubic	$\alpha = \beta = \gamma = 90^\circ$	$a = b = c$
Tetragonal	$\alpha = \beta = \gamma = 90^\circ$	$a = b \neq c$
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$	$a \neq b \neq c$
Monoclinic	$\alpha = \beta = 90^\circ \neq \gamma$	$a \neq b \neq c$
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$a \neq b \neq c$
Trigonal	$\alpha = \beta = \gamma \neq 90^\circ$	$a = b = c$
Hexagonal	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$a = b \neq c$

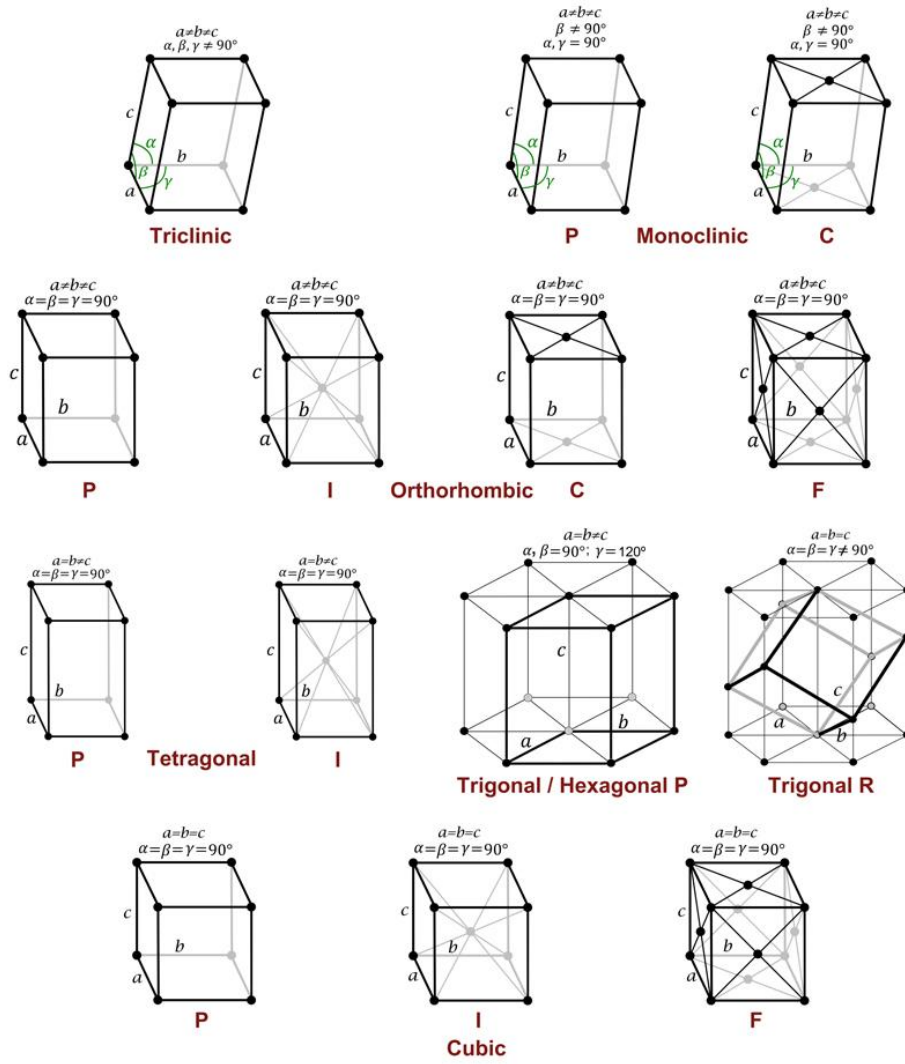


Figure 11: The 14 Bravais lattices [49]

2.3.2 X-ray diffraction and Miller planes

In 1912, Max von Laue suggested that should x-rays be scattered by a crystal to give a diffraction pattern then this would provide evidence of their electromagnetic wave nature. Furthermore, he reasoned that the wavelength of the incident x-rays must be related to the diffraction pattern and atomic separation of the crystal. In 1915, Sir William Henry Bragg and his son Sir William Lawrence Bragg created the first X-ray spectrometer, earning a joint Nobel prize for their efforts. Bragg's equation, Equation 2, describes the relationship between X-ray wavelength (λ) and the angles at which constructive interference occurs (θ).

$$n\lambda = 2d\sin\theta \quad (2)$$

Where d is a vector with magnitude equal to the separation between two parallel crystallographic planes, commonly written in the form d_{hkl} to specify the relevant plane, as shown in Figure 12. n is an integer that accounts for other parallel crystallographic planes.

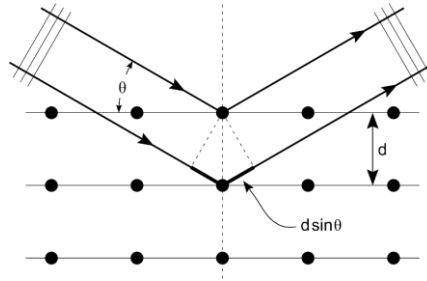


Figure 12: Representation of X-ray diffraction satisfying Bragg's law [50]

Lattice planes are represented using Miller indices h , k and l , that are defined as $h = \frac{a}{X}$, $k = \frac{b}{Y}$, $l = \frac{c}{Z}$ where X , Y and Z are the intercepts of a plane with the crystallographic axes x , y and z . The parameters a , b and c are the X , Y and Z intercepts of the parametral plane that is chosen to define the crystallographic axes and is referenced such that b is unity. The remaining crystallographic planes are described by Miller indices that indicate the reciprocal of their intercepts with the crystallographic axes.

Conventionally (hkl) represents a plane, {hkl} represents a group of planes that are equivalent to (hkl) due to lattice symmetry. [hkl] is essentially a vector with direction normal to the plane (hkl). <hkl> is a group of directional vectors equivalent to [hkl] through symmetry.

The intensity of a diffraction peak I_{hkl} is proportional to the square of the structure factor F_{hkl} which is a summation of the scattering caused by each atom in the unit cell, Equation 3. Atomic positions are represented by fractional coordinates x_j y_j z_j . The scattering factor f_j describes the strength of the scattering interaction and related to the number of electrons around the atom. The extent of long-range order is contained in N_j - the fractional occupation of equivalent positions occupied by atom j . Lower index planes exhibit both higher density of lattice points and greater d spacings, thus impacting their diffraction properties.

$$I_{hkl} \propto |F_{hkl}|^2, F_{hkl} = \sum_{j=1}^m N_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \quad (3)$$

2.3.3 Powder diffraction, polymorphism and phase identification

Powder diffraction experiments involve diffraction of X-rays by the surface layers of a polycrystalline sample (0.1 – 10 μm). Incident photons diffract upon interaction with planes of electron density resulting in diffraction in every direction. Diffraction maxima occur when the incident photon angle satisfies Bragg's law, Equation 2. Thus allowing identification of the d_{hkl} spacings present within the sample. The diffraction pattern can be collected in either one or two dimensions, with the former being a single slice of the latter in reciprocal space.

While it doesn't provide a 3D crystal structure, PXRD is an extremely valuable tool for characterisation of crystalline materials. The unique lattice parameters of different materials or polymorphs allows ready identification due to variation of d_{hkl} value. Controlling the polymorphic form of energetic materials is essential as both the hazard sensitiveness and energetic performance can vary dramatically between phases as is demonstrated by the extensive review prepared by Liu *et al.* [51].

2.3.4 PXRD peak broadening

In theory, Bragg diffraction of a photon with a given wavelength by a defined lattice plane with d -spacing should produce a sharp peak with no width at the expected 2θ value, but this is not the case. The broadening is affected by factors such as the non-monochromatic nature of the incident radiation or the axial divergence of the beams. Fortunately, these effects can be readily accounted for by recording the instrumental broadening observed when an ideal crystalline sample is used, the instrumental broadening can then be de-convoluted from the desired peaks in other experiments.

Sample broadening provides valuable information, as it is determined by crystallite domain size, lattice distortion, structural faults and concentration gradients. Scherrer's equation, Equation 4, relates the volume averaged crystallite size, L , to the broadening, B_L , via the constant K [52].

$$B_L = \frac{K\lambda}{L \cos(\theta)} \quad (4)$$

The appropriate value of K will depend on factors such as peak shape and crystallite habit, but typically it can be taken as 0.9. The reciprocal relationship between B_L and L shows that smaller crystallites give more peak broadening. It should be noted that while this equation can facilitate size calculations, it assumes that all broadening is the result purely of crystallite domain size effects and it neglects the other aforementioned factors.

Strain affecting a crystallite can be either homogeneous or inhomogeneous. Homogeneous strain, such as even compression of the crystallites reduces the d spacing to $d - \delta d$ with the associated peak shifts from 2θ to $2(\theta + \delta\theta)$, as illustrated by Equation 5.

$$\lambda = 2(d - \delta d) \sin(\theta + \delta\theta) \quad (5)$$

In the case of inhomogeneous strain where the various crystallites are strained differently, the resultant range of 2θ values present as a single broadened peak. The relationship between mean inhomogeneous strain, C_ϵ , and the strain induced peak broadening, β_ϵ , can be simplified to $\beta_\epsilon = C_\epsilon \tan(\theta)$. Williamson and Hall noted that the size and strain components of broadening depend on

$\frac{1}{\cos \theta}$ and $\tan \theta$ respectively and thus summation of the two expressions would describe the total peak broadening, β_{tot} , Equation 6 [53].

$$\beta_{tot} = \beta_{\epsilon} + \beta_L = C_{\epsilon} \tan(\theta) + \frac{K\lambda}{L \cos \theta} \quad (6)$$

Multiplication by $\cos \theta$ gives a linear relationship where the gradient is C_{ϵ} and the intercept is $\frac{K\lambda}{L}$. Such a plot of linewidth data is referred to as a Williamson-Hall plot. Unlike the Scherrer equation, the Williamson-Hall expression (Equation 7) accounts for crystallite strain, giving an average coherence length and microstrain value from broadening of the assessed peaks. This technique was developed to study highly ordered metallic domains and is it currently used widely in the classification of metallic nanoparticles [54]. However, there are examples in the literature where this technique has been applied to studies of organic crystals such as pyridine-2-carboxylictrichloroacetate [55].

$$\beta_{tot} \cos \theta = C_{\epsilon} \sin \theta + \frac{K\lambda}{L} \quad (7)$$

An improved method for deconvolution of size and strain broadening was created by Warren and Averbach. Grouping of peaks grouped by common crystallographic direction (e.g. $\langle 00n \rangle = \langle 001 \rangle$, $\langle 002 \rangle$, $\langle 003 \rangle$ where n is the order) overcomes the issue of asymmetrically sized or strained crystallites. Moreover, the separation of size and strain is aided by the dependence of strain effects on order, n , where size effects are independent of order. The results of Warren-Averbach analysis for each given crystallographic direction are an area weighted crystallite size, a parameter related to the crystallite size distribution and an average strain [56,57].

2.3.5 Lattice defects

The existence of a perfect lattice across an entire crystal is very rare. Imperfections cause deformation of the lattice and alter the chemical and mechanical properties. Classification of lattice defects is achieved through dimensionality.

Point defects are zero dimensional imperfections that occur when vacancies, interstitials or substitutional impurities are present. Edge and screw dislocations are common one-dimensional line defects that form due to stress during crystal growth. Two dimensional defects that occur when an entire lattice plane grows out of order, resulting in a dislocation (slip) of the subsequent layers from the initial stacking vector. A defect that grows in three dimensions will typically present as a void, and is often the result of growth around either a solid impurity or occlusion of solvent.

Introduction of these faults into crystals can have a variety of effects on the mechanical and chemical properties [58]. Notably, the frequency of lattice imperfections has been extensively related to the hazard sensitiveness of energetic crystals by providing a hotspot for initiation under the influence of impact or shock [59–62].

2.3.6 Crystal morphology

Since crystallisation involves the production of a novel phase from an initial bulk phase via a condensation process, an interface between novel and initial phases is produced during crystallisation. Formation of an interface entails an energetic penalty as work must be done against the cohesive bulk forces of the mother liquor. The work required to build a unit area of the interface is described by the surface or interfacial tension, γ (Nm^{-1}). Note that *surface tension* refers to solid/vapour or liquid/vapour interfaces whereas *interfacial tension* tends to relate to liquid/liquid, solid/solid or solid/liquid interfaces. Surface tensions of liquids and gasses are isotropic, thus forms such as spheres that minimise surface area are favoured. Immobile and regularly orientated molecules on crystal surfaces cause anisotropy across the surface free energy leading to asymmetric crystal growth.

Gibbs suggested that any crystal of a given volume would exhibit an equilibrium geometry that minimised the total surface Gibbs function of formation [63]. This can be summarised by Equation 8, where A_n and γ_n are the area and surface tension of the n th face. Note that this expression assumes surface tension to be constant across a given face.

$$d \sum_n A_n \gamma_n = \sum_n \gamma_n dA_n = 0 \quad (8)$$

This work was developed by Wulff, 1901, leading to his theorem that: “The minimum surface energy for a given volume of a polyhedron will be achieved if the distances of its faces from one given point are proportional to their capillary constant (surface tension)” [64]. Wulff shape predictions are often inaccurate for real crystals that rarely originate from equilibrium conditions. In general, morphology is a result of kinetic control reflective of the relative rates of growth of each lattice plane. Deliberate interference in the relative rates of growth of each face can be applied to generate a wide range of morphological differences, either through modification of the crystallisation conditions or by introduction of competitive impurities that show selective adhesion to a given face [65].

2.4 Crystallisation of materials

2.4.1 Supersaturate and metastable states

By definition, the chemical potential of two phases in equilibrium are equivalent. Differences in chemical potential between two phases represent a thermodynamic driving force for a phase transition. Supersaturation is the source of chemical potential imbalance, $\Delta\mu$, that causes crystallisation from a solution.

$$\Delta\mu = kT \ln \alpha \quad (9)$$

Where the relative supersaturation, α , is the ratio of real and equilibrium solution concentrations, C and C_0 respectively, T is the absolute temperature and k is the Boltzmann constant. This expression assumes ideal behaviour and that the entropy/enthalpy of the transitions are independent of temperature.

The unfavourable interfacial energy between the surface of a finite crystal and the mother phase provides a chemical potential in opposition to crystallisation. A solution may remain in a supersaturated state for extended periods of time, with crystallisation occurring only when further work is applied to the system. The range of conditions in which a solution may exist in a metastable state is termed the metastable zone, and the extent of the range is known as the metastable zone width.

2.4.2 Homogeneous Classical Nucleation Theory

Volmer developed classical nucleation theory (CNT) to model the first-order transition from a supersaturated phase into a crystal nucleus, the refined model is described below [48]. The nucleation rate, J , is dependent on two factors: the formation of a concentration of critical nuclei $n(i^*)$ at equilibrium and impingement onto the critical nuclei at rate W^* .

$$J = W^* n(i^*) \quad (10)$$

$$n(i^*) = n \exp \frac{-\Delta G^*}{kT} \quad (11)$$

Where n is the concentration of crystallising solute, ΔG^* is the Gibbs' free energy associated with forming a critical nucleus and the exponential term gives the probability of forming a critical nucleus.

The Gibbs' free energy of formation of a cluster composed of i monomers depends on the favourable supersaturation ($\Delta\mu$) and destabilizing product of surface tension γ_n and surface area A_n .

$$\Delta G_i = -i(\Delta\mu) + \sum_n \gamma_n A_n \quad (12)$$

Assuming the cluster is spherical, the above equation becomes:

$$\Delta G_i = -\frac{4\pi r^3}{3v_c} \Delta\mu + 4\pi r^2 \gamma \quad (13)$$

Where r is the radius of the cluster, v_c is the volume of a monomer and γ is the interfacial tension between the cluster and the mother phase. The crystallization process reduces the supersaturation of the system, leaving cluster radius as the dominant term in the expression. Gibbs' energy for crystallisation is therefore dependant on a unfavourable r^2 and favourable r^3 term. At low radius values, the second order term resulting from surface tension is dominant. At higher radius values, the third order stabilizing energy that results from bulk forces dominates.

$$\frac{d\Delta G_i}{dr} = -\frac{4\pi r^2}{v_c} \Delta\mu + 8\pi r \gamma \quad (14)$$

The differential of equation (14) shows that a maximum Gibbs' energy is reached when $r = r^*$ where r^* is the critical nuclear radius.

$$r^* = \frac{2\gamma v_c}{\Delta\mu} \quad (15)$$

Substituting the critical radius into the expression for Gibbs' free energy of formation of the critical nucleus gives:

$$\Delta G^* = \frac{16\pi\gamma^3 v_c^2}{3\Delta\mu^2} \quad (16)$$

Thus, the homogeneous nucleation rate for spherical nuclei is given by:

$$J = \Omega \exp \left[-\frac{\Delta G^*}{k_B T} \right] = \Omega \exp \left[-\frac{16\pi\gamma^3 v_c^2}{3\Delta\mu^2 k_B T} \right] \quad (17)$$

Where the pre-exponential factor Ω is related to the rate of molecular diffusion from the bulk, typical values are $10^{25} - 10^{35} \text{ cm}^{-3}\text{s}^{-1}$ [66].

2.4.3 Generalised thermodynamics

The free energy of a cluster of n monomers is a balance between favourable supersaturation, $-n\Delta\mu$, and unfavourable surface energy. The total surface energy is the product of area and specific interfacial energy at the nucleus-solution interface, $A\gamma = c(vn)^{2/3}$. The shape factor, c , is used to make this function applicable to different nuclei geometries. For small clusters, the total interfacial energy term is larger than the bulk free energy. However, as the cluster grows, the ratio of surface area to volume decreases and the bulk free energy becomes dominant. As a cluster grows it reaches a critical size n^* , often referred to as the “critical nucleus size or radius”, where the bulk free energy balances the interfacial energy. The nucleation work for homogeneous nucleation is:

$$B = \frac{4}{27} c^3 v^2 \left(\frac{\gamma}{kT} \right)^3 \quad (18)$$

Heterogeneous nucleation occurs at the interface between the solution and a spectator phase. In this case, the nucleation work depends on an effective interfacial energy, $\gamma_{HEN} = \psi \cdot \gamma$. The activity factor, ψ , describes the effect of the heterogeneous nucleation surface. When $\psi < 1$, the nucleation work is reducing and thus the surface is deemed an active template.

$$B_{HEN} = \frac{4}{27} c^3 v^2 \left(\frac{\gamma_{HEN}}{kT} \right)^3 \quad (19)$$

2.5 Solution based crystallisations

2.5.1 Generating supersaturation

As illustrated in the preceding sections, the presence and magnitude of supersaturation controls the thermodynamic feasibility of a crystallisation process. Since saturation is the ratio of concentration to equilibrium concentration of a solute in a solution, it follows that modifications of either property can be used to generate supersaturation. Evaporation of solvent, to increase the concentration of solute can be used to generate supersaturation. Alternatively, when the equilibrium solubility of a solute is dependent on temperature, saturation can be controlled thermally. The Van't Hoff isochore describes the relationship between solute activity at saturation and absolute temperature T , where ΔH_{sol} is the partial molar enthalpy of solution of the solute.

$$\frac{d \ln \alpha}{dT} = \frac{\Delta H_{sol}}{RT^2} \quad (20)$$

A commonly used technique to generate supersaturation is that the addition of competitive solutes, that may be solid, liquid or gas, resulting in a reduction of the equilibrium solubility of the initial solute. Most commonly, the competitive solute is a miscible liquid, in which the initial solute is poorly soluble – hence these are commonly referred to as antisolvent precipitations. Terms such as ‘drowning-out’, ‘quenching’ or ‘salting-out’ all refer to this process, and connote the nature of the added substance.

2.5.2 Sonocrystallisation

Crystallisation process that occur in the presence of ultrasound (US) radiation are termed sonocrystallisation, dating back to a first attempt by Richard and Loomis in 1927 [67]. Subsequently, a wide range of investigations have shown that sonocrystallisation can improve crystallisation processes in terms of crystal purity and homogeneity, whilst reducing the induction time thus allowing for faster crystallisation processes. Work conducted by Bhangu *et al.*, on the antisolvent precipitation of paracetamol in the presence of ultrasonic radiation demonstrates the versatility of sonocrystallisation effects and their value to industrial processes [68]. By conducting the same crystallisation in fields of varied ultrasound frequency and power, they were able to correlate the cavitation activity with the rate of nucleation, modify the particle size by an order of magnitude and significantly decrease the particle size distribution. Moreover, in certain cases, the application of sonication to the crystallisation process led to the formation of the metastable orthorhombic form (II) of paracetamol – an industrially desirable polymorph due to the presence of slip planes, absent in the stable monoclinic form (I), that allow for tableting without the need of binder [69]. Sonication of a liquid causes a phenomenon known as cavitation – nucleation of dissolved gasses, followed by growth into bubbles that subsequently collapse. Adiabatic compression of the gas is accompanied by instantaneous high pressure and temperature that produces localised shockwaves and turbulent conditions [70,71].

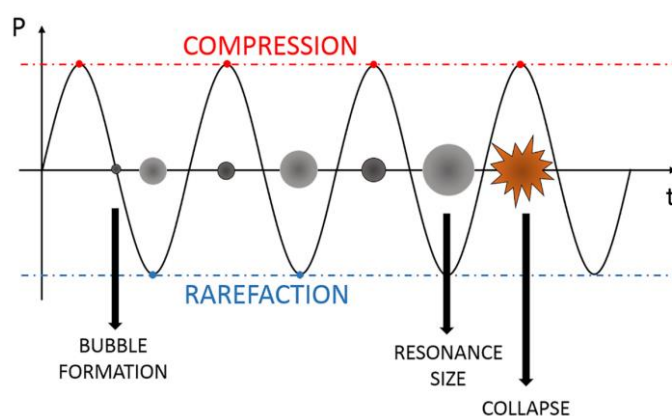


Figure 13: Representation of the cavitation process [72]

Despite a significant wealth of literature detailing the effects of sonocrystallisation on given processes, there is currently no scientific agreement on the principles underlying the effects of sonication. Between the short distances and timescales over which cavitation effects occur limiting the scope for investigation with macroscale bulk experiments, and the extreme sensitivity of sonocrystallisation (and crystallisation) processes to their conditions, literature reports are often seemingly contradictory despite technical incomparability. For a detailed understanding of the mechanisms at work in sonocrystallisation, the reader is directed towards the review by Nalesso *et al.*, [72]. An interpretation is provided below:

Three theories exist to explain the effect of cavitation on primary homogenous nucleation. Hickling *et al.*, proposed that a metastable state, sub-cooled due to proximity to evaporating gas in a cavity, may transition into a solid upon experiencing the high pressure generated by collapse [73]. Segregation theory, suggests that solute molecules are mechanically concentrated during the expansion of the cavity, leading to the formation of clusters and subsequently nuclei [74]. Finally, the energy dissipated by a collapsing bubble has been calculated as comparable to the Gibbs free energy for nucleation of a metastable solution [75]. This final possibility is closely tied to the observations of US promoting the formation of metastable polymorphs by prevention of their reversion to a thermodynamically stable form.

Other theories include the conversion of primary nucleation from homogenous mechanisms, to heterogenous nucleation at the cavity-solution interface, or acceleration of secondary nucleation rates due to sonication induced fragmentation, agglomeration and deagglomeration [72].

2.6 Spray drying

2.6.1 Introduction to spray drying and microencapsulation

Spray drying is used globally across many sectors as a means of fine particle generation. The process involves atomisation of a liquid feedstock to form droplets, exposure of these droplets to a stream of drying gas causes rapid evaporation of the carrier liquid and subsequent crystallisation. The versatility of this technique lends itself to processing a variety of liquid feedstocks: ranging from simple homogeneous solutions to multi-component and multi-phase mixtures and emulsions, restricted only by volatility and viscosity.

Using the evaporation of solution droplets is not unique to spray drying. Rapid expansion of supercritical solution (RESS) and spray flash evaporation (SFE) employ similar fundamentals to control the size and shape of product materials. While there are significant differences in the practical application of these techniques, the key difference is the rate at which supersaturation is developed during crystallisation as illustrated by Figure 14. Of the three techniques, spray drying occurs over the longest timescale, under the least harsh conditions, and offers the most scope for control over particle morphology and composition.

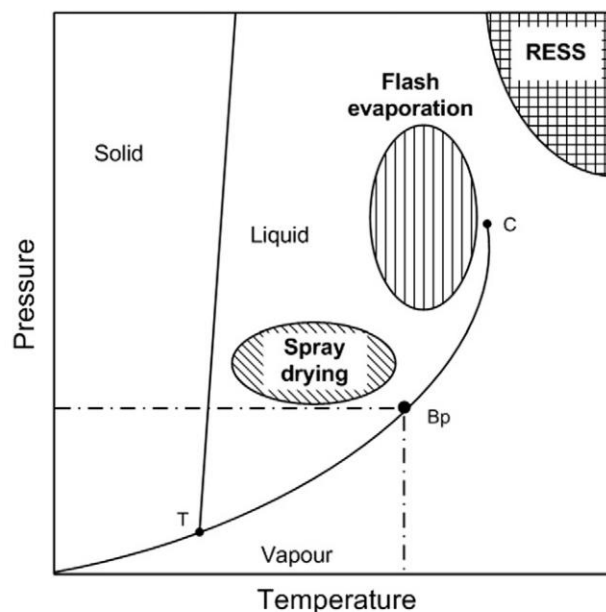


Figure 14: Comparative operation regime for spray drying, SFE and RESS [76]

2.6.2 Instrumental control over spray drying processes

Within the field, different forms of spray drier setup exist. Broadly, these may be categorised by the means of atomisation, drying and recovery.

Atomisation of the liquid feedstock into droplets is perhaps the most pivotal moment in determining properties of a spray dried powder. The following simple mass balance, Equation 21, shows the direct proportionality of a particle's geometric diameter (d_g) to the diameter of its mother droplet (d_D) [77]:

$$d_g = \sqrt[3]{\frac{c_F}{\rho_P}} d_D \quad (21)$$

Where c_F and ρ_P are respectively the concentration of the feedstock and the individual particle density.

Most industrial spray driers utilise one of the four following modes of atomisation: pressure, two/three fluid, rotary or ultrasonic [78]. Pressure atomisers operate by forcing a pressurised liquid through a fine aperture, the resultant high shear causes disruption of the liquid into droplets with sizes inversely related to the interfacial tension of the fluid. Two fluid atomisers work in a similar manner; however, feed stock is carried to the nozzle by means of an external pump and the pressure is applied by a second fluid – typically a stream of compressed carrier gas - which is combined with the feedstock prior to injection into the drying chamber. Three fluid nozzles are identical to two fluid nozzles in terms of atomisation technique, differing only in the fact that they allow multiple feedstock liquids to be mixed at the nozzle. Application of atomisation pressure by a fluid distinct from the feedstock offers the advantage of separating feedstock injection rate and atomisation pressure without the need to make modifications to the nozzle aperture size. Rotary and ultrasonic atomisers both make use of mechanical agitation and feedstock surface tension to generate droplets, with control afforded by the respective frequency of oscillation. Ultrasonic nozzles are typically employed to generate ultra-fine droplets [79]. Rotary atomisation provides access to the largest droplets [78]. Despite the array of atomisation techniques, it is important to recognise that spray drying offers access to a limited range of particle sizes: typical droplet

mass mean diameters fall into the range 10-100 μm , yielding dry particles with diameters ranging between 0.5-50 μm [80].

Co-current, counter-current or mixed-flow drying chamber configurations are illustrated in Figure 1a-1c respectively [81]. Co-current spray driers introduce the streams of drying gas and atomised feedstock at the same position resulting in rapid initial drying that is attenuated as the drying gas approaches saturation. This approach is favoured when spray drying materials that are thermally sensitive as the particles will experience temperatures equal to or lower than the wet bulb temperature of the drying gas. The shared direction of flow enables the drying gas to be used as pneumatic transport to the recovery stage. Counter-current spray drying involves the respective introduction of the atomised feed stock and dry gas inlet at the top and bottom of the chamber. In this configuration the least saturated drying gas acts upon the most dried droplets/particles, resulting in lengthier residence times, lower residual moisture and greater thermal stress for the dried particles. Since the process cannot make use of the drying gas for pneumatic transport, particles are conveyed by gravity and fines must be recovered from the drying gas exhaust. Mixed flow spray drying combines features of co-current and counter-current configurations: drying gas is introduced at the top of the tower and feed stock is atomised upwards from a position in the middle of the tower, resulting in slower initial drying and longer residence times than co-current setups whilst maintaining pneumatic transport by the drying gas and preventing the separation of fines. Typically, mixed spray drying is conducted to maximise the density of the product whilst minimising thermal stress, since the drying gas has already amassed some degree of carrier liquid vapour upon reaching the newly atomised feedstock. Various models exist that account for the moisture content of spray dried particles either as a function of residence time or position within a chamber, allowing informed decisions to be made when scaleup attempts are made [82–84].

Particle recovery methods have a less dramatic impact on powder properties, limited to modification of the particle size distribution either by design or

limitation. For systems configured either as co-current or mixed flow, in which pneumatic transport is readily possible, cyclone separators are the dominant recovery method. Counter-current systems may employ either cyclone separation or electrostatic precipitators to recover fines from the exhaust ports, while gravity is sufficient to separate larger particles.

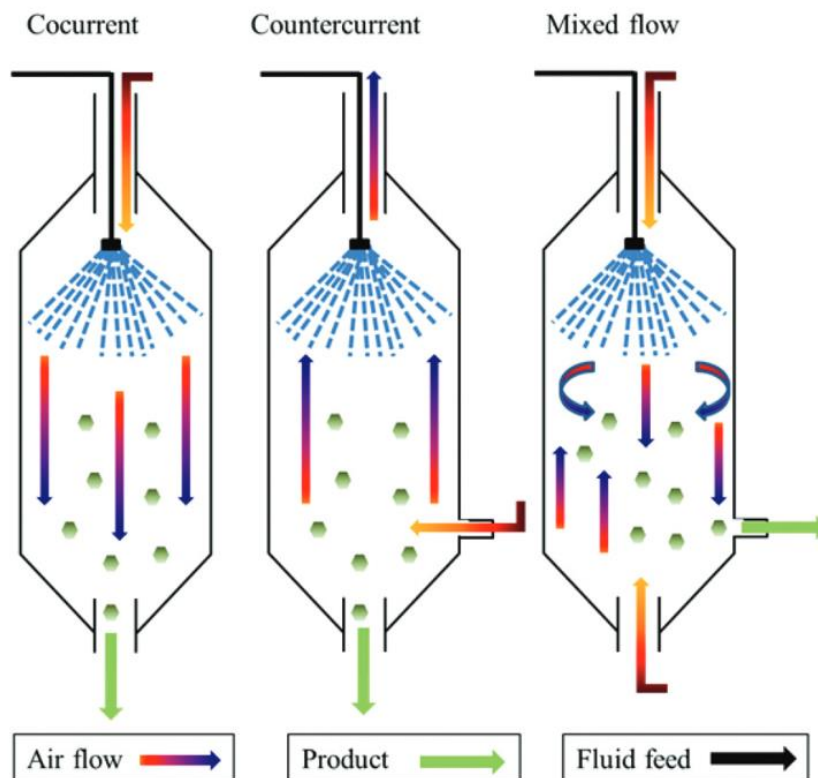


Figure 15: Common spray drying tower arrangements [81]

2.6.3 Formulation control over spray drying processes

It was previously mentioned that spray driers provide a versatile means of processing multicomponent and multiphase fluids, reliably and reproducibly converting such feedstock to a dry powder. While properties such as the size and particle size distribution are inherently dominated by the spray driers instrumental properties, other properties such as the internal and surface structure are derived from the formulation of the feedstock. Vehring's proposed terminology for describing the structure of spray dried microparticles, surmised in Figure 16, will be used throughout this thesis [80].

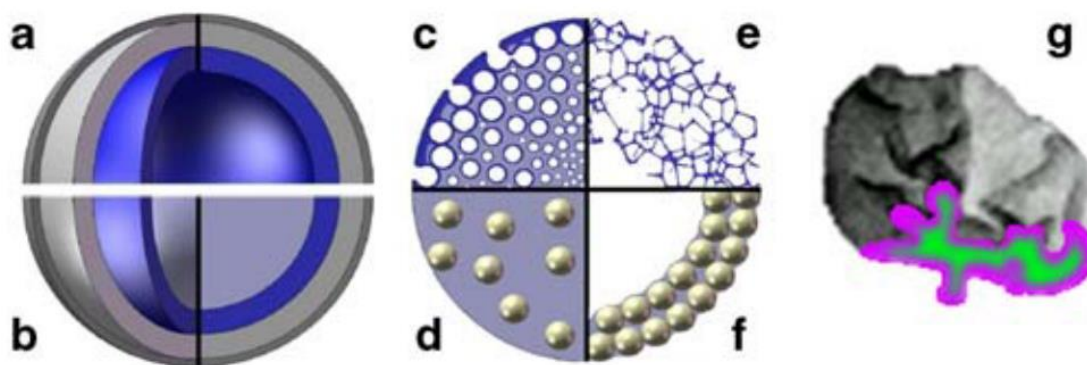


Figure 16: Illustration of spray dried particle morphologies and their description as formalised by Vehring, 2008. a) Layered with central core. b) Layered with central void, elsewhere termed crust or hollow sphere. c) Closed cell solid foam. d) Particle with embedded nanoparticles. e) Open cell solid foam. f) Composite shell, elsewhere termed crust or hollow sphere. g) Irregular particle containing external voids and internal concentration gradients. [80]

The origin of the seven distinct structures shown in Figure 16 can to some extent be rationalised in terms of the relative diffusion coefficients of components within the natant droplet from which the particle is derived. Shrinkage of the droplet due to evaporation of solvent results in concentration of the solutes in proximity to the surface and thus a diffusional gradient is formed by which material is conveyed inwards whilst species exhibiting surface activity localise at the boundaries of the droplet, the resultant radial distribution of species can thus be predicted [85]. Accurate models informed by studies using drop on demand technology to evaluate evaporation rates of isolated droplets exist [86,87]. However, the elegant simplicity Vehring's rationalisation, despite its assumptions, provides sufficient detail by which to understand the various particle morphologies produced by spray driers. A

detailed derivation of the model is not included here, but can be found in the relevant references [80,88].

Of interest for this work is the use of dimensionless Peclet numbers, Pe , relating the rate of evaporation κ to the diffusional coefficient of a given solute D_i :

$$Pe_i = \frac{\kappa}{8D_i} \quad (22)$$

Small molecular or ionic species, particularly those of high solubility in the carrier fluid, tend to locate at the core of a particle. Such species have low Peclet numbers ($Pe_i < 1$) and are highly mobile within the droplet, thus diffuse towards the centre of the droplet more rapidly than the surface resulting in low surface enrichment. For highly soluble species, with low initial saturation, the characteristic time for surface saturation is approximately equivalent to drying time – leading to the formation of particles with density equivalent to the materials crystal density ($\rho_p \approx \rho^*$).

Larger species such as polymers or nanoparticles possess high Peclet numbers ($Pe_i > 1$) ensuring that the rate of droplet shrinkage is higher than the rate at which the species can diffuse towards the centre. High Peclet number species are enriched at the droplet surface, leading to the formation of composite shells or hollow particles which may retain sphericity, collapse, or dimple.

Key to this model is the assumption that solute species exhibit diffusional properties described by Fick's second law, the partial differential expression of which is shown in Equation 23. The law describes the concentration, φ_i , as a function of both time, t , and distance, x , for a species with diffusion coefficient, D_i .

$$\frac{\partial \varphi_i}{\partial t} = D \frac{\partial^2 \varphi_i}{\partial x^2} \quad (23)$$

The model is limited in accuracy by several assumptions, most importantly, the assumption of constant of solvent evaporation rate and diffusion coefficient. The assumption motion of solutes is in abeyance of Ficks law inherently relies on the constancy of diffusion coefficients throughout the drying

process. While this is generally applicable to small species, the assumption has a tendency to fail for large species such as polymers in which complex chain-chain effects may dominate the diffusional motion. Moreover, the assumption that the solvent evaporation rate remains constant likewise assumes Fickian diffusion, this time of the solvent molecules. The drying of droplets is a particularly complex process, a detailed discussion of which is beyond the scope of this thesis. In essence however, the drying rate is purely a Fickian process, as it involves Stefan flow – the process by which vapourised solvent is driven away from the interface by successively vapourised species [87]. The motion of these materials can therefore not be described purely in terms of the diffusion coefficient which fails to include a description of volatility properties. A further complication to the drying rate description is the vaporisation of solvent within the centre of the droplet, expansion of which then leads to jetting of the surface material away from the centre of the evaporating body in a process referred to as material jetting [80].

3 Literature review

3.1 Ammonium perchlorate

3.1.1 Background information

Ammonium perchlorate (AP) is a white crystalline solid, widely used as an oxidising agent in composite propellant formulations. Manufacture of AP is achieved via neutralisation of perchloric acid by ammonia, or by double displacement of sodium perchlorate by ammonium salts. Under atmospheric conditions, crystals of AP are orthorhombic, space group Pnma, with four molecules in the unit cell ($a = 0.9202$, $b = 0.5816$, $c = 0.7449$ nm) [89]. The orthorhombic lattice is stable up to 240 °C, at which point it transitions into a cubic lattice, space group F-34m, with four molecules per unit cell ($a = 0.763$ nm) [90,91]. Phase transition in AP involves a reduction of density from 1.95 to 1.76 g.cm⁻³. The cubic form provides sufficient freedom for the perchlorate ions to exhibit molecular dynamics, whereas in the orthorhombic form only the smaller ammonium cations have mobility [92].

Thermal decomposition of ammonium perchlorate is sensitive to the environment in which the process occurs. At sustained temperatures above 130 °C the orthorhombic form will slowly decompose to a maximum of 30 % mass loss to yield porous AP. This modification is commonly used to increase the combustion rate of AP/Al composite propellants [93,94]. At higher temperatures the decomposition of the cubic form will proceed to completion, leaving no residual solids. While three mechanisms are seen as possible, initiation by protonation of the chlorate anion is generally more accepted than the theories of electron donation and Cl-O radical formation mechanisms [13]. Despite occurring via the same mechanism, low and high temperature decompositions of AP are drastically different. Low temperature decomposition of the orthorhombic occurs in subsurface interstitials, that allow for the accumulation of dissociation products whereas high temperature decomposition is a predominantly surface reaction. The effect of particle size on decomposition kinetics is complex, showing an apparent optimum minimum size.

3.1.2 Size and sphericity optimisations

The high thermal coefficient of solubility for AP in water makes cooling crystallisation an ideal method crystal preparation on a large scale. Despite this, cooling crystallisation from water poses several issues, nominally lack of morphological control and solvent occlusion. Several recent papers are presented, that have sought to optimise the parameters used for cooling crystallisation of AP with regards to the particle size and shape. Generally, these papers neglect a detailed description of particle morphology, and instead refer to numerical shape factors as representation of sphericity.

It is generally accepted that in the absence of impurities, the shape and particle size of AP formed by cooling crystallisation is dominated by agitation rate. Lakshmi *et al.* found a that reduction of average particle size and increased sphericity with increased agitation rate occurred almost independent of the cooling profile, Figure 17 [95]. Likewise, Hosseini *et al* found that increasing the agitation rate played a much more significant role in particle sphericity than cooling rate [96]. While the importance of agitation rate was contested by the work of Nair *et al.* the sample size was limited and little weight is afforded to these results [97].

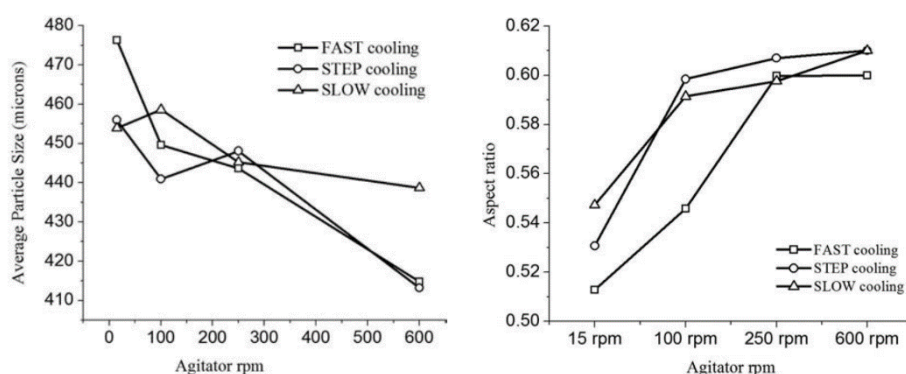


Figure 17: The dependence of AP particle size and aspect ratio on agitation rate in cooling crystallisations [95]

The effect of surfactants on sphericity appear to be highly dependent on formulation. Hosseini *et al* (2021) report that the inclusion of sodium dodecyl sulphate (SDS) provided the most substantial increase to sphericity of all assessed variables, surpassing agitation rate [96]. Development of this experiment, by the same group, to include additional surfactants (CTAB, PVA

and Tween 60) followed the same trend [98]. However, Lakshmi et al showed that the addition of 0.025 wt% surfactants (stearic acid, stearyl amine, oleyl amine and an unspecified “hydrocarbon oil”) to a cooling crystallisation of AP caused a reduction of sphericity and increased irregularity, Figure 18 [95]. Both sets of research do however agree that the inclusion of surfactants reduces the barrier to nucleation and yields lower particle sizes. The trend of increased sphericity with increased agitation rate are preserved in the presence of surfactants.

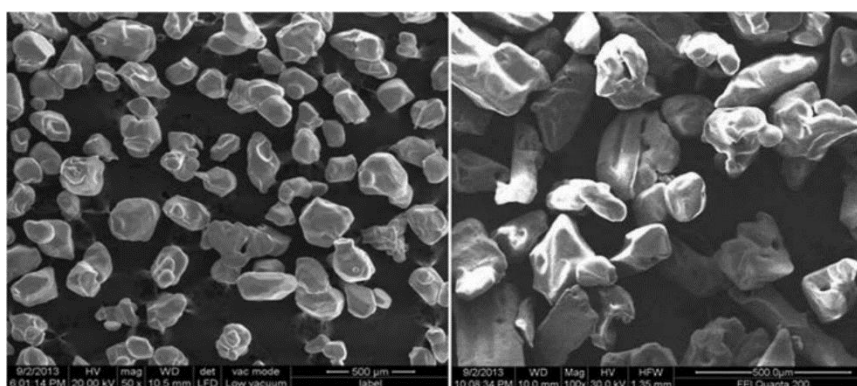


Figure 18: AP from slow cooling crystallisation with agitation at 100 RPM. (left) Pure AP (right) surfactant inclusion [95]

As mentioned at the start of this section, occluded water has been shown to migrate to the surface of particles - increasing the strength of interparticle forces due to capillary bridging and even causing recrystallisation/ripening over long periods of time. Of the optimisation papers discussed, only Lakshmi et al. attempted to account for residual moisture in their crystallisation products - finding no significant difference resulting from modification of crystallisation parameters within the error of their measurement [95].

Another interesting application of cooling crystallisation for the micronisation of AP has been reported by Zinab *et al.*, the process involves rapid cooling of undersaturated aqueous AP solution by passage under pressure through a 50m heat exchange pipe. The high surface area over which heat can be lost from the solution reportedly provides the capacity to control particle size as a function of residence time [99]. Particle sizes were reported in the range of 28.32 - 68.12 μm , however no details on the particle shape were provided.

A summary of AP cooling crystallisation parameters is shown in Table 2, note that despite the remarkably similar parameters used by Lakshmi *et al.* and Hosseini *et al.*, the resultant particle sizes were by no means similar. The results obtained by Norouzi *et al.*, used magnetic stirring whereas Hosseini *et al.* used overhead stirring - despite this significant experimental difference, due to the inclusion of surfactants they report remarkably similar size ranges.

Table 2: Summary of AP cooling crystallisation optimisation parameters. * indicates a stepped cooling profile. ** Indicated the presence of surfactants during the crystallisation.

Reference	$T_0 - T_1$ (°C)	$\Delta T/t$ (°C.min ⁻¹)	Agitation (rpm)	Size range (µm)
Lakshmi <i>et al</i> 2016 [95]	80 -15	0.25, 0.3*, 1.05	15, 100, 250, 600 (Overhead)	~ 410 - 480
Hosseini <i>et al</i> 2021 [96]	65 - 30	0.125, 0.25, 0.5	400, 500, 600 (Overhead)	~ 220 - 310 ~48 - 86**
Norouzi <i>et al</i> 2022 [98]	80 - 0	Uncontrolled	800, 900, 1000, 1100 (Magnetic induction)	~22 - 167**
Nari <i>et al</i> 2020 [97]	Not reported	0.2, 0.6	50, 500 (Overhead)	Not reported

3.1.3 Crystal habit modification of AP

Kohga and Tsuzuki investigated the effect of ethylene glycol concentration on the crystal habit of AP prepared by rapid cooling crystallisations. Increased ethylene glycol fraction resulted in a slight average particle size reduction and improved regularity of the crystal morphology, as can be seen in Figure 19. . Impact sensitiveness was adversely affected by this modification [100], but the material was later proved to increase the burn rate of AP/HTPB propellant samples without dramatically changing the thermal sensitivity of the material [15]. Interestingly, the relative intensity of the (210) diffraction peak of ethylene glycol modified AP was shown to increase linearly with ethylene glycol concentration and this was taken by the authors to be indicative of habit modification [100]. DFT modelling of the major AP lattice planes found that the (210) plane exhibited the lowest surface energy of the major planes in the presence of ethylene glycol [101].

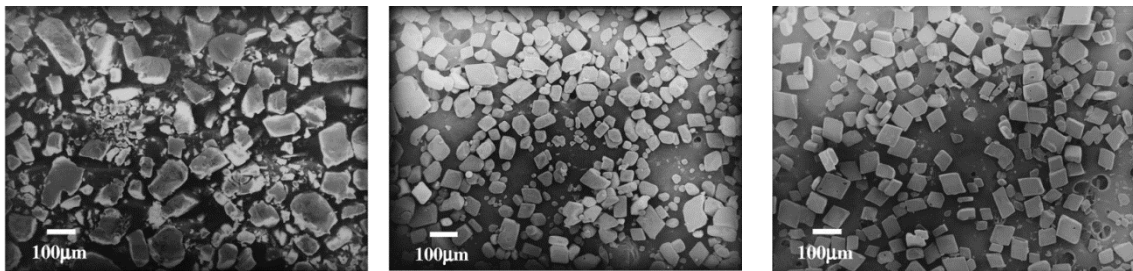


Figure 19: AP prepared by rapid cooling crystallisation (left) from pure water, (middle) water:ethylene glycol 40:60 and (right) water:ethylene glycol 20:80 [100]

Vargeese, Joshi and Krishnamurthy prepared AP by evaporative crystallisation in the presence of poly vinyl acetate (PVA), the concentration of additive was shown to increase the rectangular wedge habit modification, Figure 20 [102].

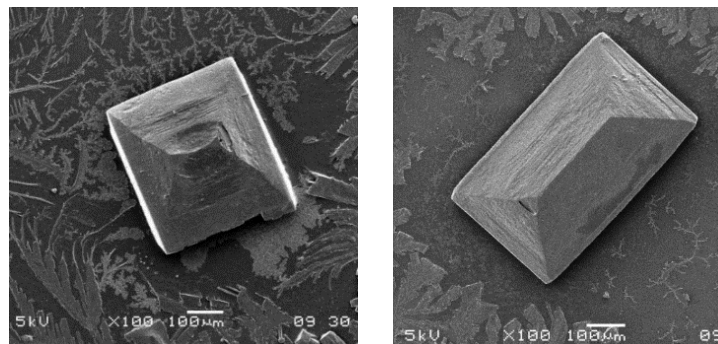


Figure 20: Rectangular wedge modification of AP by PVA [102]

Reese, Son and Groven prepared composite AP/Fe₂O₃ particles by rapid antisolvent precipitation (AcO/EtOAc) [103]. Increased heterogenous nucleation due to the inclusion of iron oxide nano particles was shown to reduce the average particle size significantly and size distribution significantly. The prismatic crystal habit of AP occurred with much higher uniformity in the presence of nano particles, Figure 21. The composite particles displayed a significantly different decomposition profile when studied by TGA, not exhibiting the typical arrest after approximately 30 % mass loss, Figure 22.

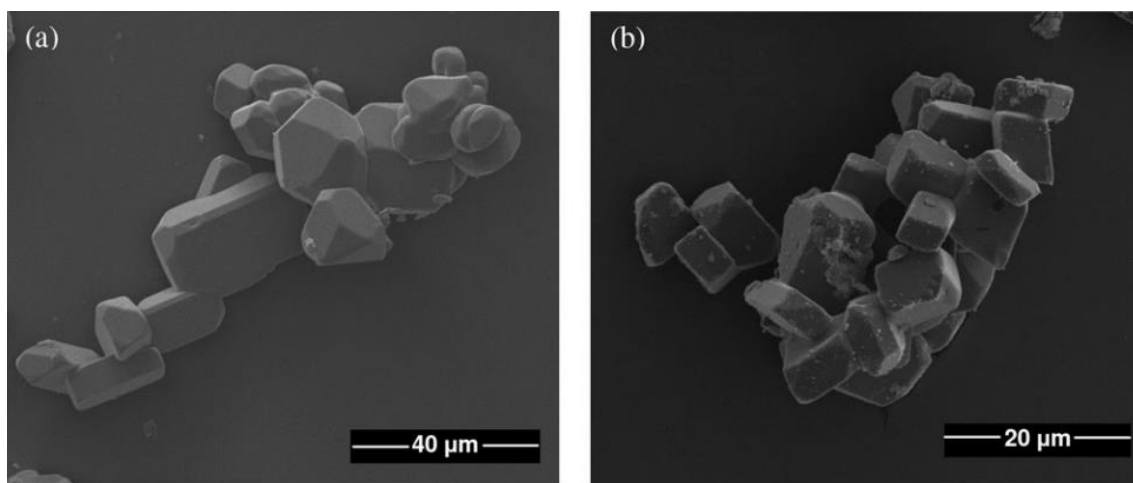


Figure 21: Antisolvent precipitated AP in the (a) without and (b) with nanoparticles present [103]

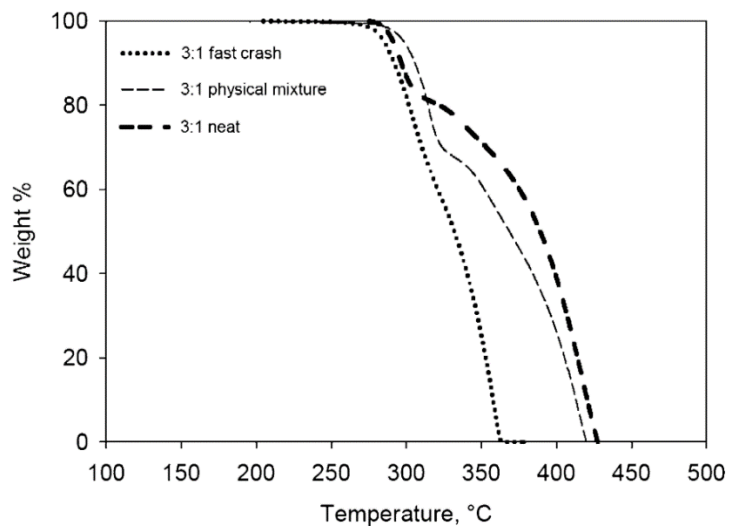


Figure 22: The effect of nano particle inclusion on AP decomposition kinetics [103]

Crystallisation of ammonium perchlorate in the presence of three different crown ethers was achieved through solvent:antisolvent crystallisation processes. The resultant prismatic AP-crown ether co-crystals were found to be monoclinic ($P2_1/n$), Figure 23 [104]. Thermal analysis of the materials showed significant reduction of the exothermic decomposition temperature.



Figure 23: Optical micrographs of AP/crown ether cocrystals (a) AP/18C6, (b) AP/B18C6 and (c) AP/DB18C6 [104]

Another interesting study investigated the effect of evaporative crystallisation of AP from mixed MeOH/H₂O solvent, within the confines of organically modified silica pores [105]. While unlikely to be a scalable process, it was demonstrated that AP could be grown in controllable nanometre length scales (4 - 30 nm) by variation of the pore size. The effect of confined growth on the material phase or morphology was not investigated, with the paper primarily focusing on the relative enthalpies of crystallisation.

3.1.4 Sonocrystallisation

Ma *et al* report sonication assisted microfluidic antisolvent crystallisation of AP from various solvents by ethyl acetate showed major morphological differences between solvent/antisolvent systems. The ultrasound intensity had a demonstrable effect on the average crystal size, following the expected trend of increased power reducing crystal size, Figure 24. Changes to the microfluidic system capillary internal diameter and US exposure time showed no significant effect on crystal size. [106]

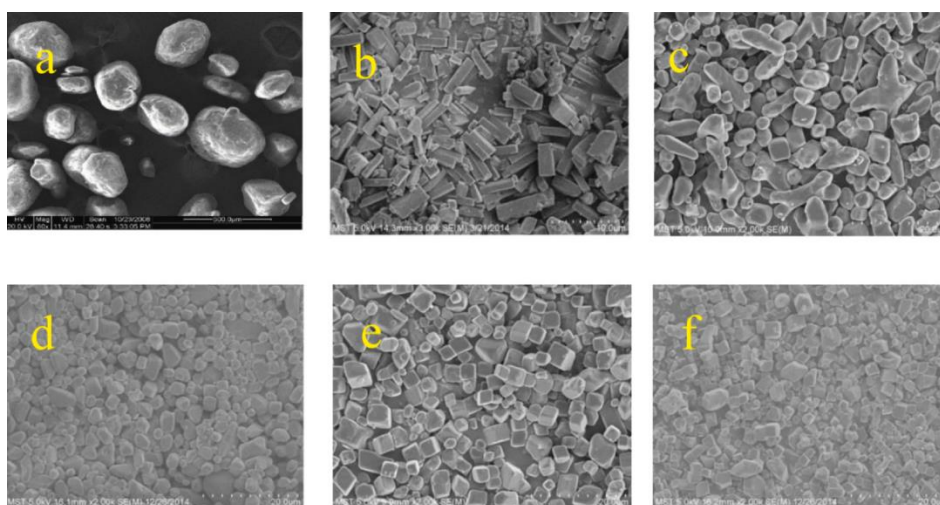


Figure 24: SEM micrographs of AP (a) raw material, (b) MeOH/EtOAc, (c) DMF/EtOAc, (d) DMF:AcO(2:1)/EtOAc, (e) DMF:AcO(1:1)/EtOAc, (f) DMF:AcO(1:2)/EtOAc [106]

Pal *et al* investigated antisolvent precipitation of AP in batch crystalliser, co-feed capillary and impinging jet reactors [107]. Use of n-propyl alcohol as an antisolvent resulted in the formation of dendritic crystals from a homogenous mother liquor, whereas n-butyl alcohol gave significantly more regular crystal growth, Figure 25. The authors demonstrated relatively crystal reproducibility through both sonocrystallisation of capillary flow and impinging jet crystallisers but noted that the latter offered significantly more scope for scalability. The authors also note that attempted capillary flow crystallisations failed in the absence of sonication due to excessive blockage at the initial mixing point.

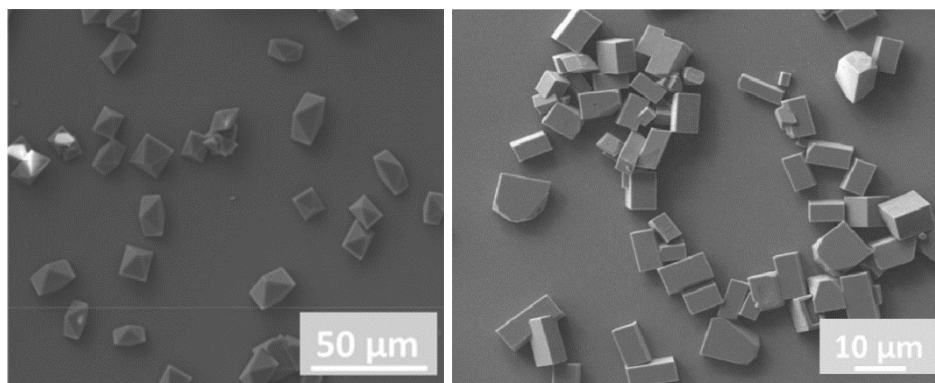


Figure 25: AP prepared by antisolvent precipitation (water/n-butyl alcohol). (left) sonocrystallisation in mixed capillary (right) impinging jet crystallisation [107]

Liu *et al.* report an interesting modification of the cooling crystallisation process of AP, in which concentrated hot AP solution is added to a low temperature saturated solution thereby controlling supersaturation by means of solution feed rate. In their first report, the setup included a gas bubbler to increase the mixing capability [108], in the later experiment this bubbling system was removed [109]. Both experiments demonstrated that a wide variety of morphologies could be prepared through variation of supersaturation rate and mixing. Crucially, the sonication during the crystallisation process caused a reduction of particle size and increased crystal regularity as a function of ultrasound power. Although not discussed in the papers, it appears from the presented images that the application of sonication also significantly reduced the extent of secondary nucleation, Figure 26.

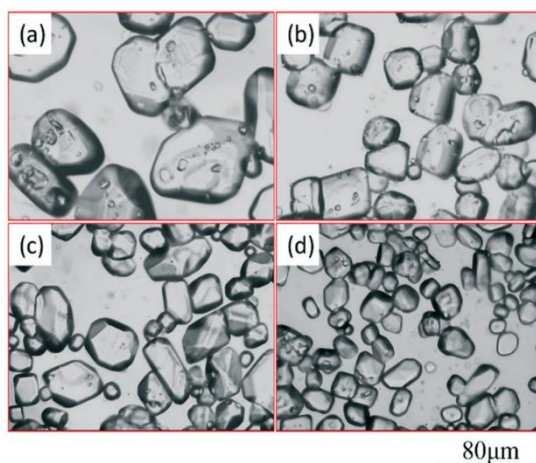
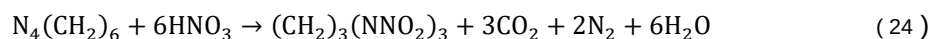


Figure 26: Solvent-solvent cooling crystallisation in a gas-liquid two phase medium. Mixing variation (a) 100 rpm magnetic stirring (b) 500 rpm magnetic stirring (c) 125 W sonication (d) 225 W sonication [108]

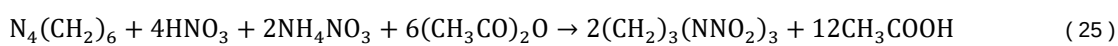
3.2 RDX

3.2.1 Background information

Cyclotrimethylenetrinitramine (RDX) was discovered in Georg Friedrich Henning and has seen extensive military application since World War II due to its explosive power and high detonation velocity. While the initial preparation of RDX was achieved by direct nitration of hexamethylenetetramine nitrate, contemporary industrial manufacture of RDX is conducted using either the Woolwich or Bachmann process. The Woolwich process, a direct nitration of hexamine by nitric acid, produces RDX alongside waste carbon dioxide, dinitrogen and water.



Whereas the Bachmann process involves nitration of hexamine, by nitric acid, in the presence of ammonium nitrate and acetic anhydride at elevated temperatures [110].



The Woolwich reaction product is typically very pure RDX, whereas the Bachmann process has a side reaction that generates approximately 8 - 12% cyclotetramethylenetetranitramine (HMX). Critically, the Woolwich reaction also produces water, resulting in dilution of the concentrated nitric acid thereby affecting the nitration rate over time. Production of HMX by the Bachmann process can be favourable, due to the excellent explosive properties of the substance. However, presence of HMX has been shown to increase the hazard sensitiveness of RDX. Commercial RDX is classified either by synthetic route, type A being Woolwich and type B being Bachmann produced, or by HMX content [111]. Type I RDX contains <5 % HMX, whereas Type II can contain 4 - 17% HMX [112]. Undesirable ring opening of the triazine core produces highly nitrated impurities that can lead to sensitisation if not purified by recrystallisation.

Like most other organic materials, the nitramines RDX and HMX, show extensive polymorphism [51]. Changes to the crystalline structure of a material

alters the detonation velocity and pressure, thermal/mechanical/chemical stability and crystal density and morphology [113]. Two polymorphs of RDX can be found under ambient conditions. The stable α form exhibits an orthorhombic crystal structure with *Pbca* space group with molecular conformers assuming two axial and one equatorial nitro groups (AAE) [114,115]. A metastable β -state form II RDX, was first reportedly produced in 1950 by evaporative crystallisation from high boiling solvents thymol and nitrobenzene [116]. Later work showed that a reduction of IR active vibrational modes was consistent with a conformational shift to three axial nitro groups, however the crystal proved too unstable for further analysis [117–119]. Subsequently, dendritic β -RDX crystals were grown and isolated for single crystal X-ray diffraction studies, allowing confirmation of the tri-axial nitro group conformation in orthorhombic *Pca2₁* space group [120].

Further polymorphism is possible for RDX, with a transition from α to γ occurring at ~ 3.9 GPa [121], yielding an orthorhombic form with *Pca2₁* space group. A high temperature-high pressure ϵ -form, initially assumed to be β -RDX due to spectroscopic similarities, has been identified as distinct [122]. δ -RDX has been observed at pressures exceeding ~ 18 GPa [123].

3.2.2 Solution crystallisations

Sensitiveness towards initiation by external stimuli is a key feature in the safety of munitions engineering. While there has been a drive towards the development of new energetic materials to satisfy the need for insensitive munitions for deployment to the battlefield, the limitations of their design restrict power and thus scope for use [124]. As such, there is a resurgence of research seeking to improve the safety of 'classical' energetics such as the nitramines.

The impact and shock sensitiveness of pure RDX and RDX/polymer composite formulations have been extensively studied, and it is generally accepted that the key contributing factors are solid particle size and morphology, the frequency and nature of crystal defects and HMX content [59,125–128]. Of these factors, particle size, morphology and HMX content can be controlled with relative ease. For example, agitation of RDX in saturated cyclohexanone solution to remove rough crystal edges [129], or selection of Bachmann RDX in combination with careful sieving to reduce HMX content [127].

Controlling the internal crystal quality cannot be done post crystallisation, and so extensive research has been conducted into minimisation of crystal defects within RDX. An excellent example of such work is provided by Kim and Kim (2010) whose crystallisations of RDX from solution in binary mixtures of γ -butyrolactone/water showed a reduction of solvent inclusion with reduced supersaturation as a function of both antisolvent ratio and cooling rate evident in both SEM and refractive index matched imaging, Figure 27 [60]. Similar optimisations are reported for AcO/H₂O, AcO/H₂O+PEG, AcO/n-hexane, DMF/n-hexane and DMF/H₂O+PEG antisolvent preparations of RDX, used to prepare crystals with a variety of morphologies and sizes [130–132].

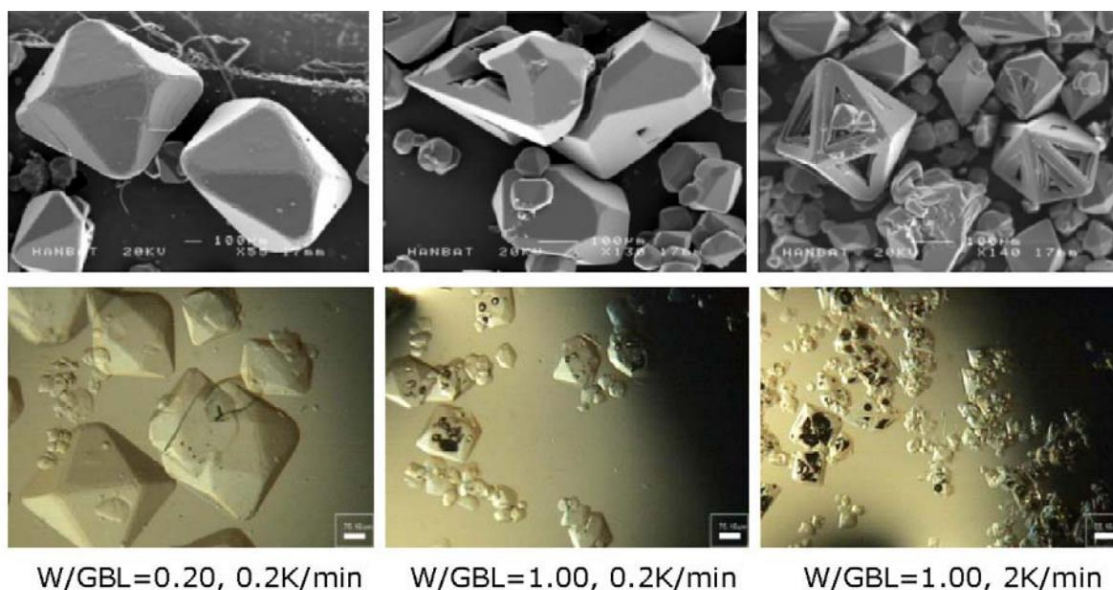


Figure 27: SEM and refractive index matched optical micrographs of RDX prepared by cooling crystallisation of RDX from binary solutions of gamma butyrolactone and water [60]

Stoltz *et al.* demonstrated that the application of sonication to evaporative crystallisation of RDX from acetone resulted in a significant reduction of solvent inclusion due to crystallisation at lower supersaturation [133]. The particles prepared also exhibited significantly more uniform size and shape, Figure 28.

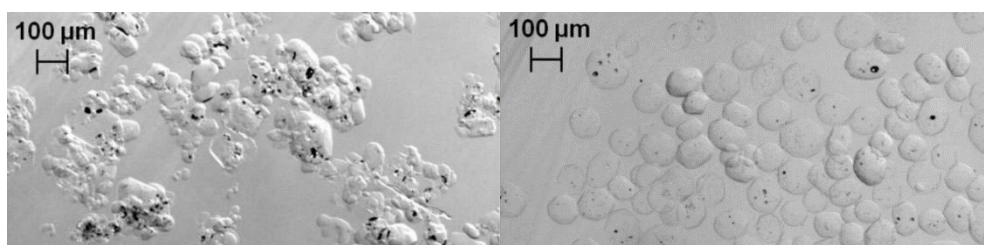


Figure 28: RDX prepared by evaporation from acetone, (left) stirring 776 rpm (right) sonication at 40 KHz [133]

Ter Horst *et al.* illustrate the significance of growth conditions on the morphology of RDX through static cooling crystallisation of RDX from a variety of polar solvents [134]. The resultant crystals, shown below in Figure 29, share commonalities such as dominant expression of the (200) and (210) planes, and limited growth of the (111) plane. However, the variation in growth produces visually distinct morphologies. It should also be noted that the crystal grown

from diethylene glycol monopropyl ether, the only protic solvent, is dissimilar from all others in not having grown with a line of vertical symmetry. These crystallisations were performed in an attempt to validate a larger molecular modelling experiment, aimed at predicting the crystal morphology through the relative attachment energy and growth rate of each crystal face – following a modification of Wulff's principle proposed by Hartmann and Bennema [135]. While the results of the modelling and experimental growths were consistent for cyclohexanone and diethylene glycol monopropyl ether, it failed to accurately predict the morphology of RDX grown from acetone or γ -butyrolactone. Further computational modelling of the relative growth rates of RDX faces was conducted by Liu et al, however, no experimental crystallisations were conducted to assess the quality of their models [136].

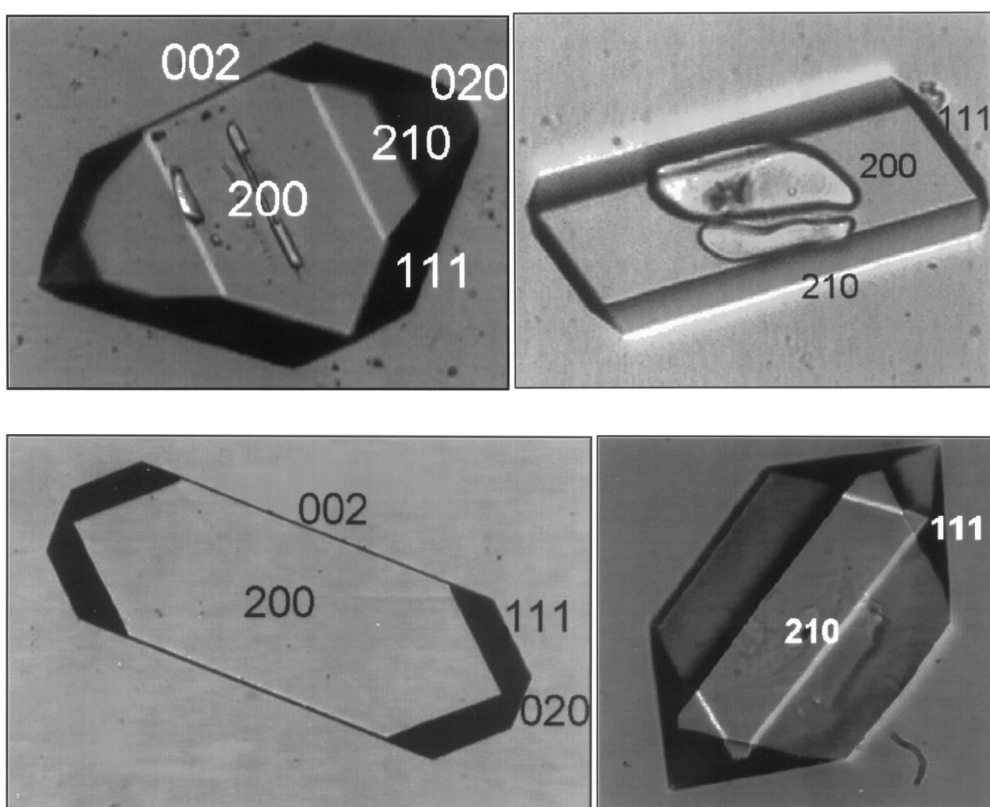


Figure 29: RDX crystals grown in static cooling crystallisations from various solvents: (top left) acetone, (top right) diethylene glycol monopropyl ether, (bottom left) cyclohexanone and (bottom right) γ -butyrolactone [134]

3.2.3 Spray drying RDX

As already mentioned, the hazard sensitiveness of RDX is highly dependent on crystal size, morphology, and quality. The above section has detailed various approaches taken to improve the quality of relatively large crystals (1-400 μm), particularly in respect to reduction of solvent inclusions. An alternative approach is, that is drawing extensive interest, is the use of nanometre scale energetic crystals.

A group at ISL, France, following their successful application of spray flash evaporation (SFE) to the production of nano-energetics, RDX and PETN [137] and subsequently RDX/TNT composites [76], investigated the impact of size reduction, from micro to nano, by spray flash evaporation (SFE) on the sensitiveness β -HMX. Impact, friction, and electrostatic discharge (ESD) sensitiveness was evaluated following the BAM guidelines, and while the micro-HMX was significantly less sensitive to impact, it was outperformed by nano-HMX in both friction and ESD testing. Further desensitisation to all tested stimuli was accomplished by reformulating the nano-HMX with licowax, however the sensitiveness to impact remained significantly higher than the uncoated micro-HMX.

Likewise, a team at Picatinny Arsenal, NJ, has for some time been interested in nano-energetics, due to their promising reduction of sensitiveness to external stimuli and the implications this has for munition safety. Work that evaluated the sensitiveness of nano-RDX, prepared by rapid expansion of supercritical solutions (RESS), revealed that there was indeed a significant decrease to shock and impact sensitiveness caused by size reduction [138]. However, the results were inconsistent with a linear trend, and it was argued that there may be an optimum size at which sensitiveness values reach a minimum.

Since then, the same group appears to have focused on spray drying as a means of reducing the sensitiveness of nitramine energetic powders. The transition from RESS to spray drying being a interesting choice, since both techniques are capable of producing nano-crystals of comparable size, distinct in their agglomeration behaviour. Where RESS produces relatively few strongly

bound agglomerates, due to the rapidity of the technique, that leads to uncontrollable weak agglomeration of dry particles. Spray drying inherently imparts a strong agglomeration amongst the many nanocrystals that result from multiple nucleation sites in each droplet that dries over a considerably longer period. Their first paper on the subject detailed an investigation of the impact of spray drying on shock sensitiveness [139]. Spray drying was conducted on a Buchi B190 spray drier equipped with an ultrasonic nozzle [Model 8700-60 Sono-Tek @ 60kHz, 1.2W] with relatively low drying inlet temperature of 55°C. The feedstock was a solution in acetone of RDX 5 wt.% and binder (PVAc or VMCC) 1 wt.%, pumped at a rate of 3ml/min. The control material was BAE 4 µm FEM RDX, slurry coated with VMCC by antisolvent precipitation of the binder from acetone by a 10 wt.% suspension of the RDX in deionised water. Results of small-scale gap testing [MIL-STD-1751A, Method 1042] show an impressive reduction of shock sensitiveness for the spray dried relative to the control, 2.5 GPa. RDX/PVAc showed the most sizeable reduction of sensitiveness, at 4.0GPa, relative to RDX/VMCC, 3.3 GPa. In discussing the reduction of shock sensitiveness, the authors comment that the reduction is a result of crystallite and void size reduction. No discussion of the relative difference between the two binders is offered despite some notable issues with the experiment.

Figure 30, shows a comparison of the spray dried particles prepared with PVAc and VMCC binders, highlighting the significant morphological differences between these materials. The RDX/PVAc microparticles exhibit a broader size distribution than the VMCC/RDX particles, with the latter particles having a significantly lower average diameter. Neither material appears to have formed perfect spheres due to premature surface saturation. The morphologies of the RDX/PVAc composites shows significant collapse of hollow spheres, whereas the RDX/VMCC particles exhibit numerous shallow dimples on each particle. Since both materials contain RDX/binder at a 5:1 ratio, and preparation was conducted using identical feedstock concentrations, the morphological differences are reflective of Peclet number differences between the two polymers (PVAc MW = ~113'000, VMCC MW = ~19'000).

The inconsistent HMX content of the two composites is likely to have been influential in the reduction of shock sensitiveness of RDX/PVAc as has demonstrated extensively in commercial products [125]. HMX, being an eight membered ring, is inherently more strained than RDX. Moreover, due the increased number of local minimum energy conformers accessible to HMX produces a much more diverse range of metastable polymorphs that can be produced by spray drying, some of which have been shown to be significantly more sensitive towards initiation by external stimuli. Note that the surface roughness of the RDX/VMCC particle, Figure 30D, is significantly higher than that of the RDX/PVAc, Figure 30B, this may be a result of early crystallisation of the less soluble HMX at surface positions [125].

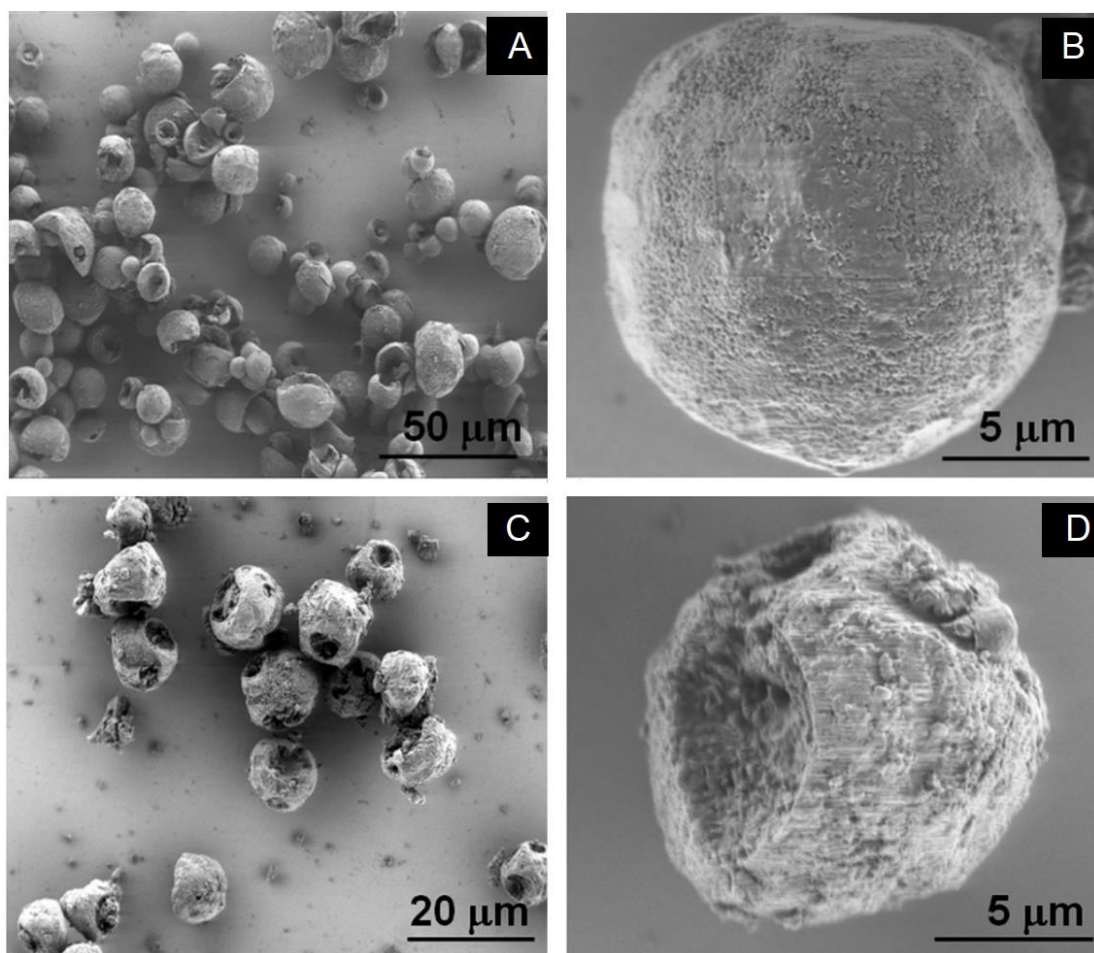


Figure 30: Comparison of microparticle morphology for (A-B) RDX/PVAc showing large collapse spheres with smooth surfaces and (C-D) RDX/VMCC showing dimpled small particles with rough surfaces [139].

One technique, unique to this paper in its employment, is the selective dissolution of PVAc by RDX saturated ethanol, which in combination with focused ion beam (FIB) milling and SEM imaging, allowed for investigation of the habits of crystals formed at the particle surface and those located in the core. Representative micrographs are shown below in Figure 31. There is an obvious increase in particle size towards the core of the particle, concurrent with the formation of a shell and subsequent slower evaporation of trapped solvents. While this was not discussed in conjunction with the material densities, it is also consistent with the reported lower density of the spray dried powders.

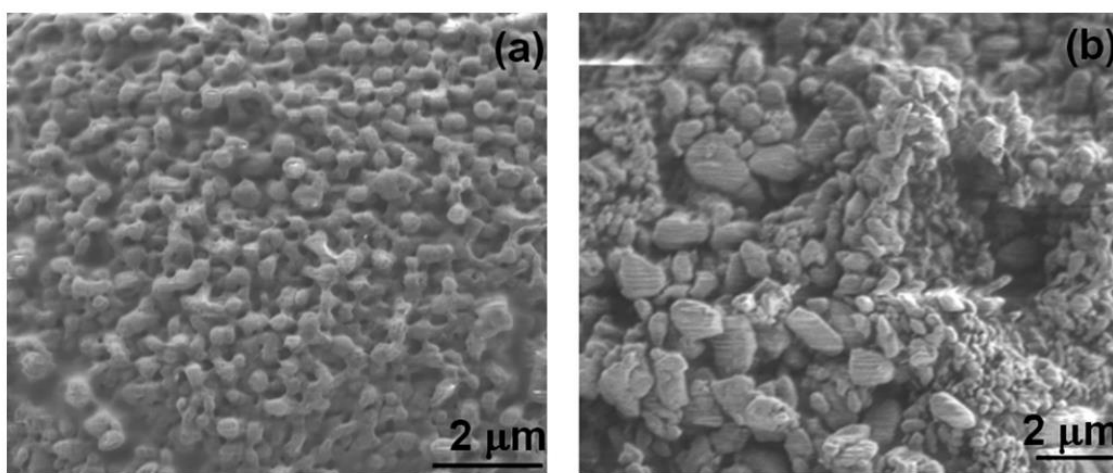


Figure 31: SEM images of spray dried RDX with binder selectively removed. (a) exterior and (b) interior crystals [139]

A paper published by the Picatinny group in 2015 sought to verify the observation of increased crystal sizes within the microspheres [140]. Again, solutions of RDX/PVAc/AcO were spray dried, but this time a comparison was made between ultrasonic nozzle (previously described) and the Buchi B290 pneumatic nozzle [(Model 044698, Buchi) @ 345 kPa N₂]. The morphologies of RDX microparticles prepared by spray drying with ultrasonic and pneumatic nozzles follow the predicts outlined by Vehring. Ultrasonic atomisation, employed to produce larger droplets and larger resultant particles, resulted in premature crust formation, and subsequent microsphere collapse. Whereas the pneumatic atomisation appears to have achieved a good balance between droplet evaporation and solute diffusion rates, resulting lower void space at the core and less prevalent collapse of microparticles. Focused Ion Beam (FIB)

milling, and SEM image revealed evidence of the crystallite size gradient in both ultrasonic and pneumatic particles, more prevalent in the larger ultrasonic particles. The external morphology and internal structure of these materials are shown in Figure 32.

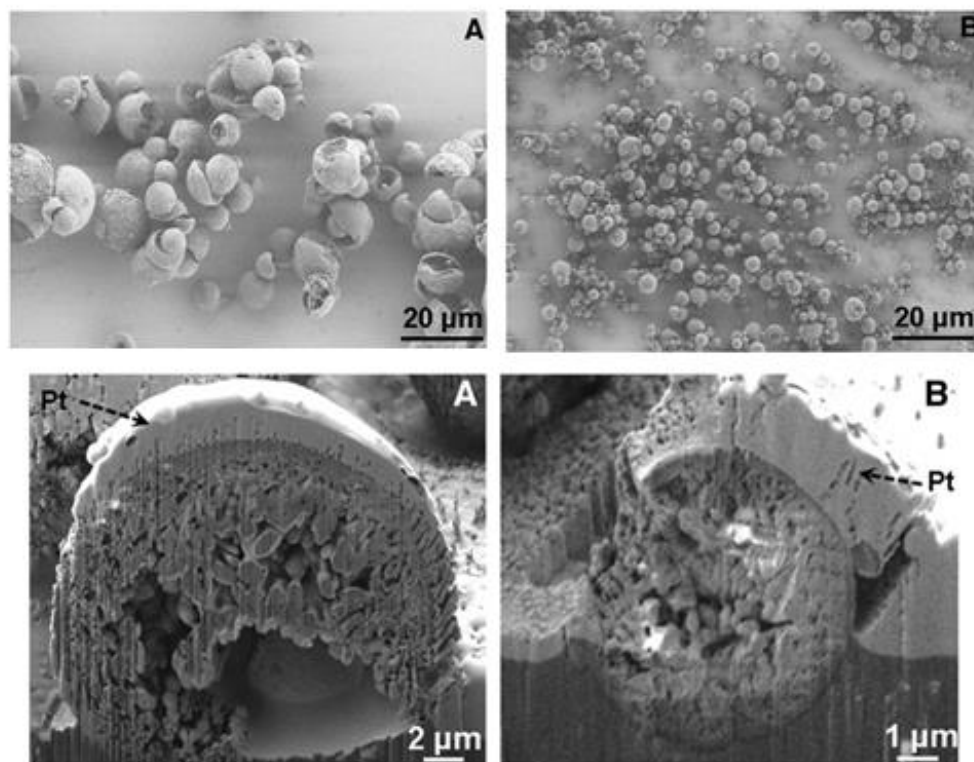


Figure 32: SEM micrographs of RDX/PVAc composite prepared using (A) ultrasonic and (B) two fluid spray drying [140]

The authors noted qualitative PXRD peak broadening, of the signal centred at $2\theta = 29.2^\circ$, in spray dried samples relative to recrystallised RDX. Broadening was more extensive in the pneumatic spray dried sample, which the authors took as evidence of lower average crystallite size.

Following their initial success with the preparation and desensitisation of RDX [138,139], and evidence that the same could be accomplished for HMX [141], the Picatinny group demonstrated the possibility of HMX/PVAc composite preparation via spray drying [142]. SEM-FIB and TEM, shown in Figure 33, indicate a significantly more dense microparticle than the earlier preparations of RDX. PXRD analysis of the spray drying product showed that a mixture of γ -

HMX and δ -HMX states were formed, neither being the militarily preferred β -HMX state, consistent with the earlier work by Zhigach *et al.* [143].

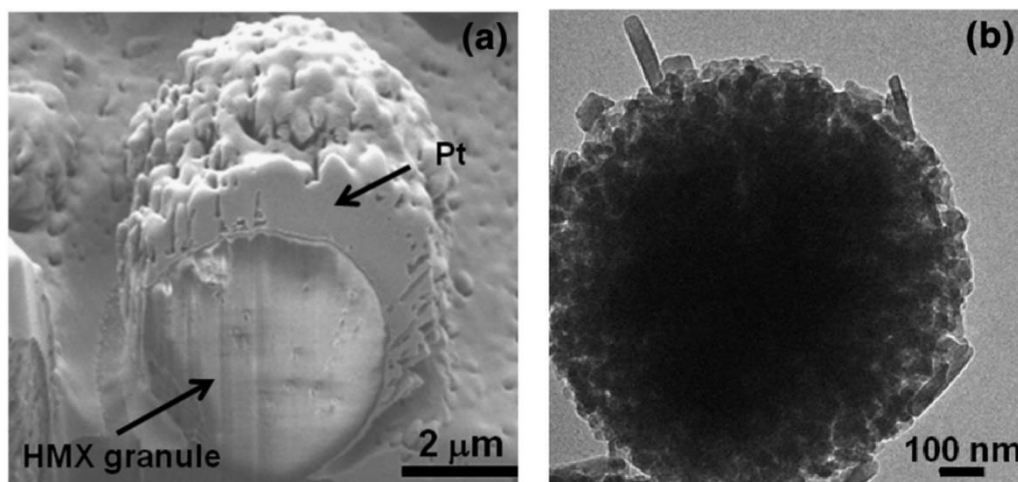


Figure 33: Two fluid spray dried HMX/PVAc microparticle structure (a) FIB-SEM and (b) TEM. [142]

Targeting the reduction of nitramine sensitiveness by microencapsulation is not unique to US research, with a recent paper from China that showed further development of the work conducted at Picatinny. Jia *et al.* compared various properties of nitramine/PVAc composites that had been prepared by spray drying and spray assisted antisolvent crystallisation (SAAS) [144]. Spray drying was conducted by atomising a co-solution of nitramines/PVAc in acetone into a drying chamber at 80°C, while SAAS was conducted by spraying the same feedstock into a vessel of antisolvent (water). RDX, HMX and CL-20 were all evaluated, and SEM images of the resultant powders are shown in Figure 34. Jia *et al.* note that both recrystallisation techniques lead to a reduction of PSD width. Attempts to investigate the average crystallite size through PXRD peak width analysis showed greater broadening in SAAS samples, which was taken to be indicative of greater strain in these materials. DSC gave evidence of more significant reduction of exotherm peak position observed in the SAAS samples relative to the spray dried samples, but both were reduced relative to the raw material. Upon impact hazard testing the raw, uncoated materials, performed worst in all cases, followed by the coated but strained SAAS materials. Spray

dried materials performed significantly better, with approximately double H_{50} value of the raw material. Since these trends of PXRD, DSC and impact sensitivity were observed in all three nitramines evaluated, it is evident that spray drying offers a means to manufacture nano-energetic crystallites that imparts significantly less stress than the more commonly used fast antisolvent methods.

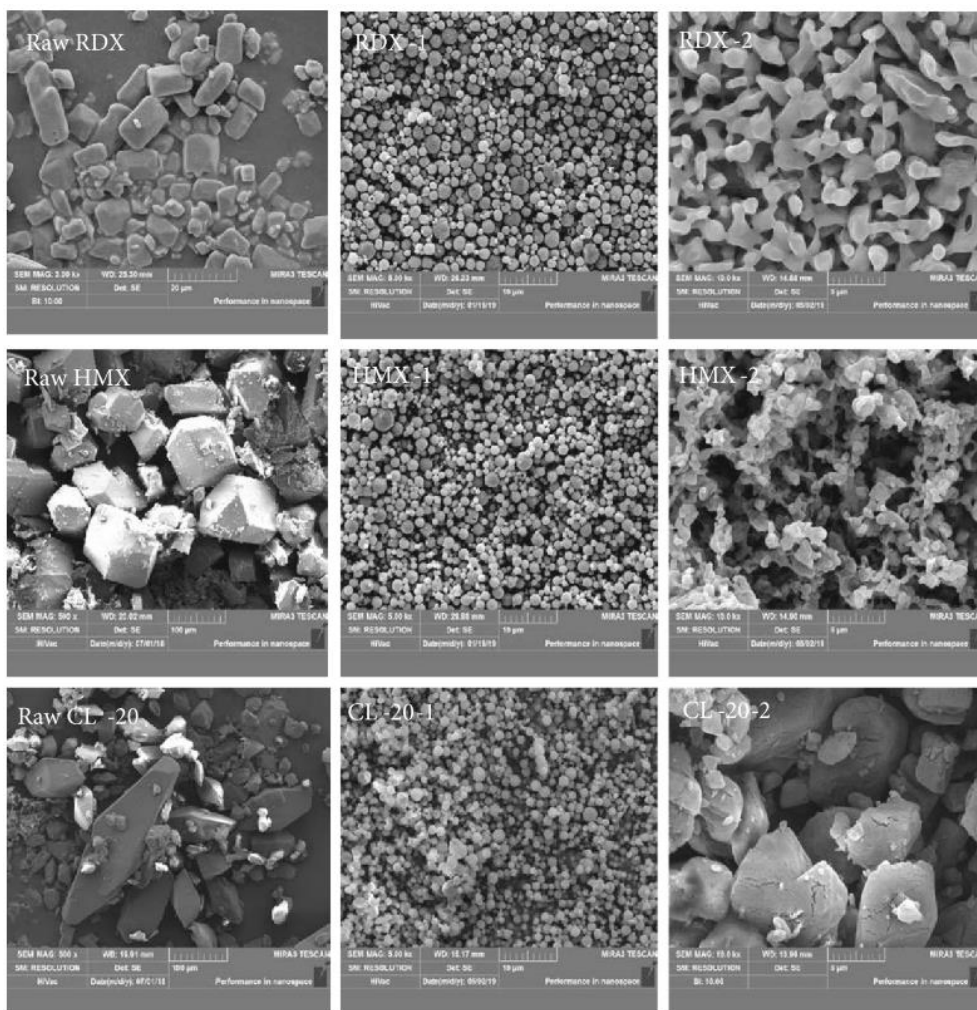


Figure 34: SEM micrographs of nitramines (left) in their raw state, (middle) spray dried from acetone with PVAc and (right) prepared by spray assisted antisolvent precipitation from acetone by water [144]

To this point, the literature reviewed has dealt with the production of nitramine composites prepared by spray drying a solution of nitramine (typically in acetone), in which polymers were typically dissolved and nanoparticles were suspended. There are however a couple of works that have employed the spray drier to improve slurry coating of fine and ultrafine nitramine powders.

For example, the Picatinny group prepared nanometric HMX powders by mechanical size reduction in a slurry of distilled water stabilised by PVOH and isobutanol. Aqueous spray drying of the slurry was conducted and the resultant powders were pressed into pellets. The mechanical properties and shock sensitiveness of these pellets were shown to improve significantly with crystal size reduction from 2 μ m to 300nm [145].

Developing the work by Patel *et al.*, Ye *et al.* prepared HMX/NC/GAP microspheres by spray drying fully and dissolved formulation (co-solution) and a slurry of HMX in dissolved binder/plasticiser [146]. The latter formulation contained nano-HMX crystals that had been prepared by SAAS. In terms of morphology, the slurry performed better, exhibiting significantly lower void space than the co-solution derived particles. Despite running the co-solution with 20°C lower drying temperature, there was insufficient residence time for a dense core to form. In the case of the slurry preparation, adsorption of binder/plasticiser onto the pre-existing HMX core gave significantly more uniform morphologies with higher density. The impact sensitiveness of the materials were assessed, and while the results indicate better performance of the slurry preparation over co-solution, both materials out performed a conventional slurry coated control. Differences in performance between slurry and co-solution cannot be attributed purely to the product morphology however, since the co-solution method resulted in conversion of the HMX from β - to δ -forms.

Zhigach *et al.*, demonstrated the versatility of spray drying in preparation of fine aluminised nitramine composite materials – a feat made non trivial by the strong agglomeration habits of nanometric aluminium powder [143]. It was shown that the degree of mixing in the composites was modifiable by choice of aluminium

surface preparation, and to a lesser extent the spray drying conditions. Polymorphic control through primarily mechanical process means was also reported, with HMX being observed in stable β -, metastable γ - and amorphous forms via PXRD studies.

A subsequent study, by Sun *et al.*, successfully employed spray drying to prepare aluminised RDX [147]. The work includes a significant investigation into the relationship between process parameters and composite microparticle morphology. SEM imaging of the powders revealed optimum particle sphericity depended significantly on aspiration rate and drying temperature, with the authors stating that maximisation of these parameters allowed for droplets to dry at a rate significantly higher than the rate of droplet collision, Figure 35. The effect of feed flow rate was assessed, but not in the context of the increased evaporative load on the system, and the results appear inconclusive. It should perhaps be noted that in Figure 35, images 1c and 2b are identical despite their reported preparation at 80°C and 70°C respectively, which, when combined with the unmentioned variation of image scale across an order of magnitude may bring into question the validity of this result.

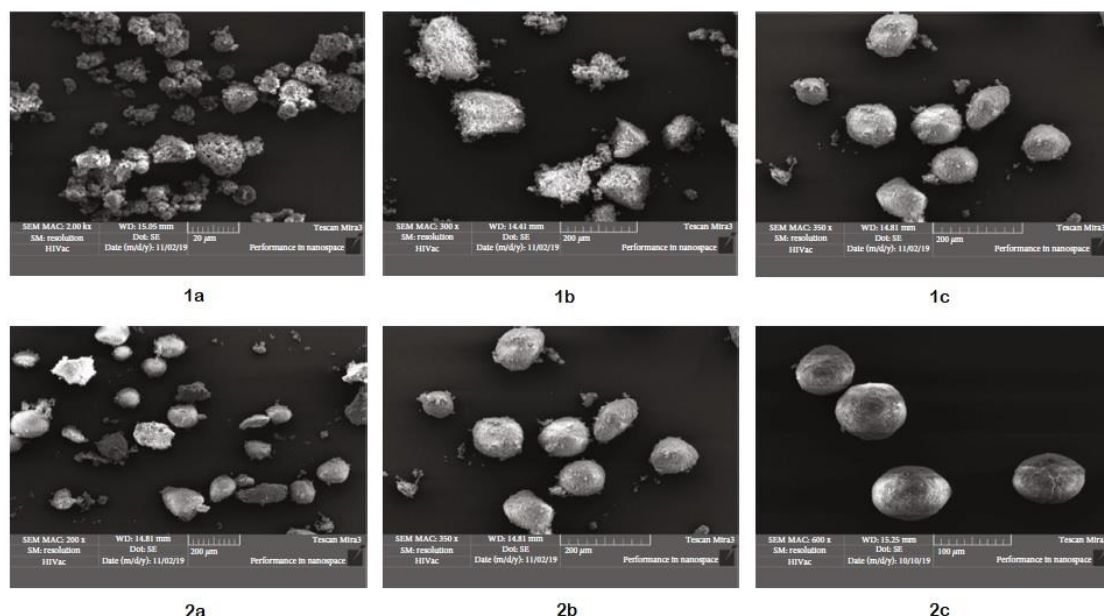


Figure 35: SEM micrographs of spray dried RDX composites. 1, Aspiration rates varied (a-c: 246, 357, 473 l.h⁻¹), T_{in} = 80°C, feed 4.5 ml.min⁻¹. 2, T_{in} varied (a-c: 60, 70, 80 °C), asp = 473 l.h⁻¹, feed = 4.5 ml.min⁻¹. [147]

Notably, this paper applied the Kissinger method to study the decomposition kinetics of spray dried composite RDX/Al/F2602 [148]. Controls of raw RDX and composite RDX/Al/F2602 were prepared by rapid antisolvent crystallization and subsequent slurry coating in the presence of aluminium. Results of the Kissinger analysis for the controls, lacking error margins, were $127.54 \text{ kJ.mol}^{-1}$ for raw RDX and $125.32 \text{ kJ.mol}^{-1}$ for the slurry coated composite. The activation energy of the spray dried composite was intermediary, at $126.63 \text{ kJ.mol}^{-1}$. Exotherm peak positions were reduced in both composite materials relative to the raw RDX, by approximately 5°C at all DSC heating rates.

The morphological observations made by Sun *et al.* were consistent with the earlier work of Kim *et al.*, who hypothesised that upward deviations in particle size resulted from collision and coalescence of droplets, which was abated by shorter residence times and high drying temperatures [149]. Extension of this theory was applied to show that inclusion of nucleation promoters (Brij 97, oleylamine) resulted in a significant increase of asymmetric coalescent growth and that by inhibition of nucleation (PVP) until after collisions had occurred, such coalescent particles grew symmetrically, as shown in Figure 36. Further affirmation of narrowed particle size distribution is afforded by Mercado *et al.*, whose work on the preparation of nano-energetics revealed the formation of trimodal distributions at low drying temperatures which were made monomodal upon reduction of drying time [119].

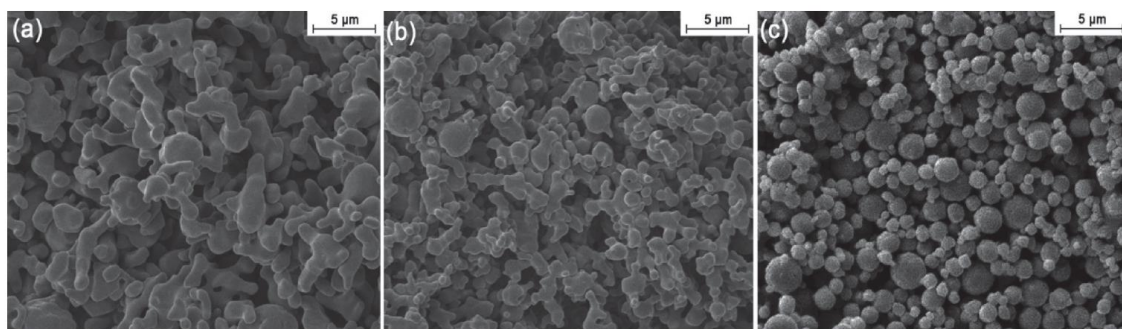


Figure 36: Micrographs of RDX spray dried by Kim *et al.* from solutions containing surfactants (a-b) and polymer (c) [149]

Table 3 contains the process parameters, resultant powder characteristics and key notes from the aforementioned papers. HMX, when spray dried, commonly exhibits phase changes. Typically recrystallising in the δ and γ forms, and infrequently the α and β forms. Despite its compositional similarity to HMX, RDX has a more rigid 6 membered ring that exists primarily in the chair conformation. Nitro groups of molecules in α -RDX assume two axial and one equatorial position, whereas molecules in the less stable β polymorph exhibit three axial nitro groups. Even with the high supersaturation rate of spray drying crystallisations (0.5 – 2 seconds) there has not been any report of the β -RDX metastable state being formed by this process.

It is generally accepted that the spray drying process can be used to reduce the shock sensitiveness of nitramines, although some issues were noted with the quality of control data upon which these claims are based. The effect of spray drying parameters has been reported to strongly influence the morphology of spray dried particles, as expected. However, the acclaimed trend of with higher temperatures thus faster drying giving the most narrow particle size range appears to contradict the theoretical basis outlined by Vehring, in which drying time should be maximised to allow for solute migration towards the core [80]. It is therefore expected that these contradictory papers, while not necessarily wrong, may contain a systematic error within the atomisation process or drying chamber fluid flow, that is increasing the rate of droplet collision to a frequency above what should be acceptable.

Table 3: Summary of key nitramine spray drying reports, parameters and results

Reference	Material / wt%	Additives / wt%	Solvent (FFR / mL.min ⁻¹)	Spray drier	Atomisation (Parameters)	Drying gas temp / °C (drying gas flow / m ³ .hr ⁻¹)	Particle size
Kim <i>et al.</i> , 2011	RDX 4 %	PVP 0.5 %, Brij 97 0.5 %, Oleylamine 0.5 %	Acetone (-)	IH	US (-)	175 (-)	0.8±0.3 µm, 2.6±0.4 µm
Sun <i>et al.</i> , 2020	RDX 0.63 %	Al 0.35 % + F2602 0.02 %	Acetone (1.5, 4.5, 7.5)	IH	US (-)	60, 70, 80 (0.25 – 0.47)	range 20-200 µm
Jia <i>et al.</i> , 2019	RDX, HMX, CL20 (-)	PVAc (-)	Acetone (-)	IH	2F (-)	80 (-)	-
Qiu <i>et al.</i> , 2015	RDX 5 %	PVAc 1 %	Acetone (3)	B290	2F (345 kPa)	55 (35)	average 5 µm
Qiu <i>et al.</i> , 2015	RDX 5 %	PVAc 1 %	Acetone (3)	B290	US (60 kHz, 1.2 W)	55 (35)	average 5 - 40 µm
Qiu <i>et al.</i> , 2011	RDX 5 %	PVAc 1 %, VMCC 1 %	Acetone (3)	B290	US (60 kHz, 1.2 W)	55 (35)	average 15 µm, range 5-30 µm
Qiu <i>et al.</i> , 2012	HMX 2 %	PVAc 0.2 %	Acetone (10)	B290	2F (345 kPa)	70 (35)	average 0.6 µm, range 0.2-4 µm
Patel <i>et al.</i> , 2015	HMX 6.80 %	PVOH 0.340 %	Aqueous slurry (-)	B290	- (-)	-	-

While not necessarily following the order of this literature review, the scarcity of reported preparations of AP by spray drying has led to this discussion being held here.

Munson and Reed spray dried ammonium perchlorate, with a variety of nanometric catalytic salts, reporting dramatic modification of hazard sensitiveness and burning performance, with some samples exhibiting explosive behaviour [25]. Likewise, Kohga and Hagihara report that the inclusion of fine porous ammonium perchlorate (FPAP) prepared by spray drying, resulted in more significant burn rate enhancement than equivalently sized fine ammonium perchlorate or porous ammonium perchlorate [5]. Neither paper provide much detail on the actual preparation procedure, with the latter citing an untranslated paper detailing the production spray dried AP [150]. From the drying temperatures involved, it is suspected that both studies used aqueous solutions of ammonium perchlorate although no concentration data is provided.

3.3 Paracetamol as an inert simulant material for RDX spray drying process development

Due to its relatively similar molecular structure, melamine is a widely used inert simulant for RDX. However, since this work focuses on recrystallisation by various means, it was decided that the lack of similarity between the solubility of RDX and melamine was sufficient grounds for replacement of the inert.

Paracetamol (acetaminophen) was selected to act as an inert simulant for various experiments involving RDX. The choice was made primarily due to the comparable solubility of RDX and paracetamol in common volatile organic solvents, summarised in Table 4. Like RDX, paracetamol exhibits both stable and metastable polymorphs under ambient conditions. The stable state, known as form I, is monoclinic while the metastable state Form II is orthorhombic. Extensive research exists, attempting to control the stabilisation of Form II, due to its preferable solubility kinetics and compatibility into tablets [151].

Table 4: Solubility data for RDX [152] and its proposed inert simulant materials melamine [153,154] and paracetamol [155,156].

Solubility (g/100g solvent)	RDX	Melamine	Paracetamol
Water	0.0012	0.323	1.739
Acetone	7.30	0.03	11.165
Methanol	0.24	Insoluble	37.161
Ethyl acetate	3.2	Insoluble	1.073

Since the primary function of paracetamol in this work was for use as an inert RDX simulant in initial spray drying experiments, it is worth noting that a similar experiment was conducted recently by McDonagh and Tajiber, using a Buchi B-290 two fluid spray drier [157]. Their experiment assessed the impact of drying temperature and solution composition (EtOH/H₂O ratio). Increasing drying temperature was shown to increase the average particle diameter and modify the volatility of the solution caused a reduction of particle size, with mean particle diameters ranging from 3.0 - 4.6 μm . It is noted by the authors that the products were strong agglomerates of much finer crystals, lacking the perfect

spherical morphology of composite microparticles, see Figure 37. The monoclinic Form I polymorph was generated in all cases.

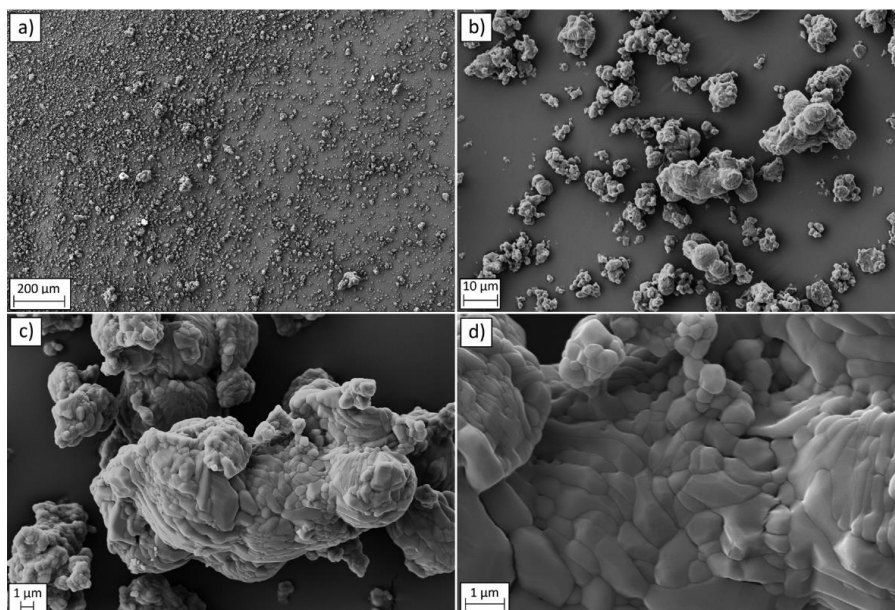


Figure 37: SEM micrographs of paracetamol spray dried from binary EtOH/H₂O solutions [157]

The flow character of various API/starch composite microparticles, prepared by rotary spray drying, was assessed by Marinopoulou *et al*, who found that composites with average particle sizes ranging from 40.48 - 55.24 µm presented with Hausner ratios between 1.2 - 1.4 [158]. Numerous other reports of spray drying paracetamol exist, but generally focus on the beneficial solubility or compressibility of paracetamol/excipient composite particles prepared by this method - these are not deemed relevant, and so will not be discussed.

3.4 Flow character modification

The flow characteristics of a powder are an ensemble effect related to the extent of internal friction between particles, resulting from interparticle forces. The flowability of a given powder is therefore intrinsically related to the particle size and size distribution, shape and shape distribution, surface roughness and humidity, and chemical composition. For dry powders, the dominant force resisting motion is usually dispersion or van der Waals forces and should the motion be driven by gravity, an expression can be written to describe the relative effects of each force on two equally sized spherical particles, Equation 26.

$$\frac{F_{vdW}}{F_G} = \frac{C_H}{4\pi\rho_s g a^2 R^2} \approx \frac{(100 \mu m)^2}{d^2} \quad (26)$$

Where the ratio of van der Waals forces, F_{vdW} , to gravitational forces, F_G , are related to the density, ρ_s , of two spherical particles with radius, R , separated by a distance, a , via the specific Hamaker constant for the system, C_H . Since attractive van der Waals forces increase linearly with particle radius, and gravitational forces increase with radius to the third power, fine particles tend to exhibit more cohesive behaviour acting to oppose flow under the influence of gravity [159]. This approximation only applies in the absence of other, generally stronger, interactions, such as capillary forces or electrostatic surface charge accumulation.

In micronized materials, the particle sizes generally fall within the bounds extremely cohesive behaviour. Assuming that the effect of capillary forces and electrostatic accumulation are either prevented, by suitable drying and handling procedures, or simply unavoidable – modifying the strength of dispersive forces between particles provides the most efficient means of reducing the internal friction of a powder [159]. Industrially this is achieved using flow modifying additives, typically with nanoparticles or surfactants, that either increase the separation of particles, a , or reduce the Hamaker constant for the interaction, C_H . Commonly used examples of flow modifiers in the pharmaceutical industry are nanometric silica (SiO_2), magnesium stearate (MgSt) and talc [160].

4 Materials and methodologies

4.1 Materials

The RDX used in this work was Chemring Type II Class 1, batch CH739/09 V87, prepared by the Bachmann process and therefore containing a nominal 4 – 17 wt.% HMX impurity, recrystallised by slow evaporation of RDX/AcO solution to remove HMX impurities. The AP used in this work was obtained from Amertek (99.3 % purity) and purified by scale static cooling crystallisation from hot (80 °C) aqueous solution. Paracetamol was obtained from SigmaAldrich, purity >99.0 %, and used without further purification. Flow modifiers carbon black, fumed silica and magnesium stearate were obtained from Sigma-Aldrich. Cellulose acetate butyrate (CAB) MW~70'000 was obtained from Merck. Potential tailor made inhibitors, 2,4-dimethyl-1-nitrobenzene (98 %), 1,2-dimethyl-3-nitrobenzene (97 %), 1,3-dimethyl-2-nitrobenzene (99 %), 2,4,6-trimethoxy-1,3,5-triazine, 6-methyl-1,3,5-triazine-2,4-diamine (98 %) were all obtained from Sigma-Aldrich and used without further purification. Solvents acetone, methanol, ethyl acetate and toluene were reagent grade, obtained from ThermoScientific, and distilled water was prepared in house.

4.2 Characterisation methods

4.2.1 Optical microscopy and ImageJ automated analysis

Stereomicroscopy was performed on a Brunel SX10 microscope, with images captured via the inbuilt 3M CMOS digital camera controlled via TCapture software [161]. The images captured on this kit proved to be unsuitable for quantitative analysis, due to the offset position of the illumination sources in both transmitted and reflective modes, and so this equipment was used primarily for qualitative inspection of samples. Polarised light microscopy was performed on a SP60P polarising microscope, with digital image capture via the trinocular mounted 1.3M UCMOS Digicam controlled via TouPView software [162]. Most samples were viewed via the x4 or x10 objective lenses, however spray dried particles were only distinctly visible via the x40 lens. Illumination was maintained at approximately 80 % capacity, and image brightness was manually controlled via exposure time. Dark and flat field corrections were enabled to prevent issues with image processing. Image gain, sharpening and colour corrections were not applied.

Particle size and shape factor analysis was performed in ImageJ/FIJI [163,164]. To preserve data quality, images were analysed without application of post processing sharpening, background removal or other modifications. While various thresholding processes were assessed, Otsu automated thresholding typically gave the best results in regards to identifying the boundaries of distinct particles without misidentification of crystal faces as distinct particles. Image measurements were performed prior to scaling, and the resultant pixel unit measurements were converted to μm using conversion factors obtained by imaging a stage micrometer at all magnifications. All optically obtained particle sizes are reported as equivalent circle diameters, not Feret diameters.

4.2.2 Scanning electron microscopy and manual sizing

Electron microscopy was performed on a Hitachi SV5000 FE-SEM operating in non-conducting mode. In the absence of a sputter coater, variable pressure experiments were conducted using sensitive beam conditions (80 Pa, 10kV) [165]. Images were obtained using the gaseous secondary electron detector as these exhibited far fewer artefacts than those obtained from the back scattered electron detector. Since the back scattered electron count is proportional to the nuclear charge of atoms imaged, and the imaged materials were primarily low nuclear mass CHNO species, the exposure time required for BSE imaging was significantly longer than SE imaging. Extension of the exposure time resulted in excessive charge build up on the sample, eventually resulting in electromagnetic repulsion or drift of the sample to produce artefacts such as the discontinuation shown in Figure 38 [165].

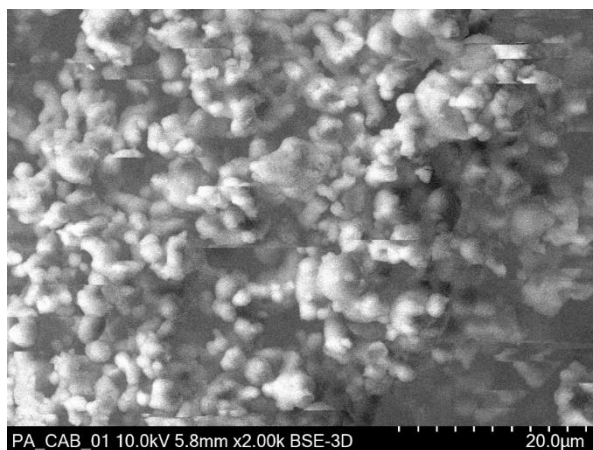


Figure 38: Artifacts observed in attempted BSE imaging of Paracetamol microparticles

4.2.3 Dynamic light scattering

Dynamic light scattering (DLS), sometimes referred to as photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QLS), is a technique that measures the size of particles suspended in a fluid. DLS experiments yield the hydrodynamic diameter, of particles by assessing the velocity of a particle subject to Brownian motion [166]. The hydrodynamic diameter and diffusion coefficient are linked by the Stokes-Einstein equation, Equation 27:

$$d = \frac{kT}{3\pi\eta D} \quad (27)$$

Where: k is the Boltzmann constant, T is absolute temperature, η is viscosity and D is the translational diffusion coefficient describing the particles velocity.

The hydrodynamic diameter is the diameter of a sphere with equivalent diffusion constant value to the sample. DLS experiments require prior knowledge of the carrier fluid viscosity and stable temperature for accurate measurements to be obtained. Errors typically arise from effects that influence the translational diffusion coefficient, such as the formation of electrical double layers, diffuse surface adhered polymers and particle shape effects [167].

DLS measurements of RDX were conducted on a Cilas 990 particle size analyser operating in small volume wet mode [168]. For RDX, the carrier fluid used was water, with Triton X (~ 0.1 wt%) as a dispersal agent. Materials with slight to high aqueous solubility (paracetamol and ammonium salts [156,169]) required the use of heptane as a carrier agent, with lecithin (~1wt%) as a dispersant.

4.2.4 Particle density

Particle densities were measured using a Micrometrics AccuPyc1330 Gas Pycnometer. An inert gas (He) was introduced to the sample cell under pressure, P_1 , while the reference cell is evacuated. The valve between the sample cell and the reference cell is opened and the pressure in each cell equilibrates at P_2 . The volume of the sample can then be found using the expression given by Equation 28 [170]:

$$V_{Particles} = V_{Chamber} + \frac{V_{Reference\ cell}}{1 - \frac{P_1}{P_2}} \quad (28)$$

Using the accurate volume measurements given by the helium pycnometer, and masses recorded on a Precisa XT 220A top pan balance, the average particle density was calculated five times per sample. Calibration was performed against a steel reference with volume 0.718655 cm³.

4.2.5 PXRD phase identification

Powder diffraction patterns were collected using a PANalytical XPert PRO Multi-Purpose Diffractometer with Cu K α radiation source. A PIXcel strip detector was used to collect data from 5°- 60° 2 θ , at intervals of 0.01313°. Peaks were fitted TOPAS using a hybrid Gaussian/Lorentzian function [171]. Phase identification was achieved by comparison of peak positions to the expected positions for each relevant polymorph obtained from the Powder Diffraction File (PDF) database.

4.2.6 PXRD peak broadening analysis

Since PXRD peaks have a tendency to be asymmetric, the peak fitting process is performed on each side separately thus yielding a full width at half maximum of the peak (FWHM) for each side. The left and right values of FWHM were then summed together to produce a “true” FWHM, that has been taken as equivalent to the total peak width, β_{tot} . The origin of this value is not exclusive to the sample, with instrumental factors such as X-ray beam width and incoherence also contributing to β_{tot} . Since broadening due to instrumental factors is largely independent of the sample, it can be measured using highly ordered materials such as silicon. Such a standardisation has been made for the equipment used here, and the expression for instrumental peak broadening as a function of diffraction angle is given by Equation 29. The peak broadening values, β , used in both Scherrer coherence length and Williamson-Hall analyses was obtained using the expression shown in Equation 30.

$$\beta_{\text{ins}} = \left[\frac{\tan^2 \theta}{10000} + \frac{\tan \theta + 0.0651}{50000} \right] \quad (29)$$

$$\beta = \beta_{\text{tot}} - \beta_{\text{ins}} = \beta_{\text{tot}} - \left[\frac{\tan^2 \theta}{10000} + \frac{\tan \theta + 0.0651}{50000} \right] \quad (30)$$

The Scherrer equation, Equation 4, was used to assess the relative coherence lengths of morphologically significant lattice planes of spray dried RDX using a shape factor, k , value of 0.9. Errors were calculated by propagation of the fit error obtained from peak fitting through the Scherrer equation.

Williamson-Hall analysis of microstrain and coherence length was used to assess the relative microstrain and average crystallite lengths of a variety of spray dried materials, via Equation 7. Peaks that displayed high fit error percentage were not used in the analysis but are shown on the Williamson-Hall plots as hollow circles. Error values for crystallite length and microstrain were calculated from the standard error associated with the applied linear fit. The MatLab script from which Williamson-Hall plots were generated is presented in Appendix A.1.

4.2.7 Flow assessment

Comparison of powder flow characteristics was conducted through conical angle of repose measurements. Piles were prepared by sieving powder into a conical funnel, held by a support at a known height above a plate. Two methods were employed for determining the angle of repose, α_R , once a pile was prepared. Initial measurements used geometric calculation, $\alpha_R = \tan^{-1}\left(\frac{h}{d}\right)$, where h was the known pile height, determined by the separation of the funnel and plate, and d was the average base width [159]. The average base width was determined from four measurements along bisecting lines, separated by 45° , made with digital vernier callipers. Issues were noted with the geometric approach, stemming from non-linear cone edges, that made repeatable determination of the base width unreliable. A new method was developed, where angles were determined from side images of the pile. Direct measurement of the angle in ImageJ was attempted, however the same issue of indeterminate lineshape was noted. As such a numerical method was developed in MatLab by which side images were converted to binary, via threshold, and the pixels corresponding to the edge of the pile were located [172]. Plotting the coordinates of edge pixels and subsequent linear fit removed the bias and improved the reproducibility of angle of repose measurements. The script used for this is shown in Appendix A.2.

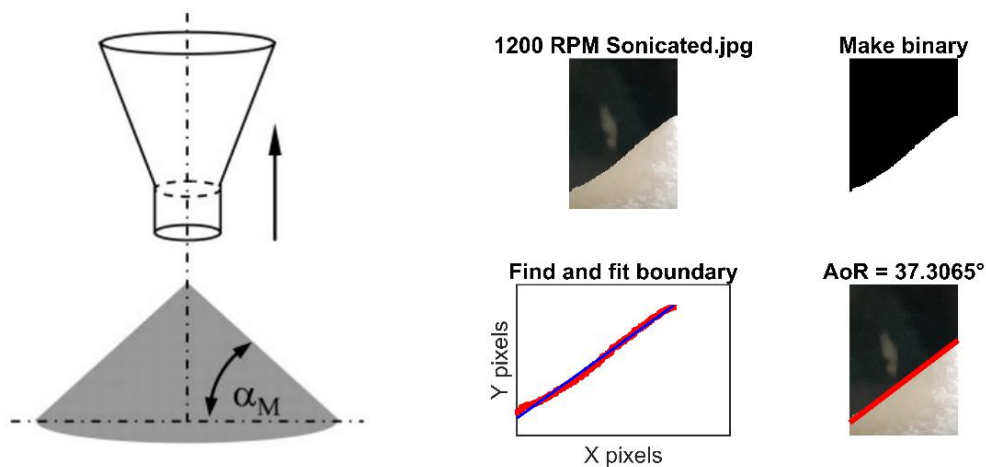


Figure 39: Conical angle of repose and image gradient fitting process [159]

The compressibility of materials was assessed by measurement of bulk and tapped densities, ρ_0 and ρ_n , from which Hausner ratios were calculated, Equation 31. The initial bulk density measurement was performed by filling a 10 cm³ graduated measuring cylinder with sieved powder and noting the mass and accurate volume [173,174]. The cylinder was then tapped manually, using a jig that allowed for 2 cm vertical displacement. The powder volume was recorded as a function of tap number until a consistent powder volume was reached. The consistent volume was then used to calculate the tapped density of the known mass of powder. Despite the majority of powders reaching a consistent volume after as few as 30 taps, all densities presented herein were calculated using volume measurements resulting from a minimum of 50 taps.

$$HR = \frac{\rho_n}{\rho_0} \quad (31)$$

Materials with angle of repose values lower than 35° flowed well, where as angle of repose measurements between 36 - 40° indicated cohesive behaviour. Materials with angle of repose > 40° were very cohesive, and typically displayed poor flow[159]. Hausner ratios indicated improved flow character as the value approached unity.

4.2.8 DSC/TGA

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were collected in tandem using a Mettler Toledo DSC/TGA 3+ instrument. Samples were prepared in aluminium pans, fitted with pierced lids, with initial sample masses measured on a calibrated Sartorius ME2155 balance. The first of experiment of each group used a blank subtraction to account for thermal drift at high temperatures. Analysis of RDX and paracetamol was conducted over the thermal range 30 - 350 °C, whereas AP was heated between 30 - 550 °C. General experiments employed a heating rate of 10 °C.min⁻¹, with N₂ purge gas (50 cm³.min⁻¹). Peak positions and integral values were obtained by fitting within the Mettler Toledo StarE proprietary software, but prepared for presentation by external export as text files.

Activation energies, E_a , and Arrhenius pre-exponential factors, A , for thermal decomposition reactions were assessed using the Kissinger relationship, Equation 32 [148]. Kissinger plots were prepared by measuring the peak decomposition temperature, T_p , at heating rates, $\beta = 20, 30, 40$ and 50 °C.min⁻¹.

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (32)$$

Selection of the Kissinger method, over the comparable Ozawa method or other modified kinetic thermal analysis techniques, was made on account of the increased literature available for comparison [175].

4.2.9 Rotter impact test

Rotter impact testing was performed by the Cranfield Energetics Materials Hazard Testing group following the procedure detailed in the EMTAP Manual of Tests [176]. Samples of energetic material, contained in brass caps, were placed on an anvil and the sensitiveness was assessed by dropping a 5 kg mass onto the sample from various drop heights. Initiation events were noted as with go or no-go for a given height. Variation of drop height followed a Bruceton staircase. The median height that caused detonation events is then converted into a figure of insensitiveness value, shown in Equation 33, to eliminate systematic differences in results.

$$\text{FofI} = \frac{80H_{50}}{RM} \quad (33)$$

Where H_{50} is the median height required to cause detonation and RM is the running mean drop height of standardised RDX testing on a given machine.

4.3 Cooling crystallisation methodology

4.3.1 Solubility plots

Ammonium perchlorate shows a very high thermal coefficient of solubility in water, making it an ideal candidate for cooling crystallisations. The solubility of ammonium perchlorate in distilled water was measured by equilibration of excess AP (100 g) in distilled water (100 ml) at various temperatures. The mixture was stirred using a submerged magnetic induction stirrer plate coupled with a stir bar in the flask. After equilibration at a given temperature for 24hr, stirring was stopped and suspended particles were given 4 hrs to settle. Aliquots ($3 \times 5 \text{ cm}^3$) of the saturated supernatant were transferred into 10 cm^3 vials and concentration was calculated based upon the dry mass. The data showed relatively good agreement with the literature values as shown in Figure 40 [169]. Linear solubility-temperature expressions for measured and literature data are provided in Equation 34 and Equation 35 respectively.

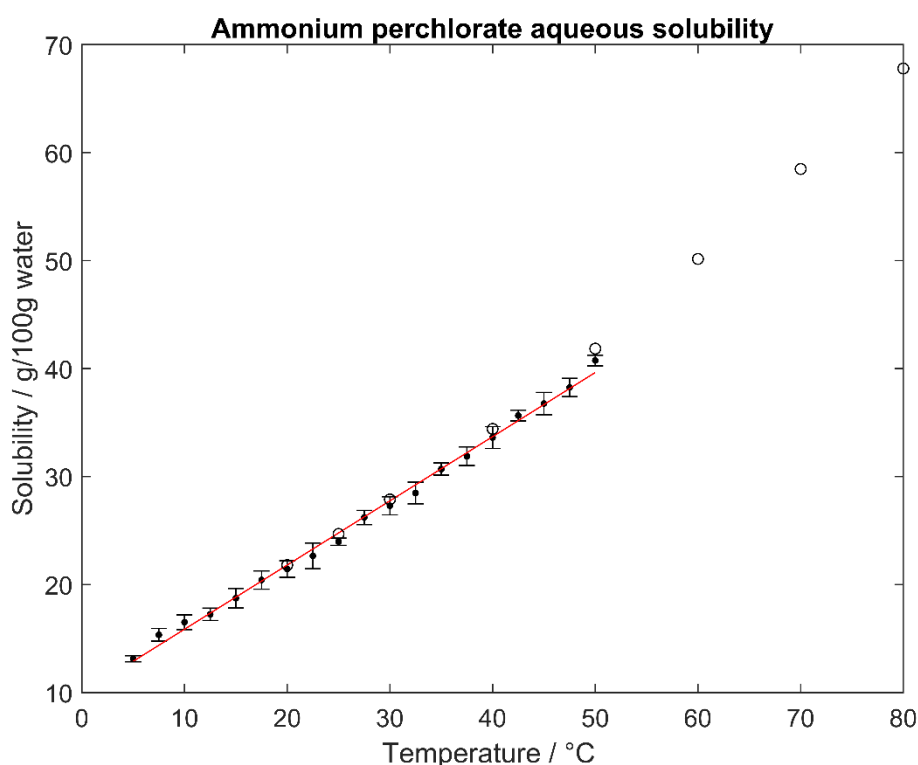


Figure 40: Aqueous solubility of AP. Measured – black points with fitted line. Literature values– hollow circles [169]

$$\text{Measured solubility (g/100g solvent)} = [0.594 \pm 0.009] T + [9.9 \pm 0.3] \quad (34)$$

$$\text{Literature solubility (g/100g solvent)} = [0.76 \pm 0.02] T + [5 \pm 1] \quad [169] \quad (35)$$

A previous variable temperature study of the solubility of AP in organic solvents was not found. Willard and Frederick Smith report the solubility of AP in a variety of solvents at 25 °C, showing it to be most soluble in MeOH, AcO and EtOH (6.862, 2.260 and 1.907 g/100g solvent respectively) [177]. Using the same procedure as before, the organic solubility of AP was measured for MeOH and AcO. The results showed decent agreement with the literature reported values. However, the thermal coefficient of solubility for AP in organic solvents was deemed insufficient for cooling crystallisations on a reasonable scale.

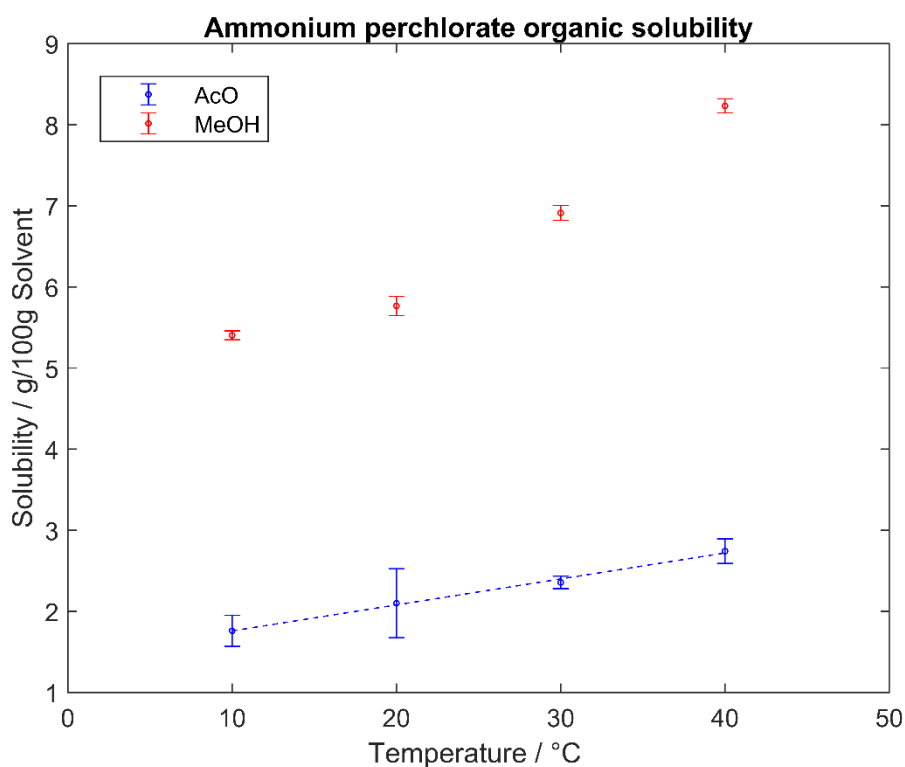


Figure 41: Equilibrium solubility of AP in acetone (blue) and methanol (red)

4.3.2 Water bath crystallisation apparatus

Preliminary cooling crystallisations were conducted using round bottomed flasks, immersed in a water bath (ThermoFisher Scientific Haake A 10B refrigerated bath combined with a ThermoFisher Scientific Haake AC200 immersion circulator), shown in Figure 42. Distilled water only was used as the thermal fluid for all experiments. This kit was chosen for the large workspace, programmable temperature profiles, internal and external thermocouples, and data logging capability via serial communications. Stirring of the crystallisation vessel was achieved using two methods, shown in Figure 43. Firstly, an overhead controller coupled with a two-paddle folding impeller. Folding of the impeller made it possible for the paddles pass through the narrow neck of the round bottomed flask. Due to the nature of these impellers, a minimum rotation rate of approximately 350 rpm was necessary to fully open the impeller. Alternatively, to assess the impact of increased crystal/impeller collision, a MIXdrive 1 eco inductive magnetic stirrer was used to drive a magnetic stirring bar within the crystallisation flask. The MIXdrive stirrer plate was designed for submersion in water and can operate at rotation rates from 400 – 1200 rpm. The inductive plate was held directly under the crystallisation vessel using an isolated aluminium bracket so that vibrational transfer into the crystallisation vessel would be minimised. Ellipsoidal bars, with different sizes and masses were assessed.



Figure 42: ThermoFisher Scientific Haake A 10B water bath fitted with AC200 immersion circulator.

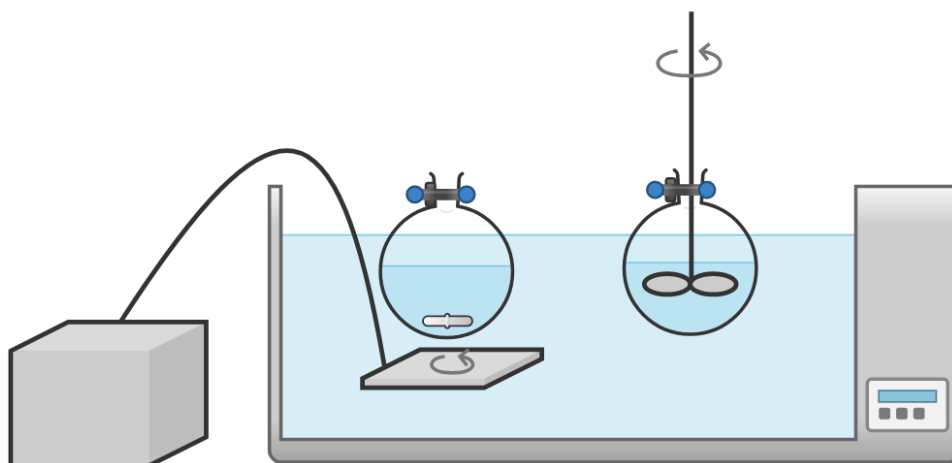


Figure 43: Submersible magnetic stirring and overhead stirring in small scale AP cooling crystallisations

Since the A10B refrigerated bath is a high-volume unit, initial experiments did reveal issues with thermal inhomogeneity. To assess this, the temperature of the bath was equilibrated at 30 °C for 1 hour. A cooling ramp was then initiated (-5 °C / hr) to a final temperature of 10 °C. Temperature readings were taken at nine positions in the bath when the internal thermocouple of the AC200 measured 20.0 °C. The inhomogeneity is represented below in Figure 44. The coldest region corresponds to the direction in which the impeller jet is predominantly directed. While the absolute temperature at different positions was noted to vary, following an initial onset, the actual rate of temperature change was consistent regardless of position. Since supersaturation in cooling crystallisations is primarily dictated by cooling rate, the inconsistencies of absolute temperature have been noted but no treatment could be found.

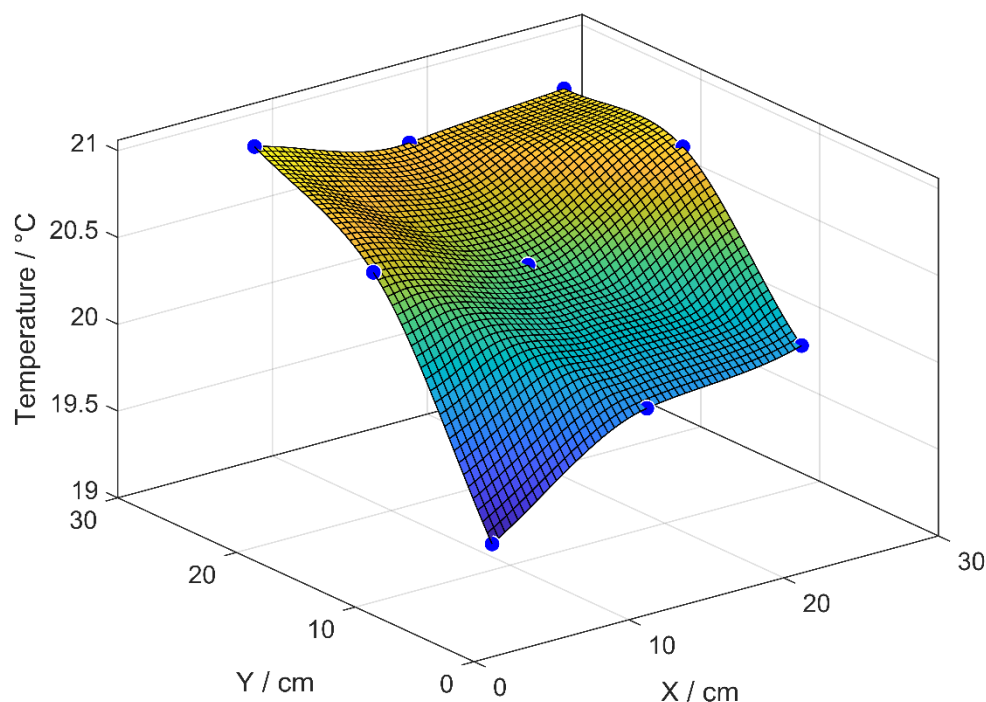


Figure 44: Surface plot of thermal inhomogeneity in the A 10B water bath as the AC200 internal thermocouple read 20 °C. The surface is generated from a cubic fit of the 9 datapoints shown by the blue circles. Note that the 0,0 position corresponds to the corner indicated by the red arrow in Figure 42.

Another issue posed by the large volume of the water bath was severe restrictions on the maximum cooling rate. To assess the maximum cooling capability of the bath, several cooling ramps were run, starting at 40°C and ending at 10 °C. The bath is programmed in steps characterised by start and end temperatures with a definable length of time between points. Setting the step time to 1 min ensured that the bath would operate at maximum power to reach the end temperature. Significant differences in the cooling capability were noted, and corresponded weakly to the ambient temperature of the laboratory, although other factors such as obstruction of cooling vents may also have played a role. The average cooling rate measured was -8.7 ± 0.3 °C/hr. To ensure consistency between experiments, a cooling rate of -7.5 °C/hr was used.

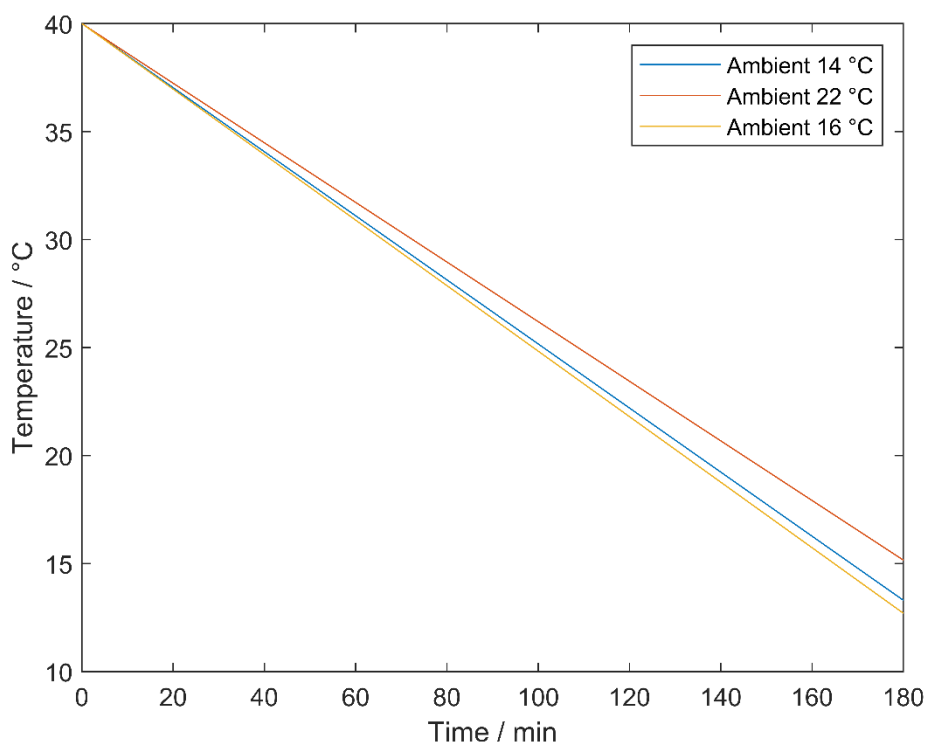


Figure 45: Variation of the maximum cooling capacity of the AC200 with ambient conditions.

4.3.3 Water bath crystallisation process

For each run, a stock solution of ammonium perchlorate (32.661 g) combined with distilled water (117.6 g) in a stoppered flask resulting in a saturated solution at 30°C, with a concentration of 27.75 g/100g solvent. The mixture was equilibrated for half an hour at elevated temperatures to ensure complete dissolution of solids (60 °C, 450 rpm). Aliquots of the solution were then taken using a preheated measuring cylinder and filtered through a preheated POR4 sintered funnel under light vacuum to reduce the chance of crystallisation that would modify the initial concentration of the solution. Filtering of the solution was conducted such that the filtrate was collected directly in the round bottomed crystallisation flask. This process was repeated for 3 x 40 ml aliquots, allowing three crystallisations to be performed simultaneously.

Solutions were prepared as described and the three crystallisation vessels were submerged in the water bath as described in Section 4.3.1. Undersaturated solutions were equilibrated at a start temperature, T_{start} , for one hour. A cooling ramp was then initiated that passed through the saturation temperature, T_{sat} , and ending at a final temperature, T_{end} . Values for the characteristic temperatures and the associated solubilities are shown in Table 5. At the end of each run, crystals were recovered by Buchner filtration and stored in a desiccator to prevent moisture ingress.

The three flasks were labelled A, B and C and were used in the same position in each separate run. Agitation of vessels A and B was achieved using submersible inductive magnetic stirrer plates with the size and mass of the stirrer bar varied to assess the effect of impeller collisions on particle formation, details of which are given in Table 6. Agitation of vessel C was achieved using an overhead stirrer fitted with a PTFE centrifugal stirrer. A mark was drawn on the shaft of the stirrer to ensure consistent submersion depths between runs.

Table 5: Characteristic points of the water bath cooling crystallisation experiments.

Characteristic point	Temperature (°C)	Solubility (g/100g H ₂ O)
T _{start}	35	30.72
T _{sat}	30	27.75
T _{end}	15	18.83

Table 6: Stirrer bar specifications for water bath crystallisations in vessels A and B

Vessel	Mass / g	Length / mm	Width / mm
A	10.793	15.3	6.2
B	40.028	25.1	10.3



Figure 46: MIXDrive submersible stirrer plate and folding implerler

4.3.4 Radleys reactor crystallisation apparatus

An improved option for crystallisation of solutions was the use of a Radleys Reactor-Ready™ Lab Reactor, shown in Figure 47. Equipment consisted of a jacketed reaction vessel, thermally controlled by the AC200 immersion circulator via the external circulation ports. Overhead stirring was provided by a Heidolph Brinkmann RZR 2021 that offered a range of agitation rates from 200 to 2000 rpm. A rigid 4 bladed agitator was used in place of the twin bladed folding stirrer. The top cap of the reaction vessel consisted of five necks, the central one being reserved for the overhead stirrer, with four remaining for various uses. Generally, the temperature of the crystallisation mixture was recorded via a Pt thermocouple, passed through one of these ports into the fluid.



Figure 47: Radleys Reactor-Ready™ Lab Reactor

4.3.5 Radleys reactor crystallisation process

Both slow and rapid cooling crystallisations were conducted and the effect of agitation rate on crystal morphology was assessed. Agitation rates were assessed at three levels, 400, 800 and 1200 RPM. Slow cooling crystallisations followed a thermal ramp ($-7.5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) provided by the ThermoScientific AC200 immersion circulator connected to the jacketed reaction vessel. These crystallisations followed ramp program that ran from $35\text{ }^{\circ}\text{C}$, through the saturation temperature ($30\text{ }^{\circ}\text{C}$) to a final temperature of $15\text{ }^{\circ}\text{C}$ at which point crystal were retrieved. Due to limitations on the maximum cooling rate provided by the immersion circulator, rapid crystallisations did not follow linear cooling profiles. Instead, the jacketed reaction vessel temperature was fixed at the end point ($15\text{ }^{\circ}\text{C}$), and undersaturated solutions were prepared and equilibrated at the desired initial temperature ($55\text{ }^{\circ}\text{C}$) in a separate water bath. A higher initial temperature was used in these crystallisations to prevent immediate crystallisation of the solution as it was added into the reaction vessel. A thermocouple was held within the crystallisation vessel to record the cooling curve, to ensure that the temperature of all rapid cooling crystallisations decayed at a comparable rate.

Solutions were prepared by mixing AP (34.69 g) with water (125 cm^3), such that the resultant solution would reach equilibrium solubility at $30\text{ }^{\circ}\text{C}$. The mixture was then heated ($55\text{--}60\text{ }^{\circ}\text{C}$) well in excess of the solubility limit to ensure total dissolution prior to hot filtration. For slow cooling crystallisations, the hot filtration was conducted directly into the Radleys reactor. In the case of rapid cooling crystallisations, the filtrate was kept in a stoppered flask fitted with a stir bar and equilibrated at the desired initial temperature in a water bath (using submersible stirrer plates to ensure homogeneity), prior to being introduced to the crystallisation vessel. For all crystallisations, upon reaching the final temperature, crystals were recovered via the drain port of the Radleys reactor, directly into a sintered funnel and washed in with cold denatured ethanol ($3 \times 5\text{ cm}^3$). All samples were then dried *in vacuo* in an effort to remove any residual moisture from the crystal surfaces.

4.3.6 Sonocrystallisation

A Heat Systems XL2020 Sonicator horn was used to generate cavitation for sonocrystallisation experiments, as shown in Figure 48. In water bath experiments, the tip of the sonication was placed in close proximity to the crystallisation vessel thus providing indirect sonication of the crystallisation medium. However, sonication experiments conducted in the Radleys reactor employed direct contact sonication. This was achieved by using the 1/2" probe in combination with the microtip extension, which was passed through one of the ports on top of the reactor vessel. Care was taken to ensure that the driver housing was clamped securely, eliminating any lateral motion of the sonicator tip that could result in direct contact with either the reactor walls or impeller. Prior to any sonication experiments, the condition of the tip and the resonant frequency tune were assessed and rectified as necessary.



Figure 48: Heat Systems XL2020 sonicator, fitted with a 1/2" probe.

By its nature, sonication of a liquid introduces a significant amount of energy to a system that is dissipated predominantly as heat. An experiment was conducted to measure the effective heat output of the sonicator, following a modified version of the disequilibrium sonication power measurement reported by [178], however the significant variation of laboratory temperature led to drift and it was decided that the results were void. A different approach was taken, that assessed whether the addition heat introduced by the sonicator would have an impact on the cooling rate of crystallisations in the rapid Radleys reactor experiments. The kit was setup as shown in Figure 48, the Radleys reactor

jacket temperature was held at 10 °C. The empty vessel was stirred at 250 rpm. Water (200 cm³) was heated to temperatures in the range of 40 – 60 °C and then poured via funnel into the reaction vessel. The resultant cooling curve was recorded via an immersed thermocouple connected as a serial object in Matlab. This process was repeated in the absence of sonication, and with the sonicator operating continuously at power levels 1 and 4. The time resolved temperature profiles were fitted to a Newtonian exponential decay, Equation 36.

$$T(t) = T_c + (T_0 - T_c) \exp(-kt) \quad (36)$$

It should be noted that the experiments involving continuous sonication were curtailed after less elapsed time to protect the sonicator from the possibility of overheating. The calculated thermal decay constants are shown below in Table 7. Fit quality was excellent in all cases, as demonstrated by the low errors. While the differences between decay constants are only marginal, they do support the expectation that sonication would reduce the rate of cooling as can be seen in Figure 49. No modification to the process was made to account for this deviation as the impact was decided to be sufficiently low.

Table 7: Summary of thermal decay constants for Radleys reactor rapid cooling crystallisations, with and without sonication.

Sonication PWL	Decay constant k
0 (off)	0.3455 ± 0.0009
1 (low)	0.3439 ± 0.0008
4 (high)	0.335 ± 0.004

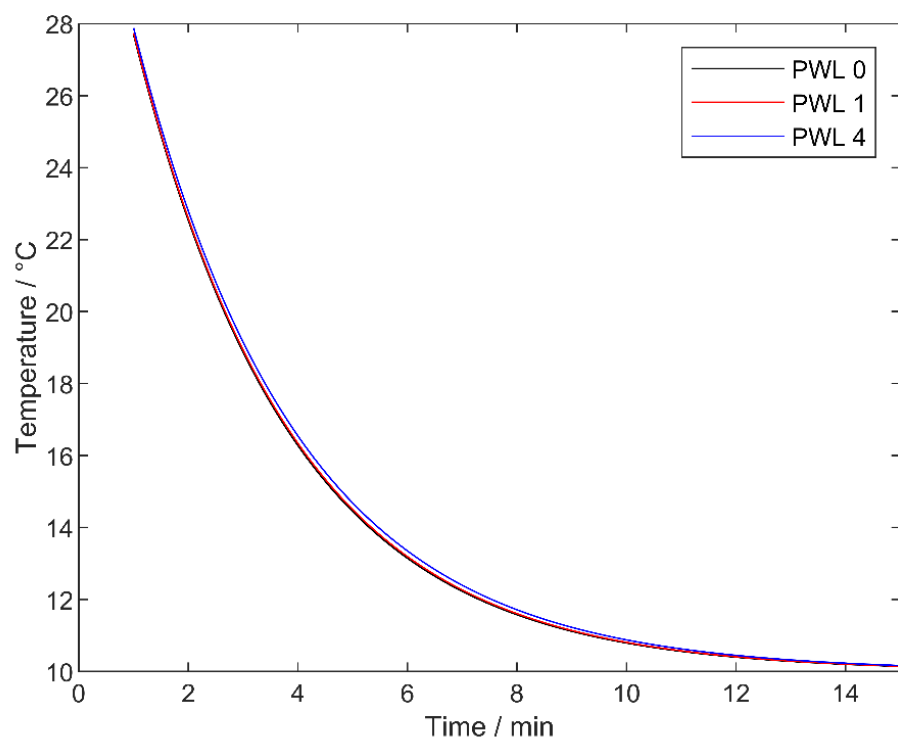


Figure 49: Stacked plot showing the effect of ultrasonic radiation on achievable cooling rates in the Radleys reactor. Cooling regimes in the absence of sonication and with low powered sonication (black and red curves respectively) were almost identical, with only a very slight delay caused by low sonication. High powered sonication caused a more pronounced delay to the cooling curve, but the effect is deemed negligible.

4.4 Spray drying and microencapsulation methodology

4.4.1 Spray drying apparatus

The spray drier used throughout this work was the commercially available laboratory scale B290 mini spray drier, manufactured by Buchi Switzerland. An annotated image of the setup is provided in Figure 50. As standard, the B290 operates using a two fluid nozzle. Notable features of this nozzle are the pneumatic nozzle cleaning functionality, which can be operated at a variety of intervals to dislodge any deposits of product obstructing the nozzle aperture. Feedstock temperature is controlled by means of a cooling circuit through which radiator fluid may be passed. This is a vital control measure to guarantee consistency within a given spray drying run, since the B290 is a co-current spray drier the nozzle is exposed to drying gasses at maximum temperature.

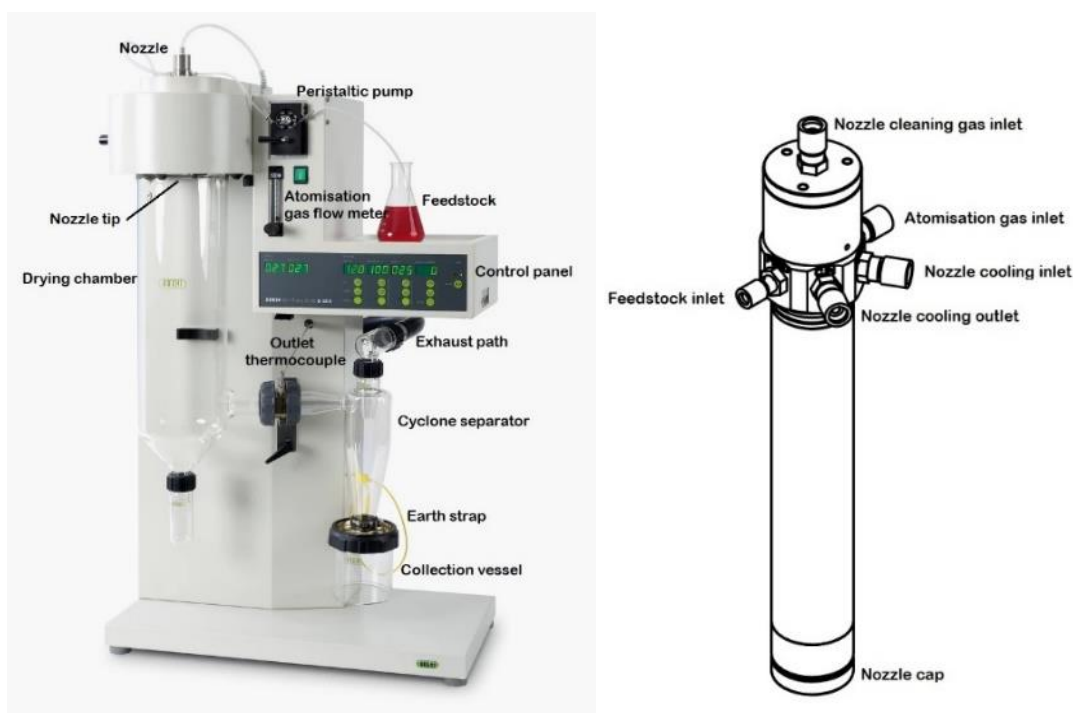


Figure 50: Buchi B-290 Mini spray drier and two fluid pneumatic nozzle

Preliminary experimentation with the B290 looked at the feasibility of spray drying aqueous AP solutions. In these experiments, AP was substituted for ammonium sulphate (an inert simulant with comparably high aqueous solubility). The kit was set up in negative pressure, open mode, using air as the atomisation and drying gas. Due to the extremely hygroscopic nature of both AP and AS, it was relatively quickly noted that the potential for drying was severely limited even at very low feed rates, with recovered powder forming a single agglomerated mass in the collection vessel.

Spray drying solutions of more volatile organic solvents required the use of an inert atomisation and drying gas, nitrogen. To prevent unnecessary waste of the inert gas, spray drying was conducted in closed negative pressure mode, with solvent vapours removed from the exhaust gasses by passage through the heat exchange unit prior to recirculation. The Buchi B295 inert loop, responsible for cleaning the drying gas of solvent vapours, is shown below in Figure 51.



Figure 51: Buchi B296

Initial experimentation with the spray drier sought to develop a baseline of machine and solution parameters, suitable for spray drying paracetamol and RDX from volatile organic solvents (primarily acetone and methanol).

Control over the feedstock flow rate and drying gas aspiration rate is afforded percentwise. Conversion from the percentage into meaningful units is possible using plots from the B-290 user manual, as can be seen in Figure 52.

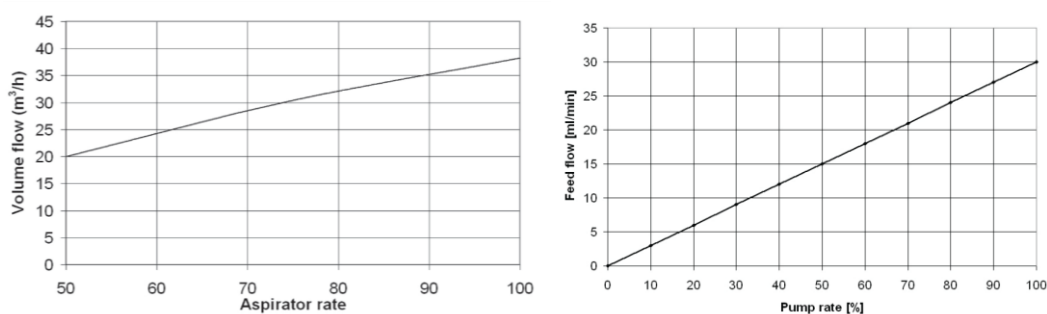


Figure 52: Conversion plots for feed flow and aspiration rates [179]

While verification of the aspiration rate can be achieved using as hot wire mass air flow (MAF) sensor, such an assessment was not undertaken in this work. Without exception, all reports of spray dried energetics that employed a Buchi B-290 spray drier, used maximum (100 %) aspiration as this gives the best yield by allowing the optimum performance of the cyclone. Lower aspiration rates may be used to increase the residence times for thermally sensitive materials that are dried at lower temperatures.

Feed flow rate is often varied, due to its high potential impact on resultant particle size and residual solvent content. As such, calibration of the peristaltic pump was performed by recording the time required for a fixed volume (10 – 90 ml) of water to be transferred by the peristaltic pump operating at various pump rates. The feed flow rate through three tubing materials (silicone, Tygon-MH2375 and Tygon-F4040A) was assessed in this manner. The experiment was repeated after one year and found that no significant deviation had occurred. The feed flow rate as a function of peristaltic pump utilisation alongside the commonly used solvents for each tubing material, is shown below in Table 8.

Table 8: Summary of peristaltic pump calibration and solvent suitability for each tubing material.

Tubing Material	FFR (ml.min ⁻¹ .% ⁻¹)	Solvents
Silicon	0.279 ± 0.004	Water Methanol Ethanol Isopropanol
F2375	0.232 ± 0.001	+ Acetone Ethyl acetate
F4040A	0.250 ± 0.003	+ Hexane

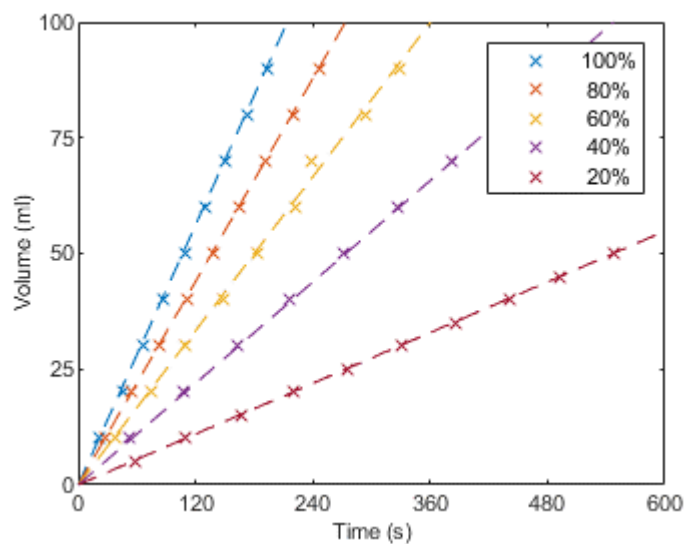


Figure 53: Feed flow rate determination for silicon tubing. Data points correspond to the time require to transfer a given volume of water at a given pump operating percentage, fitted by linear regression.

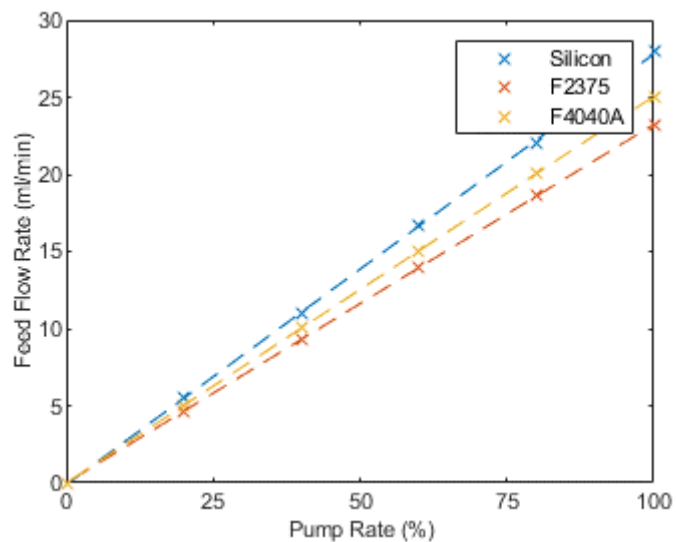


Figure 54: Comparison of feed flow rate as a function of peristaltic pump utilisation for the three tubing types used with a Buchi B-290 spray drier.

4.4.2 Spray drying process

The B-290 spray drier and B-295 inert loop was assembled in closed negative pressure mode according to the manufacturer's instructions. Aspiration was initiated at 100% and an inert atmosphere of N₂ (BOC Compressed N₂, 10 Bar series 8500 regulator) was introduced via the nozzle (40 mm, 5 – 8 bar). Nozzle cooling and cleaning (3/10) were conducted for the duration of the experiment. Upon reaching the target T_{in} value, pure solvent (acetone) was pumped through the nozzle, allowing T_{out} to reach a stable value.

The pressure drop and spray cone appearance were assessed, and when deemed of sufficient quality, the feed tube was switched from pure solvent to the stirred solution. Regular checks were made to assess the spray nozzle condition, ensuring that a constant cone was present. Cyclone performance was also monitored to ensure that no blockages occurred at the inlet or solid outlet. Upon completion of the spray drying run, the feed was reverted to pure solvent (3 x 10 cm³) following which the equipment was shut down and allowed to cool (20 min). Material was recovered from the collection vessel and dried *in vacuo* to reduce agglomeration under the influence of residual solvent and to prevent the ingress of atmospheric moisture. A threshold minimum yield of 80 % was generally applied, below which samples were rejected and remade due to the possibility of operator error. After each run the spray drier glassware, nozzle and seals were cleaned with soapy water, rinsed with distilled water and acetone then dried appropriately. The exhaust stream filter was cleaned when the pressure drop reached - 90 mbar, approximately every fourth run. A drop of - 90 mbar was deemed a reasonable cut off value for spray drying runs conducted using the more restrictive high-performance cyclone. A more stringent cut off value (- 60 mbar) was applied for use of the large volume cyclone.

Unlike the cooling crystallisations, where only adjustments to the crystallisation parameters were made, spray drying experiments were conducted using a variety of formulation and process controls. For clarity, these have been detailed within the relevant results sections.

5 Results and discussion

5.1 Small batch cooling crystallisation of AP

5.1.1 Results

Batch cooling crystallisations of AP were conducted using the apparatus described in Section 4.3.2, following the slow cooling crystallisation procedure detailed in Section 4.3.3. The effect of agitation type (magnetic stirring vs overhead), end point equilibration and indirect sonication on particle size and morphology was assessed by microscopy. While it was hoped that image analysis, as described in Section 4.2.1, could be used to obtain comparative size and shape factor values for each sample the extensive agglomeration of crystals made it impossible to reliably distinguish between particles via thresholding methods. Attempted watershed application also failed to reliably distinguish particles, as is demonstrated in Figure 55.

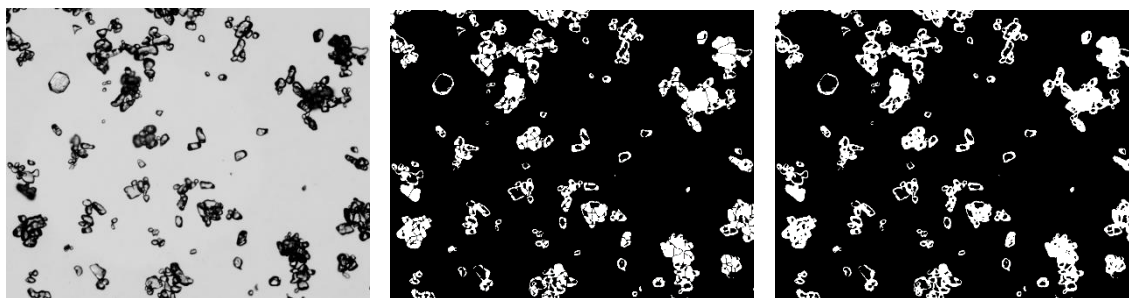


Figure 55: Left – Raw micrograph of AP crystals showing extensive agglomeration due to adsorbed moisture. Mid and right – watershed and thresholding filters applied to the raw image respectively. Both treatment processes failed to identify the boundaries between distinct crystals, favouring instead partial identification of boundaries corresponding to translucent and opaque crystal faces.

As such, this section relies on qualitative comparisons between representative images of each sample. The inherent limitation of such an approach is recognised, and so a large selection of images, intended to be representative of each sample, are presented in Appendix B.

Differences in crystal morphology due to agitation mode and rate were evident in all experiments. Figure 56, Figure 57 and Figure 58 show the effect of increased agitation rate on crystals prepared with low mass magnetic stirring, heavy magnetic stirring and overhead stirring respectively. A slight size reduction was noted when using the heavier magnetic stirring, relative to the

light 10 g bar. Agitation with overhead stirring produced crystals that were much larger crystals than those resulting from either mode of magnetic stirring. Regardless of agitation type there appeared to be a noticeable change in crystal morphology for agitation rates exceeding 400 rpm. At 400 rpm the crystals showed evident boundaries, and relatively well defined habits. Samples prepared with agitation rates of 800 and 1200 RPM showed increasingly less defined edges, increased sphericity, and reduced translucence. This effect was most pronounced for the overhead stirred samples that transitioned from large flat plates to clusters of agglomerated small crystals into very rounded particles at 400, 800 and 1200 RPM respectively.

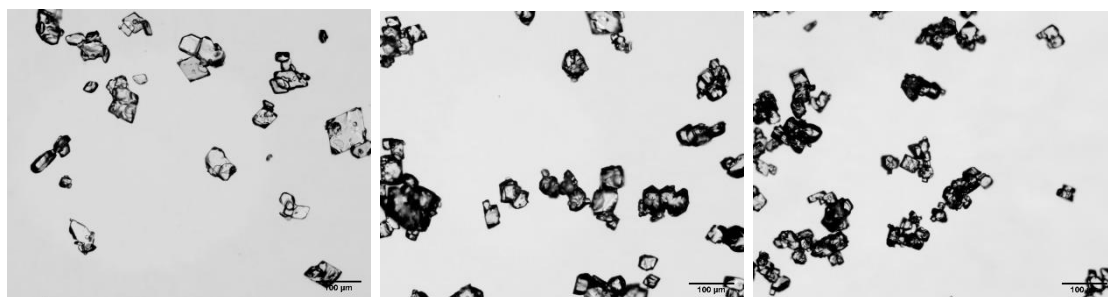


Figure 56: 10g magnetic stirrer bar crystallisations at 400, 800 and 1200 RPM (left-right) showed a tendency towards smaller particle sizes, increased opacity, and extensive secondary nucleation at higher agitation rates. Scale 100 µm.



Figure 57: 40g magnetic stirrer bar crystallisations at 400, 800 and 1200 RPM (left to right) showed a tendency towards smaller particle sizes with less agglomeration and poorly defined edges at higher agitation rates. Scale 100 µm.

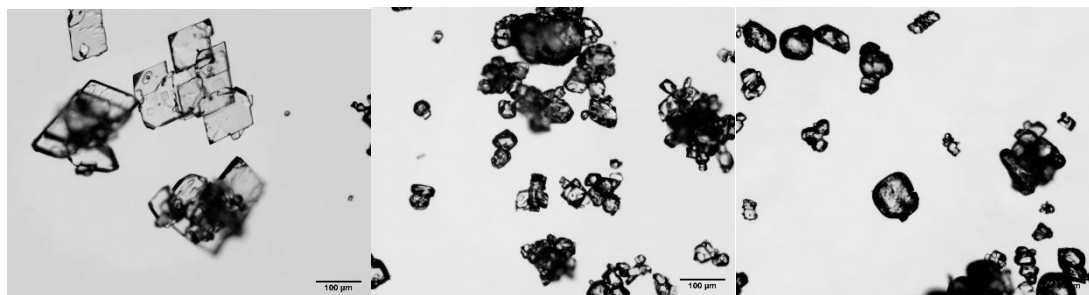


Figure 58: Overhead stirred crystallisations at 400, 800 and 1200 RPM (left to right) showed a transition from defined plates to agglomerated small rounded crystals to large spherical crystals with increased agitation rates. Scale 100 µm.

An experiment was conducted to evaluate the effect of leaving crystals to equilibrate at the final temperature of the cooling run, for 24hr, while stirring was maintained. Figure 59 shows images of AP crystals, prepared using all three modes of agitation at 800 RPM, that were recovered immediately upon reaching the end temperature. Figure 60 shows the effect of endpoint equilibration on crystals prepared under identical conditions. Crystals prepared using the 10g stir bar showed minimal evolution of morphology, but did appear to exhibit less agglomeration. Equilibration with 40g stirrer bar operating at 800 RPM likewise showed minimal evolution, although a slight size reduction and elongation was perceived. A significant evolution was observed in the crystals prepared by overhead stirring, with clusters of $\sim 30\text{ }\mu\text{m}$ crystals evolving into spherical particles on the order of $100 - 200\text{ }\mu\text{m}$.

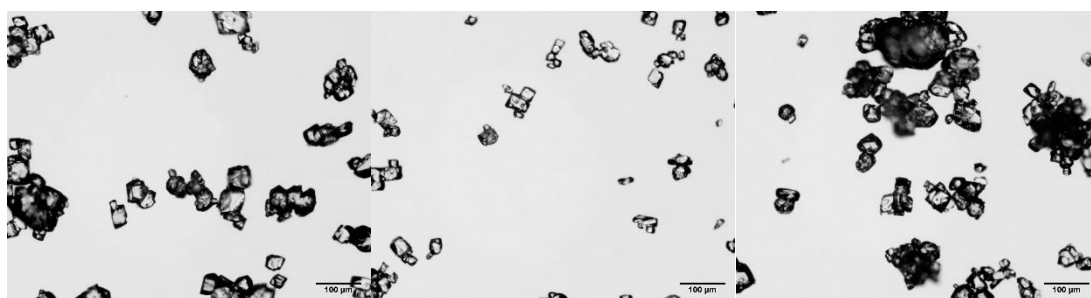


Figure 59: 800RPM 10g magnetic, 40g magnetic and overhead stirred samples recovered immediately. Scale bar $100\text{ }\mu\text{m}$.

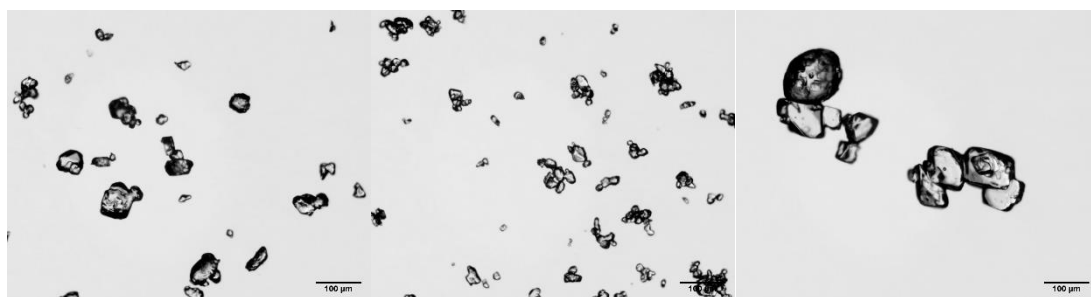


Figure 60: 800RPM 10g magnetic, 40g magnetic and overhead stirred samples, recovered after 24hrs equilibration. Scale bar $100\text{ }\mu\text{m}$.

Pulsed sonication during the slow crystallisation produced some interesting results, particularly regarding the high agitation rate samples. Where before, the high agitation rates had yielded the smallest and most spherical particles, in the presence of pulsed sonication the sizes were dramatically increased, and edges maintained. Figure 61 and Figure 62 show the significant impact of indirect sonication on crystals grown by slow cooling with high agitation rate using magnetic and overhead stirring respectively.

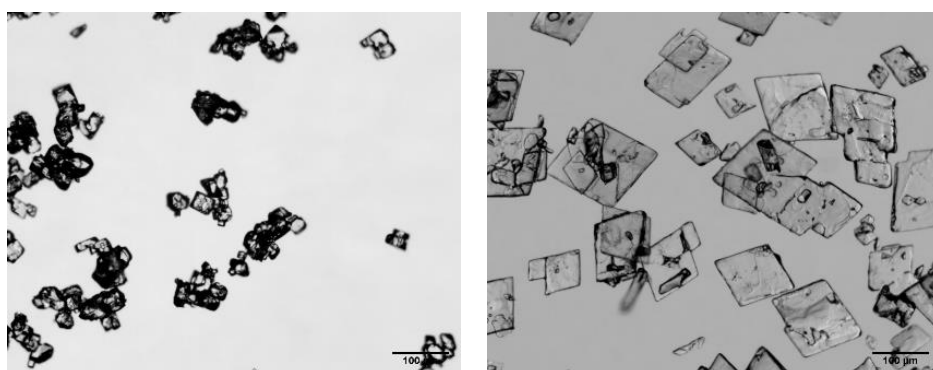


Figure 61: 1200 RPM 10g magnetic stirrer (left) no sonication (right) pulsed indirect sonication

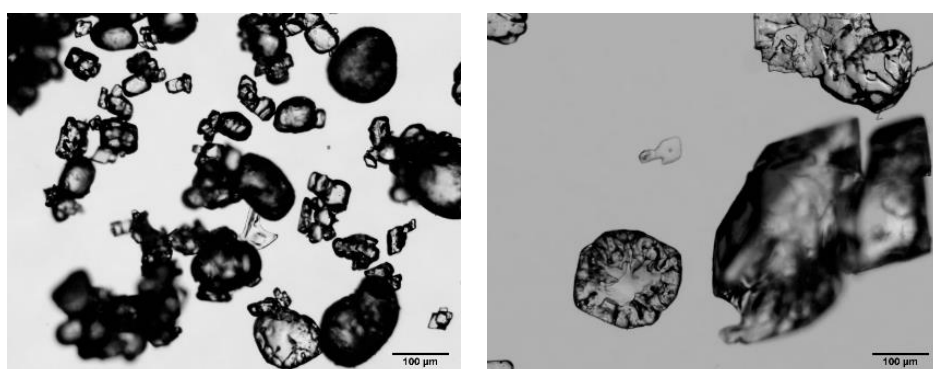


Figure 62: 1200 RPM overhead stirrer (left) no sonication (right) pulsed indirect sonication. Scale bar 100 µm.

The angle of repose was measured for each material, and the results are shown below in Table 9. In general, all of the materials showed good flow character. Notably, trends in angle of repose with agitation rate for magnetically stirred samples differed from overhead stirring. In the former case, increased agitation rate produced worse flow behaviour, due to the reduction of particle size. Using the light magnetic stirrer bar relative to the heavier bar gave significantly better flowing powders due to the difference in resultant particle sizes. The effect of agitation rate on overhead stirred samples showed the opposite trend, with improved powder flow resulting from the increased particle roundness gained at high RPM agitation.

For the 10g stirrer bar and overhead stirred samples, the effect of equilibration was a slight reduction of angle of repose. This reduction was most pronounced however for the 40g magnetically stirred sample, in which the energy of impeller-crystal collisions was expected to be greatest. Pulsed sonication showed no discernible trends, but did cause significant modification to the angle of repose.

Table 9: Summary of angle of repose modification as a result of agitating, equilibration and sonication modifiers.

Agitation	Agitation rate (RPM)	Angle of Repose (°)		
		No Modification	Equilibrate	Sonicate
Mag 10g	400	25 ± 1	23 ± 1	31 ± 2
Mag 10g	800	26 ± 1	26 ± 1	29 ± 1
Mag 10g	1200	33 ± 2	34 ± 1	22 ± 1
Mag 40g	400	36 ± 3	24 ± 1	27 ± 1
Mag 40g	800	30 ± 1	35 ± 1	27 ± 2
Mag 40g	1200	46 ± 2	32 ± 2	34 ± 2
OH	400	30 ± 2	28 ± 2	33 ± 2
OH	800	24 ± 1	28 ± 1	34 ± 1
OH	1200	27 ± 1	22 ± 1	25 ± 1

5.1.2 Discussion

As expected, the nature of stirring type produced the most evident difference in crystal morphologies, with magnetically stirred samples presenting as smaller than overhead stirred samples [95,98]. The differences resulting from changing the mass and size of the magnetic stirrer bar were also obvious, with the larger and heavier bar producing smaller crystals than the lighter equivalent. The trend for smaller more spherical particles with increased agitation rate was obvious in these samples. Unfortunately, Norouzi *et al.* provide no details of the dimensions or mass of the stirrer bar used in their experiment, which as demonstrated here could have played a more significant role in their optimisation than they realised. In samples prepared by overhead stirring, the effect of agitation rate on size was generally much less pronounced than the effect on particle shape, which was consistent with the literature reports [95,96].

Equilibration of the crystals at the final temperature for a prolonged time was expected to dramatically increase the sphericity of particles since this is effectively the same process by which RDX crystals are sphericalised [129]. In the magnetically stirred samples, end point equilibration resulted in a slight reduction of sharp edges present in the crystals, but certainly not sphericalisation. The effect of end point equilibration on overhead stirred samples is debatable, while these particles certainly did exhibit remarkably smooth morphologies, the product yields calculated were far in excess of 160 % theoretical maximum, even after prolonged drying in a vacuum oven. For these samples, it is suspected that a degree of evaporation occurred over the equilibration period. Crystallisation yields for all other processes varied between 85 - 95% theoretical maximum, calculated for samples dried in a vacuum oven (40 °C, - 800 mbar, 48 hrs). In general, the equilibration step improved the flow character of AP powders.

Pulsed sonication produced the most dramatic effect on crystal morphology. Light weight magnetically stirred samples showing a trend of size and angularity increase with increased agitation rate, contradicting the observed trend in the absence of sonication. Pulsed sonication of overhead stirred samples caused a

very significant increase of sample size, and increased crystal angularity, with no discernible dependence on agitation rate. Generally, the application of pulsed sonication produced results that were undesirable for both energetic sensitiveness and powder flow character reasons. However, it should be noted that all samples prepared in the presence of sonication showed significantly reduced agglomeration. Application of pulsed sonication to the crystallisations had a varied effect on each form of agitation. Light weight magnetically stirred samples exhibited higher angle of repose values because of pulsed sonication, whereas heavy magnetically stirred samples showed significantly lower angle of repose values. The angle of repose for samples prepared with overhead stirring was unaffected by pulsed sonication. Unfortunately, no literature reports of AP cooling crystallisation in the presence of pulsed sonication were found, limiting the scope for comparison.

5.2 Scale up cooling crystallisations of AP

5.2.1 Results

Scale up cooling crystallisations of AP were conducted in a 250 cm³ jacketed reaction vessel, as described in Section 4.3.4. Details of the slow, rapid and sonocrystallisation procedures can be found in Section 4.3.5.

Slow cooling crystallisation produced large single crystals, showing extensive secondary growth or twinning, with excellent preservation of the sharp lattice edges. The expected reduction of crystal size with increased agitation rate was not observed, as can be seen in Figure 63. At low and high agitation rates, the crystals presented mostly as cuboids, with a high degree of agglomeration of secondary nucleation. At the intermediate agitation rate however, the crystals appeared to favour growth over secondary nucleation, resulting in large flat looking plates.

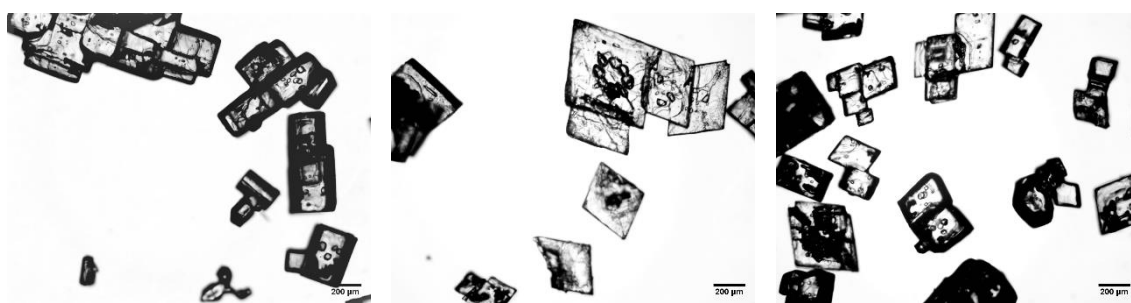


Figure 63: The effect of increased agitation rate (400, 800 and 1200 left to right) on slow cooling crystallised AP. Scale bar 200 µm

Increasing the rate of cooling had a very dramatic effect on the morphology of crystals and produced a significant size reduction as can be seen in Figure 64. While it is not entirely accurate to speculate on the 3D habit of an object based on 2D information such as the micrographs shown in Figure 64 the morphology observed in these samples tended towards that of a square bipyramid, particularly at low agitation rates. Increased impeller rotation rate appeared to cause elongation of crystals and smoothing of the edges. Unlike the slow cooling experiment, the degree of secondary nucleation was appeared to increase with agitation rate.

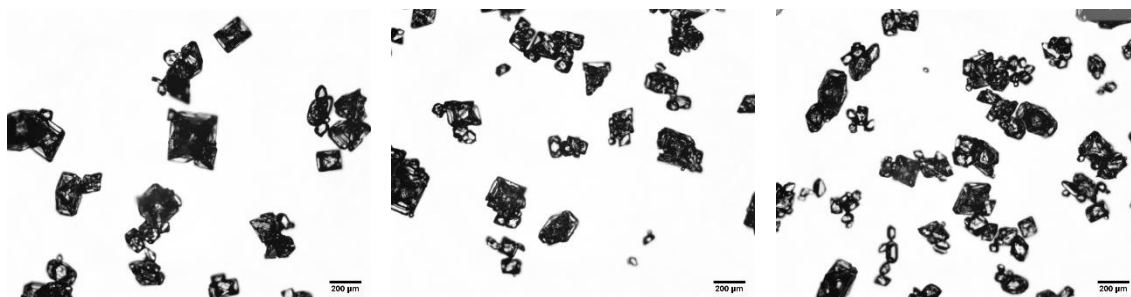


Figure 64: The effect of agitation rate (400, 800 and 1200 right to left) on crystal morphology. Scale bar 200 μm

Crystals prepared by rapid cooling crystallisation in the presence of direct contact constant sonication, Figure 65, were significantly smaller and more rounded than those prepared in the absence of sonication, Figure 64. Sonication appears to have accelerated smoothing of the crystals, presumably by an exaggerated effect similar to that of impeller collisions. As expected, the high conditions of high supersaturation provided by the ultrasonic radiation rapidly increased the nucleation rate relative to growth rate; resulting in a dramatic crystal size reduction compared to the non-sonicated fast cooling crystallisations.

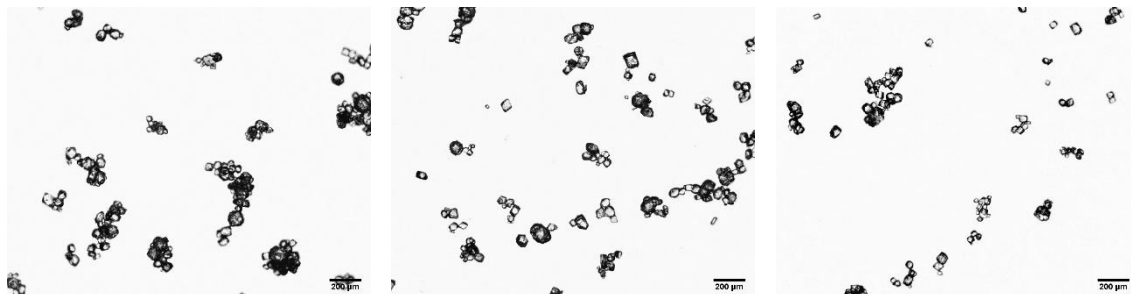


Figure 65: Sonocrystallisation of AP at 400, 800 and 1200 RPM (right to left) Scale bar 200 μm .

Differences in crystal size were quantified by digital image analysis following the procedure detailed in Section 4.2.1 and the results are shown in Table 10. Angle of repose values were calculated via the linear fit image analysis procedure described in Section 4.2.7, the results are presented in Table 11.

Table 10: Optical image analysis particle sizes of ammonium perchlorate, prepared by fast cooling crystallisation in the presence and absence of ultrasonic radiation and employing a range of agitation rates

Production parameters		Optical image analysis (equivalent circle diameter)			
Agitation (RPM)	Sonication (PWL)	d10 (μm)	d50 (μm)	d90 (μm)	d90 - d10 (μm)
400	0	13.8	152.3	272.4	258.5
800	0	13.8	79.1	237.4	223.7
1200	0	15.3	104.5	268.4	253.1
400	4	13.9	43.4	98.9	85.0
800	4	17.3	39.3	89.3	72.0
1200	4	13.4	33.5	83.0	69.6

Table 11: Summary of average angle of repose measurements, calculated by digital gradient fitting

Production parameters		Angle of repose (image analysis)		
Agitation (RPM)	Sonication (PWL)	Average left ($^{\circ}$)	Average Right ($^{\circ}$)	Average Both ($^{\circ}$)
400	0	38.8 ± 1.2	39.5 ± 1.9	39.1 ± 1.7
800	0	33.2 ± 0.9	33.0 ± 0.8	33.1 ± 0.8
1200	0	31.1 ± 1.6	32.6 ± 1.5	31.8 ± 1.7
400	4	28.7 ± 1.1	31.0 ± 3.9	29.9 ± 3.1
800	4	33.1 ± 3.3	34.1 ± 2.8	33.6 ± 3.1
1200	4	31.7 ± 2.6	33.7 ± 5.1	32.7 ± 4.2

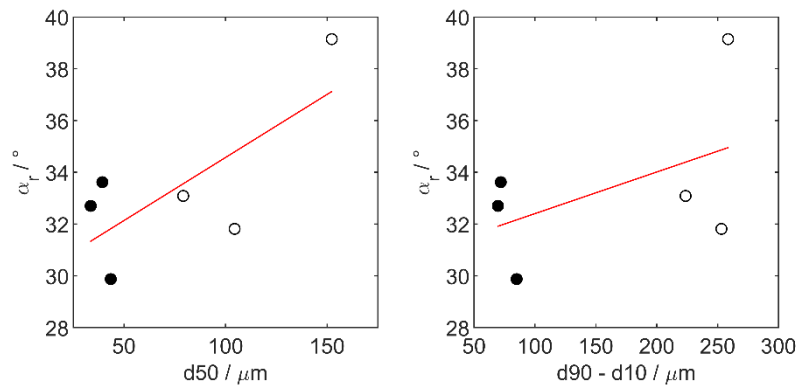


Figure 66: Plots showing a lack of correlation between particle size (left) and PSD width (right) to angle of repose. Solid black data points correspond to sonocrystallisation samples. Hollow black circles correspond to rapid cooling crystallisation samples. A linear fit, shown in red, demonstrated the poor correlation

A plot comparing the DSC traces of AP prepared by slow, rapid and sonicated cooling crystallisations is shown in **Error! Reference source not found.**Figure 67. All traces correspond to 20 °C/min heating rate. Ammonium perchlorate shows three characteristic thermal transitions, associated with the orthorhombic-cubic transition, low temperature decomposition and high temperature decomposition respectively. All three transitions were clearly evident in the slow cooling and sonocrystallisation samples. The low temperature exotherm, of the sample prepared by rapid cooling crystallisation, was suppressed almost entirely. Sonocrystallisation of AP shifted the position of the low temperature exotherm up by 9.05 °C, a result that was not expected considering the size reduction caused by the sonication process. High temperature exotherm peak positions were relatively unaffected, however it is evident from the peak shapes in **Error! Reference source not found.**Figure 67 that the nature of the high temperature decomposition was drastically influenced by the crystallisation process.

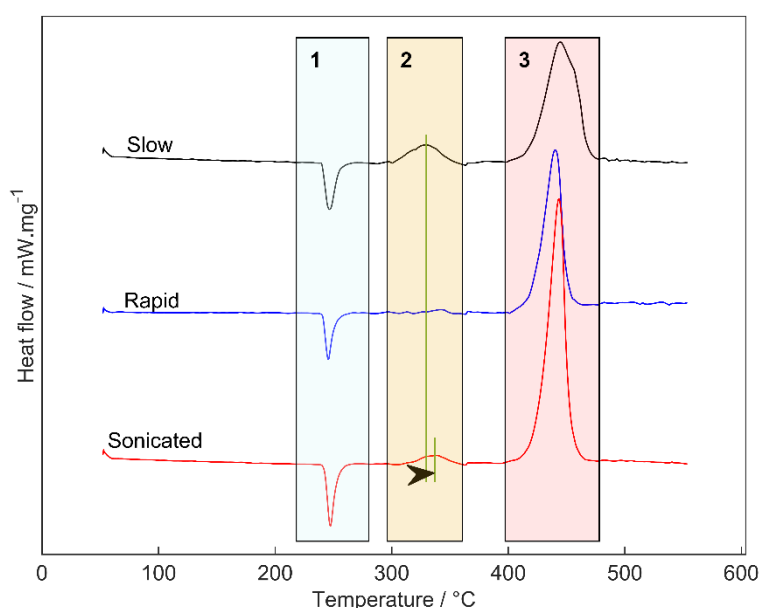


Figure 67: Comparison of DSC traces corresponding to slow cooling, rapid cooling and rapid sonocrystallisation produced AP. Data recorded with a heating rate of 20 °C/min under standard DSC conditions. The plot contains three regions, corresponding to : (1) orthorhombic – cubic phase transition, (2) low temperature partial decomposition and (3) high temperature full decomposition. The green lines in region 2 represent the shifted peak position observed in the sonicated sample relative to the slow crystallised sample.

Kinetic activation energies were calculated using the Kissinger method detailed in Section 4.2.8. Figure 68 to Figure 76 show the DSC traces at each heating rate for each sample and the accompanying Kissinger analysis plot. Data corresponding to the high and low temperature exotherms are shown in red and blue respectively. Modification to the DSC traces shown in Figure 68 to Figure 76 was restricted to normalisation of heat flow by initial sample mass, no scaling factors were applied. Variation in the separation of the lines was an unavoidable consequence of inconsistent baseline values.

A summary of the Kissinger analysis results is shown in Table 12. Error values were calculated by propagation of the standard error associated with the gradient of the linear fits on the Kissinger plots. For the low temperature decomposition, the error magnitude was well within tolerability, however, errors calculated for the high temperature exotherm were non-trivial. Inspection of the high temperature data on the Kissinger plots shows the poor fit from which these errors derive.

Table 12: Summary of Kissinger analysis results for the low and high temperature decompositions of ammonium perchlorate

Production parameters			Decomposition activation energy	
Agitation (RPM)	Rate	Sonication (PWL)	~350 °C E_a (kJ.mol ⁻¹)	~450 °C E_a (kJ.mol ⁻¹)
400	Slow	0	102± 8	100± 130
800	Slow	0	113 ± 6	180 ± 50
1200	Slow	0	119 ± 5	110 ± 120
400	Rapid	0	132 ± 6	200 ± 70
800	Rapid	0	129 ± 12	280 ± 50
1200	Rapid	0	118± 14	330 ± 220
400	Rapid	4	141± 19	410 ± 130
800	Rapid	4	113± 8	180 ± 30
1200	Rapid	4	123 ± 16	250 ± 30

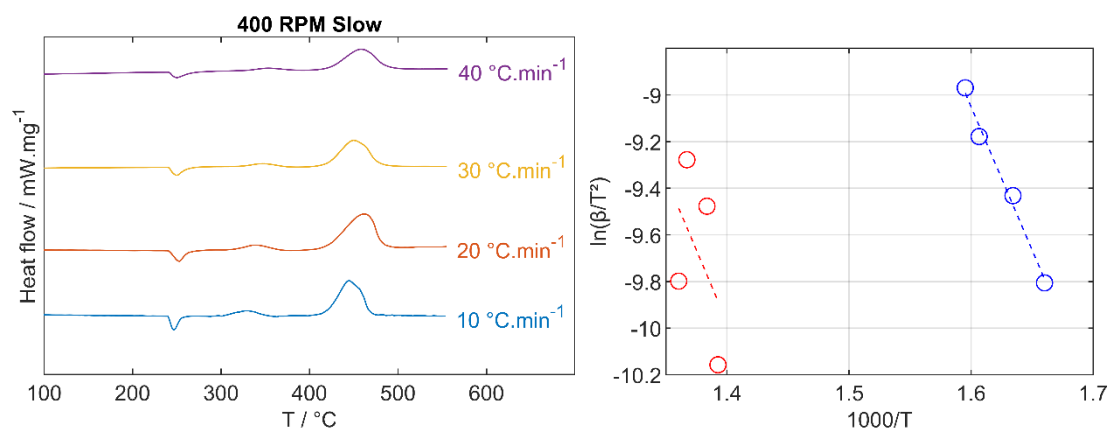


Figure 68: Kissinger analysis of AP prepared by slow cooling, agitated at 400 RPM, gave activation energies for the 350 °C and 450 °C exotherms, shown in blue and red on the Kissinger plot respectively.

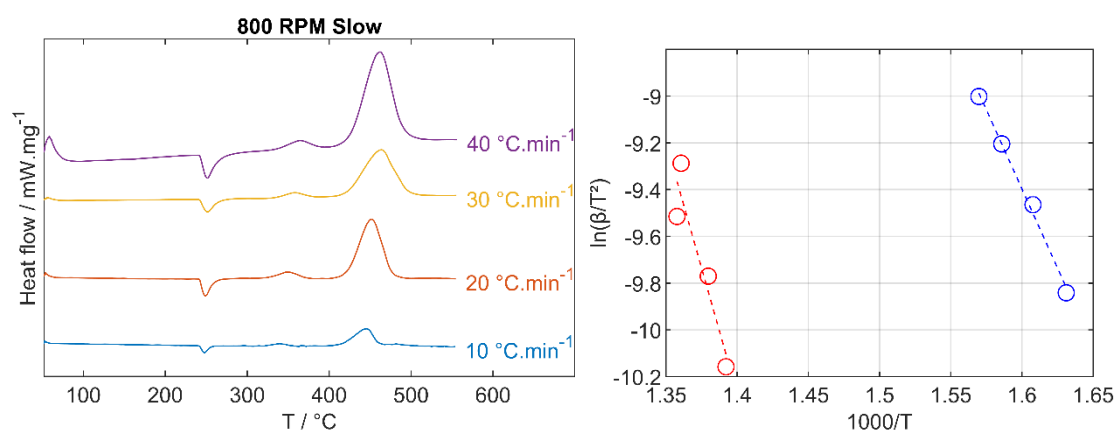


Figure 69: Kissinger analysis of AP prepared by slow cooling, agitated at 800 RPM, gave activation energies for the 350 °C and 450 °C exotherms, shown in blue and red on the Kissinger plot respectively.

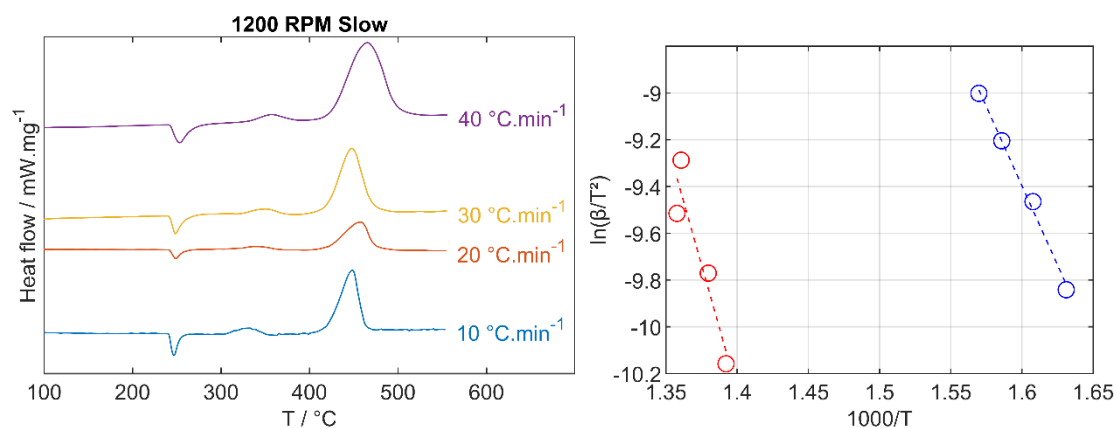


Figure 70: Kissinger analysis of AP prepared by slow cooling, agitated at 1200 RPM, gave activation energies for the 350 °C and 450 °C exotherms, shown in blue and red on the Kissinger plot respectively.

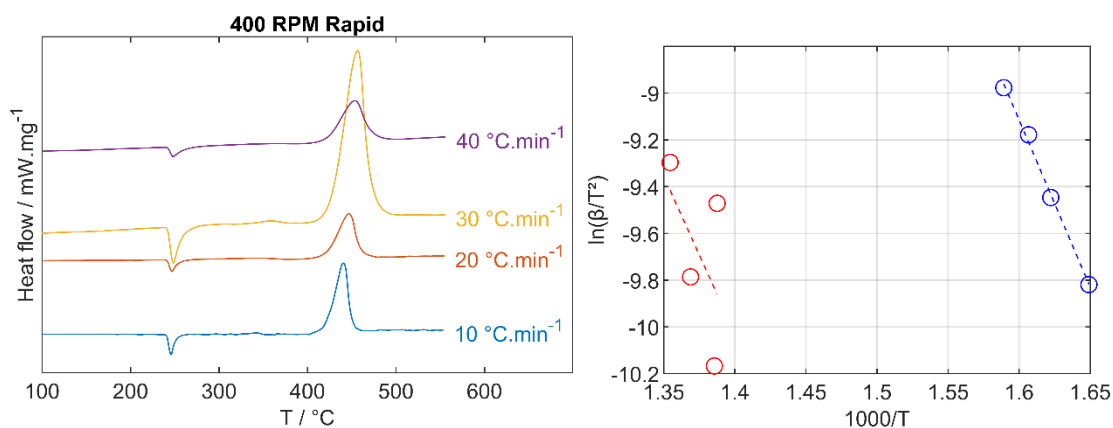


Figure 71: Kissinger analysis of AP prepared by rapid cooling, agitated at 400 RPM, gave activation energies for the 350 °C and 450 °C exotherms, shown in blue and red on the Kissinger plot respectively.

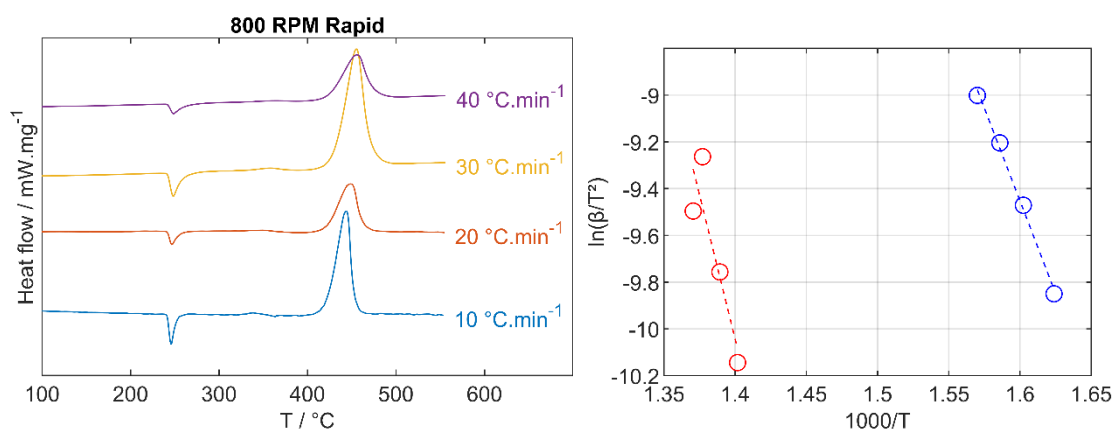


Figure 72: Kissinger analysis of AP prepared by rapid cooling, agitated at 800 RPM, gave activation energies for the 350 °C and 450 °C exotherms, shown in blue and red on the Kissinger plot respectively.

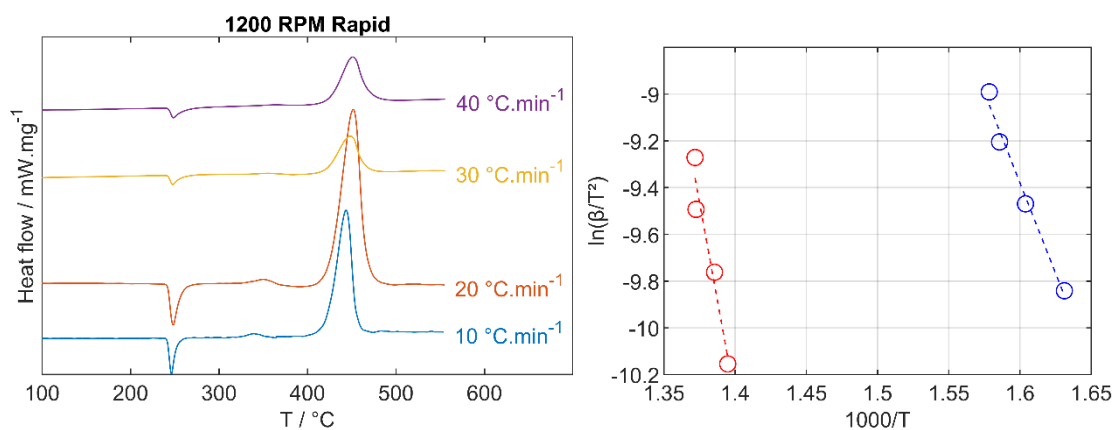


Figure 73: Kissinger analysis of AP prepared by rapid cooling, agitated at 1200 RPM, gave activation energies for the 350 °C and 450 °C exotherms, shown in blue and red on the Kissinger plot respectively.

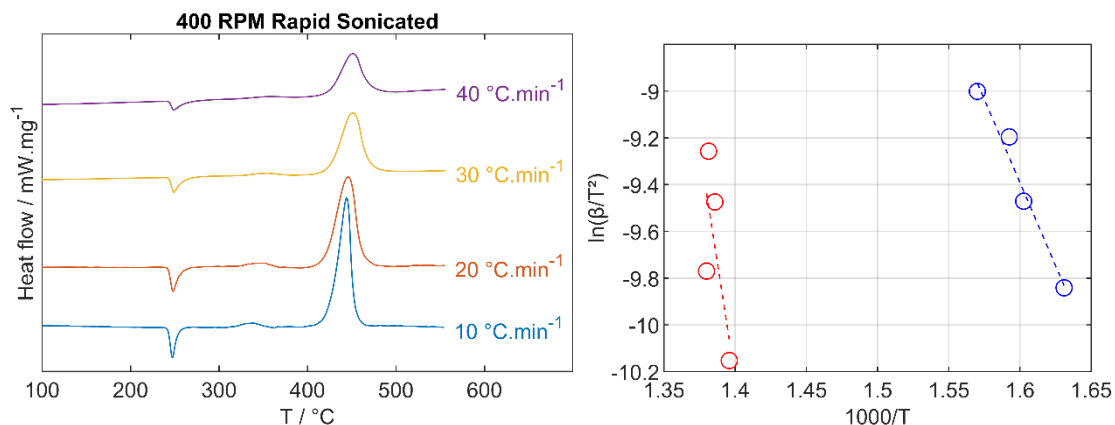


Figure 74: Kissinger analysis of AP prepared by rapid cooling, agitated at 400 RPM with direct sonication, gave activation energies for the 350 °C and 450 °C exotherms, shown in blue and red on the Kissinger plot respectively.

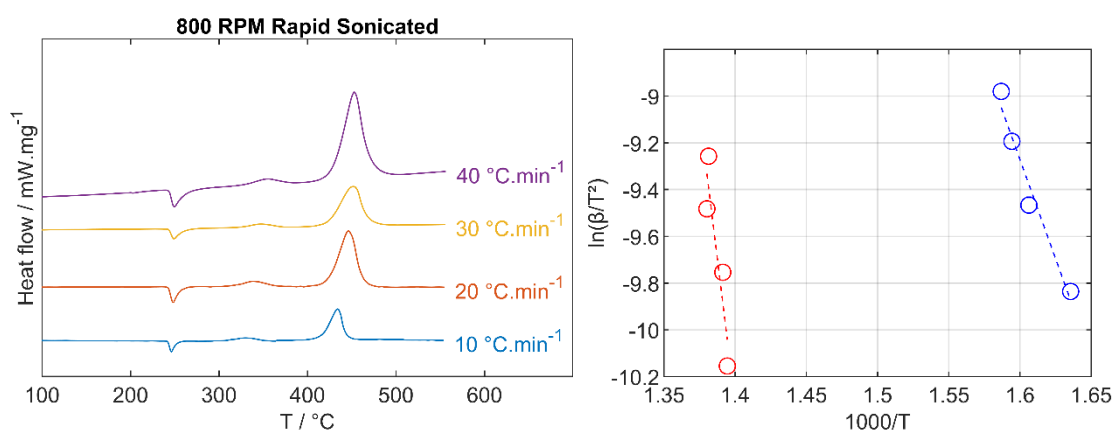


Figure 75: Kissinger analysis of AP prepared by rapid cooling, agitated at 800 RPM with direct sonication, gave activation energies for the 350 °C and 450 °C exotherms, shown in blue and red on the Kissinger plot respectively.

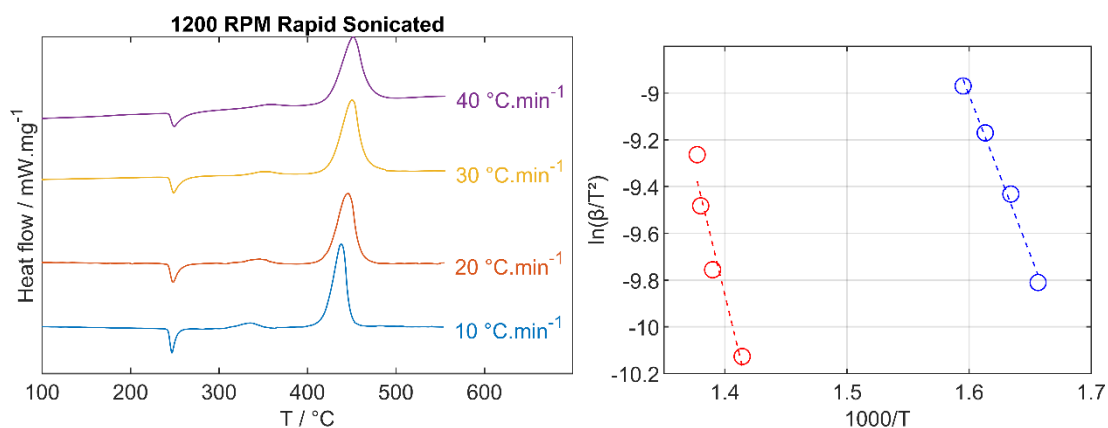


Figure 76: Kissinger analysis of AP prepared by rapid cooling, agitated at 1200 RPM with direct sonication, gave activation energies for the 350 °C and 450 °C exotherms, shown in blue and red on the Kissinger plot respectively.

5.2.2 Discussion

Slow cooling crystallisation gave large crystals that were extensively agglomerated. The extent of agglomeration or secondary nucleation did not appear to correlate with agitation rate, and samples prepared at 400 RPM closely resembled those prepared at 1200 RPM. Agitation at 800 RPM instead seemed to allow for further lateral growth, with slightly less secondary nucleation. Increasing the rate of cooling crystallisation significantly impacted the morphology of crystals, leading to the formation of square bipyramidal habits in preference to the prismatic crystals observed in slow cooling crystallisations. Under these conditions, agitation at 800 RPM produced crystals with the lowest median diameter (79.12 μm).

The cooling crystallisations of AP conducted by Lakshmi *et al* used remarkably similar equipment, including paddle depth within the mother liquor and paddle diameter to reaction vessel diameter ratio being identical [95]. Despite the intended similarity to this experiment, crystals prepared here by rapid cooling were significantly more angular and defined than those prepared by Lakshmi *et al*. In their experiments, Lakshmi *et al.*, ran a thermal ramp from 80 °C to 30 °C with the solution prepared such that saturation was reached at 75 °C - i.e. ΔT was significantly higher than what was used in this work. Hosseini *et al* used a more comparable ΔT to this work, and this is reflected in the near identical crystal sizes obtained here [96].

The morphology of AP prepared by rapid cooling crystallisation in the presence of ultrasonic radiation did not reflect either the prismatic or square pyramidal crystals. Instead, crystal faces were generally un-identifiable in these near spherical particles. Twinning and secondary nucleation was very rarely observed in sonocrystallisation samples, presumably due to the relative ease of “homogeneous” nucleation caused by cavitation. The morphology and sizes of crystals were similar to those reported by [108,109], but produced in significantly greater abundance. As expected, the application of sonication to the rapid cooling crystallisation significantly reduced the average particle size. The average d50 of standard rapid was $112 \pm 30 \mu\text{m}$, whereas with sonication

this average was reduced to $38.7 \pm 4.1 \mu\text{m}$ (average of 400, 800 and 1200 RPM values). Likewise, the particle size distribution was significantly narrowed by sonocrystallisation. The value for $d_{90} - d_{10}$ was averaged across the three agitation rates used, and without sonication the PSD width was $245 \pm 15 \mu\text{m}$, reduced to $75.5 \pm 6.7 \mu\text{m}$ by sonication.

The effect of particle size and particle size distribution width on the angle of repose is plotted in Figure 66. In general, the data follows no correlation, and the linear fits are only present to aid identification of trends. Plotting all the data in a single fit ignores the impact of morphology. Within the sonicated sample datapoints (solid black circles) there appears to be a region of linearity that would be consistent with decreasing angle of repose as particle size increases [180]. However, due to the small sample size, a fit containing only three data points was deemed inappropriate. Similar trends were identified, but discounted due to small sample size. Notably these other trends contradicted the expected result, so expansion of this data set would be sensible.

All of these samples did exhibit extensive agglomeration. Despite efforts to dry the samples immediately upon recovery, with ethanol washing and *in vacuo* drying, it nearly impossible to remove the occluded water. Chen and Chou (1993) suggested that the application of anti-caking agents could negate the issues of AP agglomeration over time. However, they found that surfactants caused the formation weak dendritic crystals. Their frustration appeared sufficient for the authors to suggest that modification to the crystallisation process would be preferable [181].

Error! Reference source not found. showed how the low temperature exotherm position and integral varied depending on the crystallisation method. Suppression of this exotherm is widely used in propellant systems to improve safety by prevention of a reignition mechanism, however it is more commonly achieved using catalysts such as ammonium hexafluorophosphate in combination with thermal pre-treatment [182].

Application of the Kissinger DSC analysis was achieved successfully retrieving activation energy values for the low and high temperature exotherms of AP

decomposition, Table 12. A summary table, showing the average activation energy by type of crystallisation is given below, Table 13. Included in the table are examples of Kissinger activation energies from the literature, showing relatively poor agreement.

Table 13: Summary of measured Kissinger activation energies with comparison to literature values

Data source	Decomposition activation energy	
	~350 °C (kJ.mol ⁻¹)	~450 °C (kJ.mol ⁻¹)
Slow cooling	111 ± 7	131 ± 34
Rapid cooling	126 ± 6	270 ± 50
Sonocrystallisation	126 ± 11	282 ± 97
Domínguez (2019) [183]	87 (293 °C)	198 (420 °C)
Jacobs (1969) [184]	91	229

However, there are several limitations to the experiment that could account for these discrepancies. Properties of the AP crystals, such as size and morphology, significantly impacted the results. Comparison of the activation energy for the low temperature exotherm shows disagreement between slow and rapid cooling, whereas rapid and sonicated gave excellent agreement. The discrepancies are significantly more extensive for the high temperature exotherm, the decomposition of which is dependent on crystalline changes that occurred during the preceding transition. Manipulation of the low temperature decomposition has been extensively used to modify the burning characteristics of AP, predominantly thought the formation of porosity during sublimation [5,93,94]. Secondly, the Kissinger approach to measuring activation energies is a purely kinetic theory, and applies only to first order transitions, however the complexity of AP decomposition is known to not always act as a first order transition [13].

5.3 Inert simulant spray drier optimisation

5.3.1 Material preparation

Following initial setup and familiarisation with the operation of the B-290 spray drier, attempts were made to simulate its application to the Micronisation of both AP and RDX – using inert simulants ammonium sulphate and paracetamol. Small amounts of each material were prepared by spray drying aqueous solutions of ammonium sulphate and organic solutions of paracetamol respectively. The quality of spray dried powder flow was assessed, by simple attempts to pass the material through the solid hopper of the printer. These initial experiments in revealed the inherent difficulty of making such fine powders flow in the printing system. Generally, a small amount of material would dispense (< 0.1 g) before compaction led to blockages at the nozzle. As previously discussed, the flowability of a powder can be modified through both formulation and morphological controls. This section details the attempts made, using both approaches, to improve the flowability of fine cohesive spray dried paracetamol powders. Spray drying of ammonium sulphate, while achieved, was not pursued as an area of research due to the numerous issues that occurred as a result of incomplete drying. All attempts to spray dry ammonium sulphate led to blockage formation at either the cyclone intake or collection exit choke points.

Since particle size and size distribution are reportedly facile to control using the wide array of parameters involved in spray drying processes, a full 2^4 factorial experiment was conducted to investigate the effect of production parameter variables on these responses. The variables are listed here along with a rationale behind their choice. Increased concentration of solute in a droplet will produce larger particles assuming the viscosity of the solution is not significantly changed and so the atomisation of proceeds as it would have at lower concentrations. Decreasing the atomisation pressure and increasing the nozzle diameter has been shown to increase the size of droplets, and a large droplet will yield a larger particle than a smaller droplet with equivalent initial

solute concentration. Buchi reports that a higher feed flow rate will result in higher particle sizes [179].

The 2^4 factorial experiment was conducted with most parameters using fixed values, shown in Paracetamol (5.00 g) and acetone (95.00 g, 121.2 ml or 66.67 g, 85.0 ml) were combined in a stoppered conical flask. The mixture was magnetically stirred (RT, 400rpm, 0.5 h), with occasional swirling of the flask to ensure that no residue formed on the glass. The mixture was spray dried according to the standard operating procedure for organic solutions detailed in Section 4.4.2. The experiment involved conducting 16 runs, which are presented by nested variables in Table 16, the order of preparation was randomised using a random number generator.

Table 14. The variable parameters were used at high and low values, shown in Table 15. The high and low values were chosen to balance the most extreme values possible with feasibility. For example, the atomisation pressure was varied from 5 to 8 bar – values equivalent to the min and max operating conditions of the spray drier. Whereas, while the high value for concentration was chosen to be as near to saturated as possible, the low value was not as dilute as possible since this would entail extremely long spray drying runs to produce sufficient material for testing. Likewise, the feed flow rate (FFR) high value (5 ml/min / 22 %) was chosen as it represents the maximum value that never produced condensation in the cyclone when spray drying at 100 °C. Nozzle diameter corresponds to the size ruby aperture cut in the nozzle cap, typically a larger aperture is used to aid in spray drying more viscous solutions, or to improve the drying performance when aqueous solutions are spray dried by modification of the atomisation process.

Paracetamol (5.00 g) and acetone (95.00 g, 121.2 ml or 66.67 g, 85.0 ml) were combined in a stoppered conical flask. The mixture was magnetically stirred (RT, 400rpm, 0.5 h), with occasional swirling of the flask to ensure that no residue formed on the glass. The mixture was spray dried according to the standard operating procedure for organic solutions detailed in Section 4.4.2. The experiment involved conducting 16 runs, which are presented by nested variables in Table 16, the order of preparation was randomised using a random number generator.

Table 14: Control parameters for paracetamol full factorial experiment

Control measure	Value
Inlet temperature	97-105°C
Outlet temperature	~ 60°C
Atomisation and drying gas	N ₂
Gas flow rate	40 mm
Aspiration rate	100 %
Solute/Solvent	Paracetamol/Acetone
Cyclone	High performance

Table 15: High/Low variables used in 2³ full factorial paracetamol spray drying experiment.

Level	FFR / ml.min ⁻¹	C / wt.%	d _n / mm	p _n / bar
-1	2.5	5.0	1.4	5
+1	5.0	7.5	1.6	8

5.3.2 Results

Conditions and key responses of the full factorial experiment are shown below in Table 16.

Table 16: Summary of factorial experiment conditions and key response variables.

Sample	p_n (bar)	FFR (ml/min)	d_n (mm)	C (wt%)	D50 (μm)	Span (N/A)
PA 01	5	2.5	1.4	5	13.82	1.851
PA 02	5	2.5	1.4	7.5	11.31	1.922
PA 03	5	2.5	1.6	5	14.37	1.999
PA 04	5	2.5	1.6	7.5	11.92	1.874
PA 05	5	5	1.4	5	15.50	2.024
PA 06	5	5	1.4	7.5	9.6	2.074
PA 07	5	5	1.6	5	13.97	2.053
PA 08	5	5	1.6	7.5	20.47	2.014
PA 09	8	2.5	1.4	5	10.01	1.778
PA 10	8	2.5	1.4	7.5	13.68	1.904
PA 11	8	2.5	1.6	5	13.40	2.041
PA 12	8	2.5	1.6	7.5	13.63	1.863
PA 13	8	5	1.4	5	9.27	2.014
PA 14	8	5	1.4	7.5	15.31	2.122
PA 15	8	5	1.6	5	12.73	1.875
PA 16	8	5	1.6	7.5	16.92	1.947

Fitting the size and span data into a multivariate models, limited to first and second order interactions, was performed in JMP [185]. A summary of the statistical quality descriptors for both models is given in Table 17. Coefficients for each term in the size and span models are tabulated below, in Table 18 and Table 19 respectively.

Table 17: Summary of quality descriptors for diameter and span models.

Goodness of fit	Diameter model	Span model
R ²	0.658	0.838
F ratio	0.9621	2.5913
Prob > F	0.554	0.1525

Beginning with discussion of the quality of the diameter model, it is apparent from the descriptors in Table 17 that this model is of low statistical quality. The omnibus test result shows that the model is not significantly different from random. Moreover, the F ratio being close to unity indicates that across the ranges tested, there was no significant impact of any variable on the measured average particle diameter. Finally, the R² value indicated that the overall correlations within the data, while present, are not strong. Inspection of the standard error associated with each coefficient reveals that all errors are of the same order of magnitude with many exceeding the coefficients.

Goodness of fit values for the model describing the dependence of PSD breadth (span) on production parameters indicate that this model is of much higher quality than the former average diameter model, Table 17. While the values are not ideal, the omnibus test is far removed from the chance value seen previously. Moreover the F ratio indicates that variation of the parameters led to meaningful variation in span values. The R² value is much closer to unity as the correlations are more pronounced. Standard error values associated with each coefficient are high.

Despite these faults, inference can be drawn from this model about the relative significance of each parameter. However, it should be noted that the accuracy of predictions based on this model will be severely lacking.

Table 18: Coefficients for the model representing the impact of atomisation pressure, feed flow rate, nozzle diameter and solution concentration on the volume average particle size of paracetamol prepared by spray drying.

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	-7.850104	12.05275	-0.65	0.5436
p_n (bar)	-0.250292	0.481245	-0.52	0.6252
FFR (ml/min)	0.58125	0.577493	1.01	0.3604
d_n (mm)	11.824375	7.218668	1.64	0.1623
C (wt.%)	0.48885	0.577493	0.85	0.4359
$(p_n - 6.5) * (FFR - 3.75)$	-0.153833	0.384996	-0.4	0.706
$(p_n - 6.5) * (d_n - 1.5)$	-0.867083	4.812445	-0.18	0.8641
$(p_n - 6.5) * (C - 6.25)$	0.6165667	0.384996	1.6	0.1702
$(FFR - 3.75) * (d_n - 1.5)$	4.9575	5.774934	0.86	0.4299
$(FFR - 3.75) * (C - 6.25)$	0.4754	0.461995	1.03	0.3507
$(d_n - 1.5) * (C - 6.25)$	3.5815	5.774934	0.62	0.5623

The absolute value of t-ratio gives an indication of significance for each term, with $|t \text{ ratio}| > 1.96$ and $|t \text{ ratio}| > 1.65$ corresponding to significance at the 95% and 90% confidence intervals. While none of the terms in the above model can be treated with such confidence, a discussion of their relative import is non trivial. Nozzle diameter is shown to have the most significant impact on the particle size, with larger aperture diameter producing larger particles. This result appears intuitive, the ratio of aperture areas being 1:1.306 for the 1.4:1.6 mm nozzle caps. The significant difference in cross sectional area over which the atomisation pressure acts evidently has a large impact on the size of droplets formed. Coefficients of the $(d_n - 1.5) * (C - 6.25)$ and $(FFR - 3.75) * (d_n - 1.5)$ had high magnitudes, but low statistical significance. Again, these indicate that the nozzle diameter plays a critical role in determining the particle size. The influence of atomisation pressure was unexpectedly low, despite being consistent with reduction of pressure at the nozzle leading to larger particle formation. Terms such as feed flow rate, $(FFR - 3.75) * (C - 6.25)$ and $(p_n - 6.5) * (C - 6.25)$ showed fairly high statistical significance, but low overall impact on particle size.

Table 19: Coefficients for the model representing the impact of atomisation pressure, feed flow rate, nozzle diameter and solution concentration on the breadth of the particle size distribution (represented as span) of paracetamol prepared by spray drying.

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	1.8599375	0.280588	6.63	0.0012
p _n (bar)	-0.011125	0.011203	-0.99	0.3663
FFR (ml/min)	0.04455	0.013444	3.31	0.0212
d _n (mm)	-0.014375	0.168051	-0.09	0.9352
C (wt.%)	0.00425	0.013444	0.32	0.7647
(p _n - 6.5) * (FFR - 3.75)	-0.0049	0.008963	-0.55	0.6081
(p _n - 6.5) * (d _n - 1.5)	-0.067083	0.112034	-0.6	0.5754
(p _n - 6.5) * (C - 6.25)	0.0057	0.008963	0.64	0.5528
(FFR - 3.75) * (d _n - 1.5)	-0.3335	0.134441	-2.48	0.0558
(FFR - 3.75) * (C - 6.25)	0.01188	0.010755	1.1	0.3196
(d _n - 1.5) * (C - 6.25)	-0.3125	0.134441	-2.32	0.0677

The baseline of span values, given by the intercept, is 1.8 ± 0.3 and it should be noted that none of the measured results fell outside of that error range. As such, interpretation of this model should be restricted to relative importance of parameters, as it was for the diameter model. Of the various parameters, feed flow rate was shown to have the most likely impact on span, however, the magnitude of the direct correlation is small, with an increased flow of 10 ml/min resulting in an increased span of only 0.4455. Secondary terms, $(d_n - 1.5) * (C - 6.25)$ and $(FFR - 3.75) * (d_n - 1.5)$ were both statistically significant and highly impactful, with small increase of either product resulting in marked reduction of particle size distribution width. It should be noted that nozzle diameter is once again involved in both terms. Of the primary terms, solution concentration displayed the least effect on span width, which is a reasonable result considering the paracetamol solute concentration has little impact on the solution viscosity, the only means by which this would impact the atomisation process.

Congruent with size analysis of the spray dried paracetamol samples, analysis of various characteristic flow indicators was conducted. The results are tabulated in Table 20, scatter plots representing this data are shown in Figure 77.

Table 20: Flow characteristics of spray dried paracetamol

Sample	Factorial level [p _n FFR d _n C]	D50 (μm)	Span (N/A)	Angle of Repose (°)	Hausner Ratio (N/A)	Pycnometer density (g/cm ³)
PA 01	- - - -	13.82	1.851	49.2	1.54	1.297
PA 02	- - - +	11.31	1.922	56.4	1.50	1.299
PA 03	- - + -	14.37	1.999	47.5	1.56	1.311
PA 04	- - + +	11.92	1.874	53.7	1.41	1.304
PA 05	- + - -	15.50	2.024	52.3	1.46	1.300
PA 06	- + - +	9.60	2.074	55.1	1.47	1.304
PA 07	- + + -	13.97	2.053	48.1	1.48	1.305
PA 08	- + + +	20.47	2.014	49.3	1.57	1.301
PA 09	+ - - -	10.01	1.778	51.1	1.56	1.297
PA 10	+ - - +	13.68	1.904	56.1	1.42	1.312
PA 11	+ - + -	13.40	2.041	50.4	1.51	1.312
PA 12	+ - + +	13.63	1.863	51.8	1.59	1.306
PA 13	+ + - -	9.27	2.014	55.7	1.54	1.293
PA 14	+ + - +	15.31	2.122	47.6	1.46	1.314
PA 15	+ + + -	12.73	1.875	52.1	1.45	1.297
PA 16	+ + + +	16.92	1.947	47.2	1.43	1.314

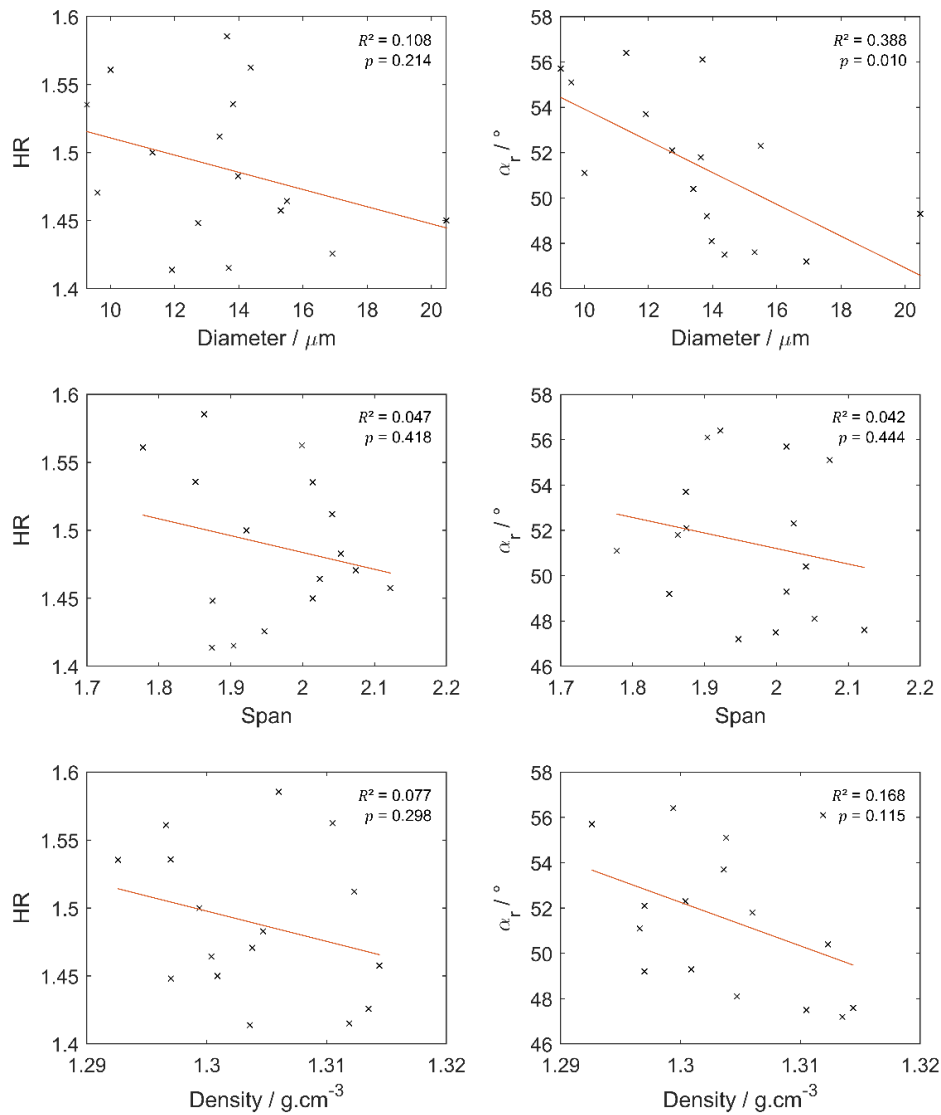


Figure 77: Scatter plots of Hausner ratio (left) and repose angle (right) against measured powder properties, the orange line represents the linear best fit to the data points. Statistical fit descriptors are shown for each plot and these indicate that only the relationship between angle of repose and particle median diameter are significantly correlated (90 % CI).

Of the six relationships assessed for correlation, shown in Figure 77, only the relationship between angle of repose and particle diameter showed a significant result at $\geq 90\%$ confidence interval. While the quality of the linear fit was not excellent ($R^2 = 0.388$), it does follow the expected trend that increasing particle size leads to reduced internal friction and improved flowability, as indicated by a constant of proportionality between the angle of repose and diameter of -0.7 ± 0.2 ($^\circ/\mu\text{m}$). No discussion will be provided of the direction and magnitude of the remaining linear fits due to the associated lack of statistical significance, although these are tabulated in Appendix C.1.

Particle size analysis by DLS is often convenient for comparison of a range of powders, since many particles from a relatively large sample are measured. As such, provided a sensible sampling procedure is followed, there is limited scope for misrepresentation of the particle size. However, DLS intrinsically assumes that the particles measured are spherical, or at least the output data takes the form of equivalent volume sphere diameter. Description of each particle by a single value is convenient for comparison, but a large amount of detail is lost in the process. Therefore, SEM imaging of samples 01-08 was performed to investigate whether the flow characteristics, previously discussed, were a result of variations in particle size and size distribution or whether particle morphology played a dominant role. Images were acquired by the method detailed in Section 4.2.2. All samples presented as nodular particles with aspect ratios approaching unity. Significant differences between the interparticle agglomeration were observed, that may account for variation of spray dried powder angle of repose.

Samples PA01 and PA03 that had shown relatively low angle of repose measurements presented as small clusters of agglomerated particles, as shown by Figure 78. A high magnification image of an unbound particle from sample PA03 showed high degree of sphericity with relatively long protrusions from the body. This sample exhibited the least agglomeration and lowest angle of repose.

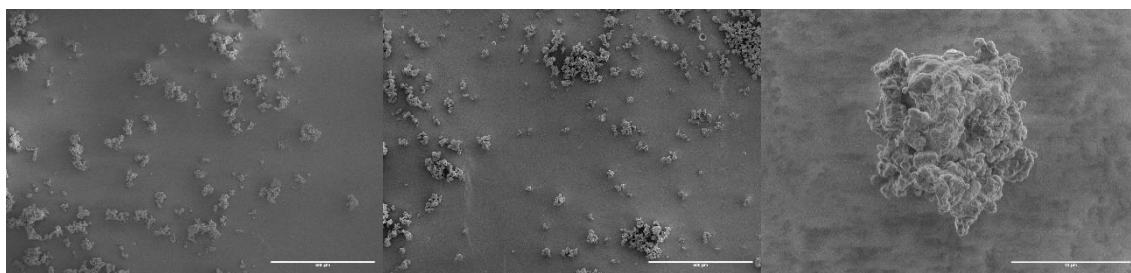


Figure 78: Low α , samples PA01 (left) and PA03 (middle and right) exhibited small agglomerate clusters. A high magnification image of an isolated particle showed sharp protrusions from a nearly spherical body. Scale 500 μm , 500 μm and 10 μm left to right.

Increased agglomerate size was observed in samples PA07 and PA08, Figure 79, and this was accompanied by slight increase of repose angle. While the radial distribution of crystallites in the microparticle was less regular when compared to the samples PA01 and PA03, the formation of large flat surfaces lacking point like protrusions likely gives these materials a high surface area of interparticle attraction. However, there were significant voids near to the particles centre of mass that likely reduce the overall effect of bulk dispersive forces.

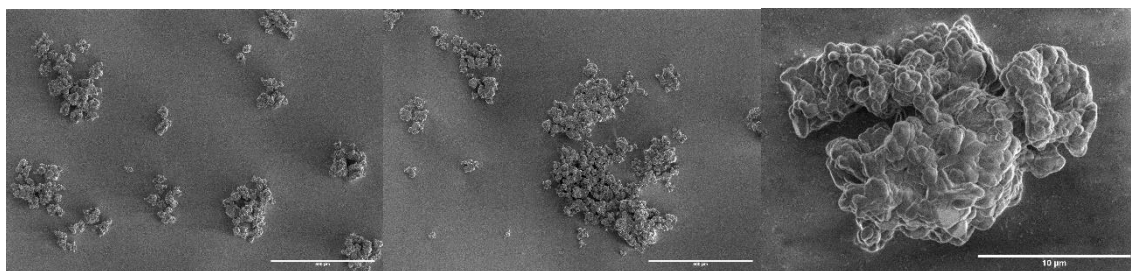


Figure 79: Moderate α , samples ($\sim 53 - 53^\circ$) PA07 (left) and PA08 (middle and right) presented as large agglomerate clusters ($\sim 200 - 600 \mu\text{m}$). Isolated particles showed irregular morphologies with significant void space towards the centre of mass of the particle. Scale $500 \mu\text{m}$, $500 \mu\text{m}$ and $10 \mu\text{m}$ left to right.

Sample PA02 gave the highest angle of repose, and SEM imaging revealed this sample to be distinctive due to the formation of an extensively branched network of agglomerates, Figure 80. Particles from this sample lacked both the protrusions observed on PA03, and the central voids observed in PA07 and PA08 the combined effect of which may be responsible for the formation of such extensive agglomeration. Attempted to imaging of samples PA04 and PA06 failed at high magnification due to excessive charge build up on the materials.

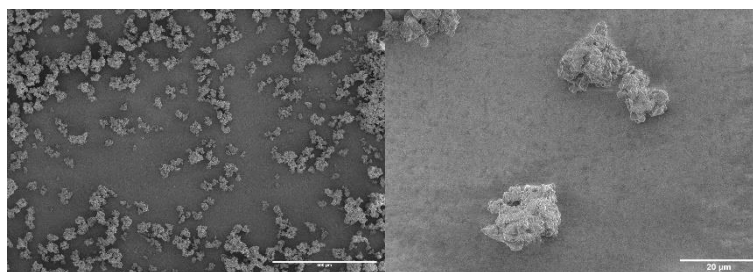


Figure 80: High α , samples ($> 56^\circ$) PA02 showed a network of agglomerates with individual particles showing dense spherical bodies lacking protrusions. Scale $500 \mu\text{m}$, $500 \mu\text{m}$ and $20 \mu\text{m}$ left to right.

Rationalisation for the nature of agglomeration is based on the assumption that interparticle forces are dominated by dispersive forces, not solvent/capillary forces. The assumption that solvent forces can be dismissed is made on the basis that spray drying was conducted with conditions sufficiently high as to remove all solvent, this was confirmed by the lack of yield change upon sample drying *in vacuo*. Since van der Waals force often dominates interactions between bodies of this size, in the absence of solvent forces, and since dispersive forces decay inversely to the sixth power of separation distance surface roughness can be used to rationalise the interaction energy. It should also be noted that the irregular void containing particles gave significantly lower Hausner ratios than either the spiked or smooth solid spherical particles. This result is consistent with the better packing efficiency of the latter morphologies. While a low compressibility may indicate better flow performance in a vibrationally mediated hopper such as that employed by the novel powder bed printer, it would likely introduce issues with the hazard sensitiveness of printed parts should these voids persist through the binding stage.

Having encountered difficulties modifying the flow characteristics of spray dried paracetamol using isolated production parameters, an investigation of the effectiveness of glidants was undertaken. The parameters used were equivalent to those used to prepare PA03, one of the lowest angle of repose samples that showed the least agglomeration, shown in

Table 21. The effectiveness of three known glidant materials was assessed by angle of repose measurements following the calliper method outlined in Section 4.2.7. Feedstock was prepared by suspending glidant nanoparticles, at a range of concentrations, in acetone (95 g) under sonication with a HeatSystems XL2020 Sonicator, before addition of paracetamol (5 g). Acetone was then added to return the total mass of solution to 100 g.

The results are plotted below in Figure 81. Data points are the average of five angle of repose measurements made on a single spray drying run and the plotted error bars correspond to the standard deviation of these measurements. Silica offered the best improvement to flowability at low additive content; however, data was not obtained at high content due to issues with unbound silica passing through the cyclone and resulting in filter blockages. Magnesium stearate offered limited scope for improving the flowability of spray dried paracetamol, at times actually causing a worsening of powder flowability. Nanoparticles of magnesium stearate failed to disperse well into the acetone, and it is thought that the variability is reflective of heterogenous mixture passing through the spray drier. Runs with high concentrations of magnesium stearate did not result in blockages at the filter, but significant material was recovered from the feed line. Carbon black dispersed readily in acetone at all concentrations used, and this was reflected in the results. Concentrations of carbon black above 1.5 wt.% offered little gain, and caused some darkening of the filter membrane indicating limits to adhesion.

Table 21: Paracetamol/glidant spray drying parameters

Control measure	Value
Inlet temperature	97-105°C
Outlet temperature	~ 60°C
Atomisation and drying gas	N ₂
Gas flow rate	40 mm
Aspiration rate	100 %
Solute/Solvent	Paracetamol/Acetone
Cyclone	High performance
Pressure	5 bar
FFR	2.5 ml.min ⁻¹
Nozzle diameter	1.6 mm
Concentration	7.5 wt. %

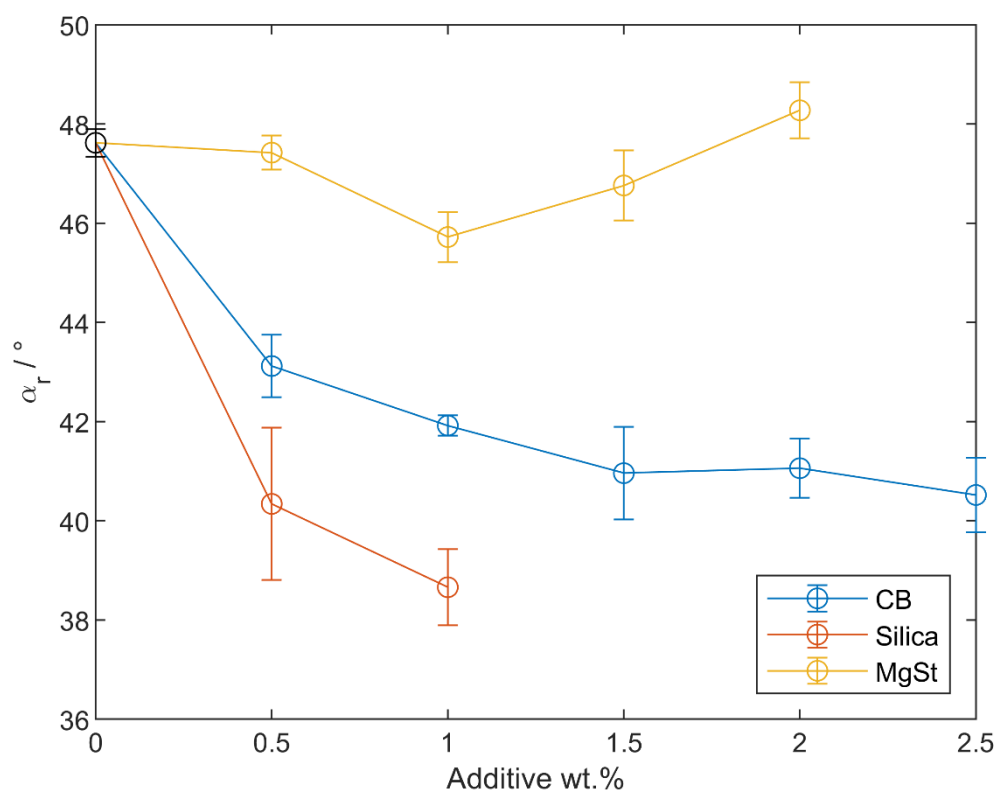


Figure 81: The effect of glidant addition on spray dried paracetamol flowability

5.3.3 Discussion

Overall, the attempt to model particle size and size distribution as a function of various process parameters was unsuccessful, with results showing limited coherence. Of the two models that were constructed to better understand the effect of pressure, FFR, concentration and nozzle diameter on particle properties, that which modelled span appears to be of better quality. Neither model should be used to make accurate predictions for future runs. The validity of the models could be tested, given sufficient time to replicate several runs under identical conditions. Such validation was not attempted because the initial results conclusively showed that process parameter optimisation, while potentially critical for other fields of research, offers little advantage in comparison to formulation change with regards to modification of flowability characteristics. Moreover, due to the batch-to-batch reproducibility of spray drying experiments, it was decided that further work on these models would be of little benefit. Despite the statistical weakness of the particle size factorial model, there was notable adherence to the logical mass balance arguments outlined by Vehring [80]. Particle size enlargement was achieved through two means, primarily modification to the atomisation and secondarily by concentration increase. While the scope for modification of particle size was expected to be higher, particularly by modification of nozzle pressure from 5 to 8 bar, it is recognised that the average particle sizes fell within limit of particle sizes expected from this two fluid atomisation setup (2 – 20 μm) [157,179]. A significantly wider range of particle sizes would be accessible by rotary or ultrasonic atomisation.

Particle size distributions were significantly wider than expected for a spray dried powder, based on numerous literature reports of narrow distributions. This is perhaps the most discouraging information retrieved from this dataset as it may indicate a systematic issue with the experiment. The drying temperature (T_{in}) was 97 – 105 °C, which is an usually high temperature when acetone is the solvent. The purpose behind this high temperature was to ensure that the exhaust temperature remained at 60 °C – preliminary experiments showed a significant reduction of product agglomeration under these conditions as

residual solvent content was negligible. This reasoning was consistent with the SEM investigation of particle morphology revealed that most particles were not the smooth, nodular and roughly spherical shape expected. But instead, there was a range of shapes from spiked spheres to irregular globules. The irregularity of particle morphology can be explained by the excessive drying temperatures which may have raised the droplet temperatures above the wet bulb temperature, resulting non-Fickian mass transfer such as material jetting. Since the solute was small, soluble organic molecules, it is unlikely that the observed morphologies were a result of premature crust formation.

Since the flowability data was derived from poorly fitting models of size and span, it was not expected to reveal any idealised behaviour. Six relationships between independent variables (median particle size, size distribution span and average particle density) and dependant flow characteristics (Hausner ratio and angle of repose) were examined. Of which, only the relationship between particle size and angle of repose was statistically significant (p -value = 0.010). The correlation, while weak ($R^2 = 0.388$), followed the expectation that increased particle size would yield better flowing powder. The constant of proportionality for this relationship was of relatively high magnitude (-0.7 ± 0.2 $^\circ/\mu\text{m}$). This result implies that, should rotary or ultrasonic spray drying be used to generate larger spray dried particles, these would exhibit significantly better flow properties. Following the extrapolation of this data, should particles with an average diameter of 50 μm be produced, the expected angle of repose values would be $\sim 26^\circ$ - which would be firmly within the region of good flow behaviour. It is however recognised that this model was extremely limited in both breadth of particle sizes, and accuracy – so such an extrapolation, while tempting, should not be prioritised over alternate methods of flow improvement.

Pycnometer densities of the paracetamol were accurate to within the standard error provided by the gas pycnometer, the average of all pycnometer densities measured was 1.304 g.cm^{-3} (cf. lit. density = 1.23 – 1.40 g.cm^{-3} [186,187]). Such significant variation between pycnometer density was unexpected, the range spanning 1.293 to 1.314 g.cm^{-3} is not explained by the standard error on

volume measurements given by the pycnometer ($\pm 0.0005 \text{ cm}^3$) nor the error in sample mass obtained from the balance ($\pm 0.00005 \text{ g}$).

Generally the spray dried paracetamol particles resembled the images shown in the literature, being nodular agglomerates of nanocrystals [157]. The results of the SEM investigation were interesting and may explain some of variation observed when attempting to correlate particle properties with flow characteristics. Agglomeration of the spray dried powders was distinguishable into three types, short- and long-range discrete agglomerates were shown to result in significantly lower angle of repose measurements than powders which formed networked agglomerates. In all samples, very few un-agglomerated particles were found, and a tentative hypothesis is proposed based on the small sample size observed. Weak agglomeration between rough/spiked microparticles resulted in the best flow character. Stronger interactions between irregular particles resulted in further ranged agglomeration, and subsequently worse flow characteristics. The strongest interactions, between smooth surfaced particles appeared to be sufficient to maintain strong agglomeration in low density networks of particles. These networked agglomerates showed the worst flow characteristics.

As expected, the introduction of known glidant nanoparticles into the spray dried formulation had a very significant effect on the flowability of the materials as expected [160]. While silica appeared to offer the best reduction of internal friction, lack of adhesion between the nanoparticles and paracetamol in the absence of binder caused significant issues with spray drying this composition. In one run, a fibrous mass of silica was recovered from the product collection vessel. Flow modification using magnesium stearate nanoparticles was likewise unsuccessful. Issues with poor dispersibility, and tendency to localise at boundaries between solution and vessel or solution and feed tube, resulted in an increased variation of spray dried material character. Carbon black was successfully employed as a flow modifier for spray dried paracetamol, at a range of concentrations. Performance as a modifier was lower than silica but showed a defined progression to a steady state after 1.5 wt.%.

5.4 Spray drying RDX

5.4.1 Material preparation

RDX microparticles were prepared by spray drying using a small range of conditions employed for the full factorial optimisation of paracetamol spray drying, discussed in Section 5.3.1. The controlled parameters are shown in Table 22 and the variables are shown in

Table 23.

Table 22: Control measures employed for spray drying pure RDX from acetone.

Control measure	Value
Inlet temperature	97-105°C
Outlet temperature	~ 60°C
Atomisation and drying gas	N ₂
Nozzle pressure	5 bar
Gas flow rate	40 mm
Aspiration rate	100 %
Solute/Solvent	RDX/Acetone (5 wt.% solid)
Cyclone	High performance

Table 23: High and low variables used to spray dry four distinct RDX samples.

Level	FFR / ml.min ⁻¹	d _n / mm
-	2.5	1.4
+	5.0	1.6

Prior to use, RDX was recrystallised by evaporation of an undersaturated solution in acetone to reduce HMX impurity content by selectively using large high quality crystals. As with spray drying paracetamol, the experiment was conducted in closed negative pressure mode following the procedure outlined in Section 4.4.2. Solutions were prepared by dissolving RDX (1 g) in acetone (19.0 g, 25.5 cm³) in a stoppered conical flask. The solution was equilibrated at room temperature with stirring (200 rpm, ~30 min) prior to use. Visual checks of the spray drying process, cone shape and pressure drop, were conducted as before. Upon completion of each run the kit was switched off and allowed to cool for approximately 30 minutes as this was found to reduce issues with static adhesion of the spray dried material to the collection vessel. Transfer of RDX was conducted using an anti-static horn/resin spatula.

5.4.2 Results

The particle sizes of spray dried RDX, shown in Table 24, were lower than paracetamol prepared using the same conditions, Table 16. However, the RDX size data was collected by thresholding image analysis of optical micrographs, following the procedure described in Section 4.2.1, while the paracetamol data was collected using the DLS procedure described in Section 4.2.3. Data collection by DLS was attempted for RDX, but issues were encountered while attempting to disperse spray dried RDX particles in water which necessitated the use of small quantities of dispersal agent, Triton X. Unfortunately, this then led to rapid dissociation of the agglomerated crystals that composed a single spray dried particle as was evidenced by a rapid increase of laser obscuration over time. As such, optical microscopy, being significantly less destructive, was employed for particle size analysis. Unlike DLS, which provides a volume distribution, the optical microscopy result is a number distribution that was skewed towards the more abundant small particles [188]. The majority of particles presented with diameters within the bounds of 2 – 20 μm , as expected for two fluid spray drying [179]. Some upwards deviation was observed in the SD 01 sample which was unexpected considering this sample was prepared using the low flow rate a smaller nozzle diameter.

Table 24: Summary of optical microscopy particle size analysis, percentiles corresponding to number distribution.

Sample	d_{10} / μm	d_{50} / μm	d_{90} / μm
SD 01 (- -)	2.28	7.13	25.92
SD 02 (+ -)	2.04	5.14	20.89
SD 03 (- +)	2.02	5.14	13.73
SD 04 (+ +)	2.04	6.08	16.64

Fitting a model to the data showed that neither the feed flow rate or nozzle diameter had a significant impact on the average particle size within the error of the coefficient. The summary of effects for the 2² model are presented Table 25.

Table 25: Summary of 2² modelling of diameter in terms of FFR and nozzle diameter.

Term	Estimate	Std Error	t Ratio
Intercept	10.5975	11.22901	0.94
FFR	-0.21	0.586	-0.36
d _n	-2.625	7.325	-0.36
			Prob > F
			R²
			0.8920
			0.2044

The model quality indicators show this to be a poorly fitting model, further evidencing the difficulty of representing such a complex system by such reductive means. Unlike the 2⁴ model representing the diameter of spray dried particles, which possessed a negative intercept with positive effect coefficients, this model begins with an intercept close to the true diameter of the particles and the effect of feed flow rate and nozzle diameter are subtractive. Note that the errors associated with the intercept and effects are sufficiently high as to encompass a change of sign.

Table 26: Summary of thermal analysis and pycnometer densities for spray dried and raw RDX samples.

Description			ρ_{pyc} g.cm ³	T _{endo} peak / °C	T _{exo} onset / °C	T _{exo} peak / °C	ΔH / kJ.g ⁻¹
Type II Class 4			1.7946	206.0	208.2	232.0	2036
Label	FFR	d _n	Spray dried				
SD 01	2.5	1.4	1.7341	204.9	207.9	234.7	2124
SD 02	2.5	1.6	1.7781	205.6	208.5	234.2	1732
SD 03	5	1.4	1.7472	205.1	208.3	234.8	1690
SD 04	5	1.6	1.7650	205.1	208.5	234.4	1830

Herein, the pycnometer densities of spray dried pure RDX spanned a range of 1.7341-1.7781 g.cm⁻³, corresponding to 95.28 – 97.70 %TMD using an RDX crystal density of 1.82 g.cm⁻³ [189]. Maximisation of density is preferable as it evidences a reduction of internal void spaces, which have been shown to negatively influence the shock and impact hazard sensitiveness of energetic materials. Such maximisation was achieved by increasing the drying time of a given droplet, as evidenced by the dramatic effect of nozzle diameter on the pycnometer densities shown in Table 26. It appears that slight control over the particle density is also indirectly provided by increasing the feed flow rate. However, the range over which this variable was modified limited this effect by intention since the reduction of residual solvent in particles was prioritised.

DSC results for the starting material and spray dried materials are shown in Table 26. All spray dried RDX samples showed a very slight reduction of DSC exotherm onset temperature relative to the Type II Class IV starting material. This result was expected due to the significant crystal size reduction that significantly modified the ratio of destabilising surface and stabilising surface energies. The overall magnitude of the reduction was sufficiently low that no safety concerns were raised. The enthalpies of decomposition showed significant variability, with SD01 and SD03 providing the highest and lowest energy densities respectively. While values of decomposition enthalpy appear to correlate positively with the average particle size, no meaningful causality has been identified for this observation. The DSC traces showed no evidence of low temperature solid-solid transitions that would be expected for the β to α relaxation.

Powder X-ray diffraction studies showed that all spray dried RDX samples retained the stable α -polymorph, Figure 82. The significant differences in peak intensity are a result of preferential orientation of relatively coarse Class IV crystals. Peak positions were unchanged in either sample relative to the PDF. Note that the Class IV sample crystals were too large for PXRD, necessitating size reduction by careful grinding in a smooth marble pestle and mortar using a

rotary motion. Sufficient material for study was prepared by repetition of the grinding process in small batches (5 x 0.2 g).

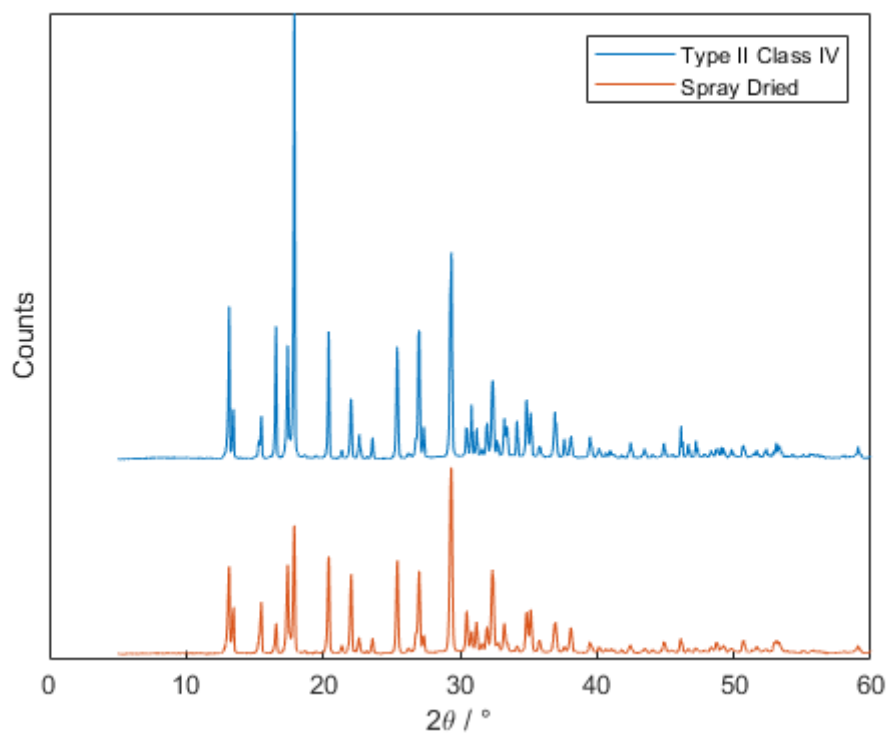


Figure 82: PXRD traces of RDX starting material and spray dried RDX showing both to be the stable

Williamson-Hall analysis was conducted on both the ground starting material and the spray dried sample that showed the most significant change of energy density (RDX SD03). Microstrain and coherence length calculation was achieved following the analysis procedure detailed in Section 0. Since many peaks were overlapped, making deconvolution and the associated errors unavoidable, an error limit was imposed. Data points in which the peak width error exceeded 10 % of the FWHM were not included in the analysis but are shown in the figures below as hollow circles. The analysed data points are shown as filled black circles. Williamson-Hall analysis requires linear regression of the data shown on the plots in Figure 83 and Figure 84, and this is represented by the solid red line. The dashed purple lines indicate a two standard error boundary above and below the line, corresponding to a confidence interval of 95 %. Errors on the final microstrain and coherence length value were propagated from the linear regression fit errors.

Langlie approximated Rotter tests were performed for the Class IV starting material and the RDX SD03 sample, following the EMTAP standard test detailed in Section 4.2.9. The results are presented as either GO or NOGO, corresponding to the identification of an initiation event. In the event of a GO, the drop height is reduced in the subsequent run. This is continued until a NOGO is observed, at which point the drop height is reduced. While initiation can be identified by studying the residue in the anvil, the setup used employs expelled gas as a more reliable indication.

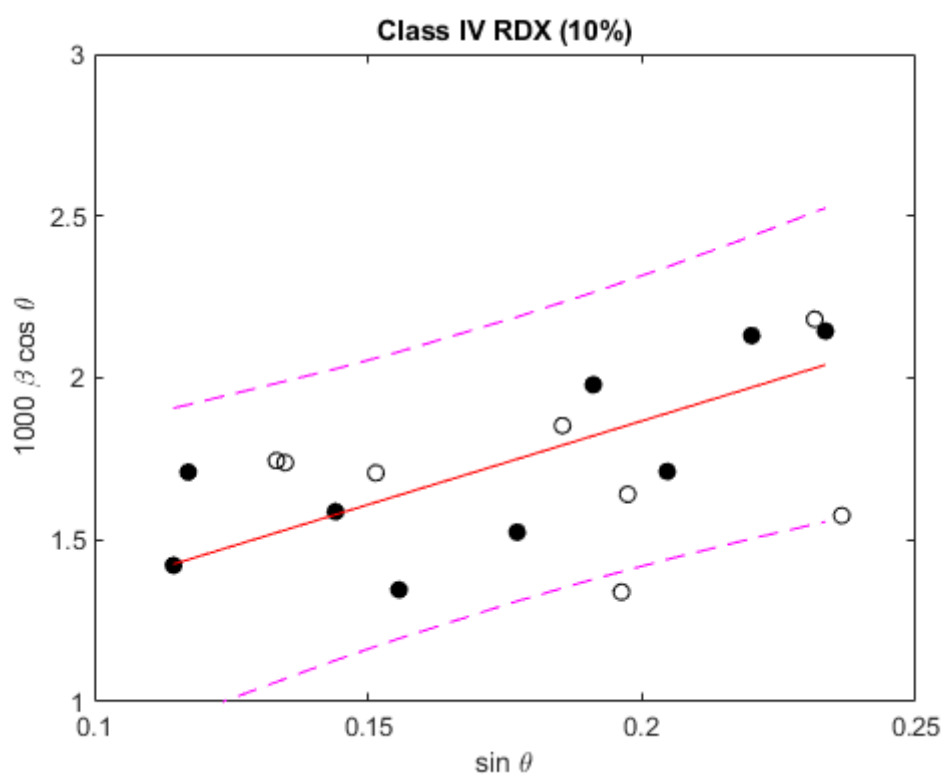


Figure 83: Williamson-Hall plot for Class IV RDX was consistent with appropriate use of the technique. Overall the data (black circles) fell within the a 95 % confidence interval (purple dashed lines). The linear fit is shown by the solid red line.

Table 27: Results for Class IV RDX Rotter impact test, performed using Langlie scaleup approximation, showed a significant reduction of sensitiveness relative to the standard sample.

Run	Height	Result	Gas produced / ml
1	77	GO	1
2	56.9	NOGO	0
3	66.1	GO	1
4	61.3	NO GO	0
5	63.7	GO	1
6	62.5	NO GO	0
7	63.1	NO GO	0
8	94.3	NOGO	0
9	115.3	GO	2
10	104.3	NOGO	0

RDX STD	97.4
Median Height	96.9
F of I	79.6

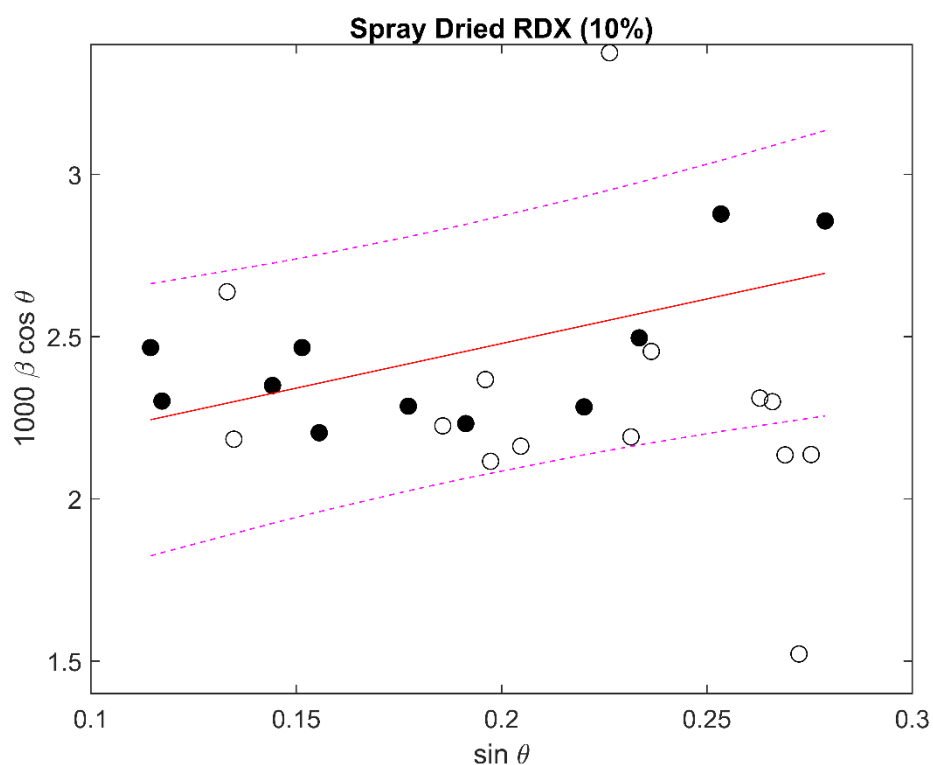


Figure 84: Williamson-Hall plot for spray dried RDX showed significantly higher variation of broadening with each peak, but generally the valid data points (solid black circles) fell within 95 % confidence intervals (purple dashed lines). The linear fit is shown by the solid red line.

Table 28: Results of the spray dried RDX Rotter impact test, performed using the Langlie 10 shot approximation, showed no noticeable change relative to the starting material Class IV RDX.

Run	Height	Result	Gas produced / ml
1	77	NO GO	0
2	104.2	GO	1
3	89.5	NO GO	0
4	96.6	GO	1
5	93	NO GO	0
6	94.8	GO	1
7	93.9	NO GO	0
8	94.3	GO	1
9	94.1	NO GO	0
10	94.2	GO	1

RDX STD	97.4
Median Height	94.15
F of I	77.3

Table 29 contains a summary of Williamson-Hall microstrain and coherence length data both for the RDX samples discussed above, and their simulant paracetamol equivalents. Except for Class IV RDX, all samples were used as generated. As previously detailed, crystals of the Class IV RDX starting material were found to be excessively large for PXRD so were ground in a pestle and mortar.

Table 29: Summary of Williamson-Hall strain and coherence length values, with errors taken from the standard error of linear regression.

Sample	1000 x $C\epsilon$ / a.u.	1000 x Error	L / nm	Error	F of l / a.u.
Class IV RDX	5.2	1.7	166	61	79.6
Spray dried RDX	2.8	1.1	71	8	77.3
Raw paracetamol	2.0	0.3	69	11	---
SD paracetamol	2.1	0.2	67	8	---

It is thought that the action of manually grinding the class IV starting material introduced a significant amount of strain to the crystals involved. Indeed, out of all the samples, the manually ground RDX sample showed the highest microstrain. The coherence lengths of Class IV RDX and raw paracetamol showed the highest error values, indicative of limited control in these production processes that led to both a wide particle size range, but also variety in the crystal habits. Whereas the coherence length error for spray dried RDX and spray dried paracetamol were very consistent.

5.4.3 Discussion

Comparison of the RDX and paracetamol factorial models unfortunately held limited meaningful results, primarily due to the significant difference in size data used. Regardless of this, the errors associated with the RDX model are significant, and could perhaps be reduced by increasing the range over which variable were modified. As it is presented, the intercept value was by far the most dominant term within the model, with process parameters offering very marginal scope for size control. Notably, the particles measured by optical microscopy had diameters around 5 μm , proximate to the lower limit of resolution and subject to diffraction error.

Pycnometer densities of spray dried RDX showed a slight reduction relative to crystal density potentially indicating void formation although the magnitude of density change was much less than was reported by Qiu *et al*, for RDX/PVAc and RDX/VMCC composite spray dried particles [139]. Since the above RDX was spray dried in the absence of a binder coating, it is not possible to attribute the increased density to a reduction of central void volume, as it may simply be a more permeable structure analogous to an open cell foam.

Formation of α -RDX by spray drying, as indicated by DSC and PXRD, was consistent with all literature reports. Williamson-Hall analysis was employed successfully to calculate microstrain and coherence length in samples of RDX and paracetamol that were prepared by spray drying under identical conditions. Impact testing, by Langlie ten shot approximation of the standard Rotter procedure was applied to spray dried RDX and the raw material Class IV RDX. It was expected that microstrain values, being a relative measure of lattice imperfection density, should correlate to the presence of hotspots responsible for initiation. The dependence of shock and impact sensitiveness on lattice imperfections has been demonstrated in a range of energetic materials [59,126,128,190]. The results in Table 29 appear to suggest the opposite to the proposed hypothesis. However, the strain value for Class IV RDX cannot be observed independent of recognising that much of this was imparted by the grinding process.

The measured Fofl value for spray dried RDX was lower than expectations based on the accounts of [139,140], whose investigation of the shock sensitiveness of spray dried RDX led them to hypothesise that the spray drying process reduced the prevalence and relative size of lattice imperfections, leading to improved sensitiveness. While it is not possible to attest to the relative reduction of lattice imperfections as a result spray drying, due to lack of an adequate control sample, it can be inferred from the Williamson-Hall analyses that this spray dried sample contained relatively little strain compared to samples prepared by milling processes. Despite possessing low crystallite strain, spray drying pure RDX was shown to increase the sensitiveness relative to the standard used, a result that contrasts much of the work in this field. Application of small-scale gap testing, to assess the impact of spray drying on shock sensitiveness would potentially allow for better comparison against the literature.

5.5 Microencapsulation of RDX

5.5.1 Material preparation

Before preparation of any composite RDX/CAB composite materials by spray drying, a compatibility test was conducted by comparison of DSC traces for a sample containing the raw material (0.9 mg) and a 50:50 mixture of the raw RDX and CAB (1.8 mg combined mass), as outlined in STANAG 4147 [191]. The result showed the materials to be compatible, with an onset reduction of 3.1 °C resulting from the addition of CAB, as is shown by Figure 85 **Error! Reference source not found.** It should be noted that the RDX used for this test was Type II, indicating a possible HMX content of 4 – 17 % HMX. The HMX content is evident from the DSC trace due to the additional endotherm at 193.5 °C corresponding to a transition from γ - to δ -HMX [192].

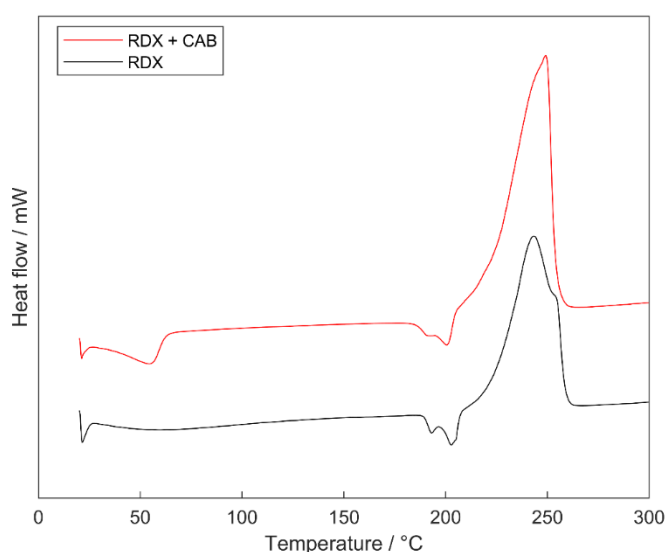


Figure 85: DSC traces for RDX and RDX/CAB mixtures showed a slight reduction of exotherm onset position in the latter, within the range of compatibility defined by STANAG 4147. Note the initial settling of the DSC is expected, however the red RDX+CAB trace contains an endotherm (45-60 °C) corresponding to the glass transition of CAB.

The spray drier was set up in close negative pressure mode, as described in Section 4.4.1. Purified RDX (12 g) and CAB (1.2 g) were combined with AcO (646.8 g, 825 cm³) in a stoppered flask. The mixture was gently stirred (300 rpm, 18 °C) until no solids were visible, after which the mixture was stirred for a

further 30 mins. The solutions were then spray dried following the procedure detailed in Section 4.4.2, the key process parameters are shown in Table 30. Accumulated static in the product was allowed to dissipate (30 mins) before the product was transferred into a pre-weight anti-static sample bag.

The exact same procedure was conducted for preparation of paracetamol/CAB inert samples, although these were produced in lower quantities. Each solution was composed of paracetamol (2 g) and CAB (0.2 g) in acetone (107.8 g, 137.5 cm³).

Table 30: Summary of spray drying and feedstock parameters for the production of RDX/CAB and paracetamol/CAB composite microparticles.

Control measure	Value
Inlet temperature	55, 70, 85, 100°C
Atomisation and drying gas	N ₂
Feed flow rate	50 ml.min ⁻¹
Nozzle pressure	5 bar
Nozzle diameter	1.4 mm
Gas flow rate	40 mm
Aspiration rate	100 %
Core/Binder	RDX/CAB, PA/CAB 10:1
Total solids in solution	2 wt. %
Cyclone	High performance

Comparison of RDX/CAB composite microparticle yield before and after desiccation of the sample revealed that a significant amount of solvent remained either trapped/adsorbed/dissolved in the product. The residual solvent content was recorded as a function of drying gas temperature in **Error! Reference source not found.** It appears that complete removal of solvent during the spray drying process is not feasible by isolated modification of inlet temperature within reasonable bounds and would likely require a simultaneous reduction of feed flow rate, **Error! Reference source not found.**

Table 31: The relationship between drying temperature and residual solvent in spray dried RDX/CAB composite microparticles

$T_{in} / ^\circ\text{C}$	$T_{out} / ^\circ\text{C}$	Wet mass / g	Dried mass / g	Solvent / %	Yield / %
55	31 - 33	10.730	10.571	1.48	86.65
70	36 - 38	11.062	10.965	0.88	89.88
85	41 - 44	9.659	9.612	0.49	78.79
100	52 - 58	11.033	10.989	0.40	90.07

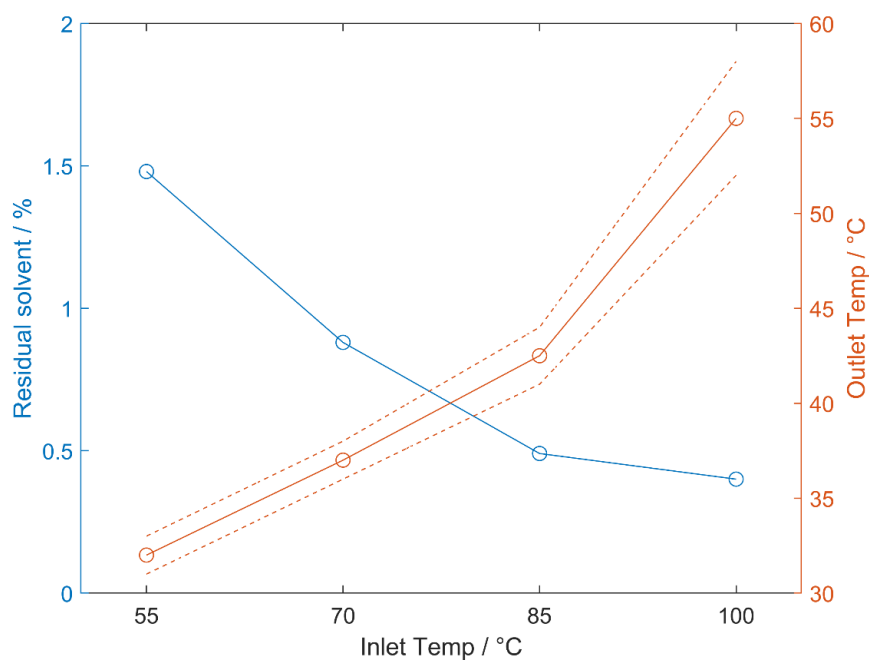


Figure 86: Plot showing the diminishing impact of inlet temperature (black) on residual solvent content (blue). With the inverse effect being observed on the outlet temperature (orange), which begins to increase more rapidly as the boiling point of acetone is reached. The dashed orange lines mark the upper and lower variation of outlet temperatures observed while inlet temperature and feed flow rate were maintained at constant values.

5.5.2 Results

As previously discussed, prohibition of energetic sample investigation using the available SEM has necessitated the use of paracetamol/CAB inert samples from which inferences of microparticle morphology are drawn. Image acquisition details are provided in Section 4.2.2.

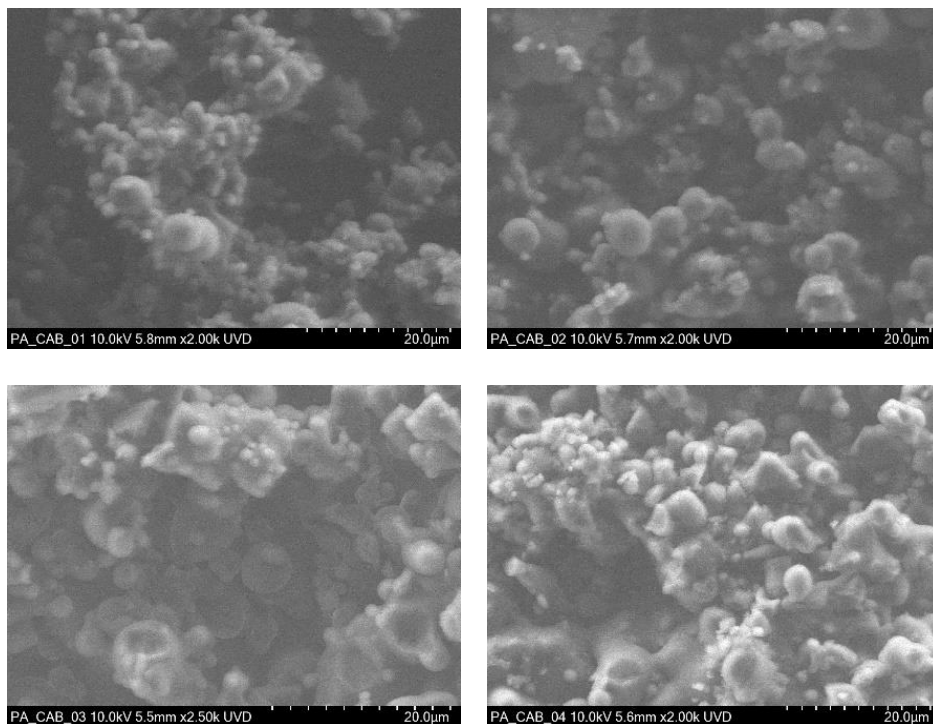


Figure 87: PA/CAB composite microparticle prepared by spray drying with varied inlet temperatures: (a) 55 °C, (b) 70 °C, (c) 85 °C and (d) 100 °C

The SEM images of paracetamol/CAB microparticles showed an evident trend towards larger particle size with increasing drying temperature. The samples prepared with $T_{in} = 55\text{ °C}$ and 70 °C are composed primarily of distinct spherical particles, whereas the higher temperature samples showed excessive bridging to the point where regions of continuous binder phase were observed. The sample resulting from $T_{in} = 85\text{ °C}$ showed numerous examples of both dimpled and collapsed hollow spheres resulting from premature crust formation. The sample prepared using $T_{in} = 100\text{ °C}$ contained particles exhibiting the lowest degree of sphericity and the most irregularity. Since this sample was prepared using drying conditions under which the droplet temperature likely exceeded the wet bulb temperature, it is likely that the morphology deviated from the expected Fickian diffusion result due to combined mass and heat transfer processes.

Microparticle size analysis was conducted using line length measurements applied to diameters noted by visual inspection of the image. While this method has inherent issues regarding bias and boundary determination error, attempts to apply a more comprehensive thresholding approach were unsuccessful due to the overlapped nature of the microparticles. Particle diameters for the four samples are presented below as independent histograms, Figure 88, to which lognormal distributions were fitted to aid comparison, Figure 89.

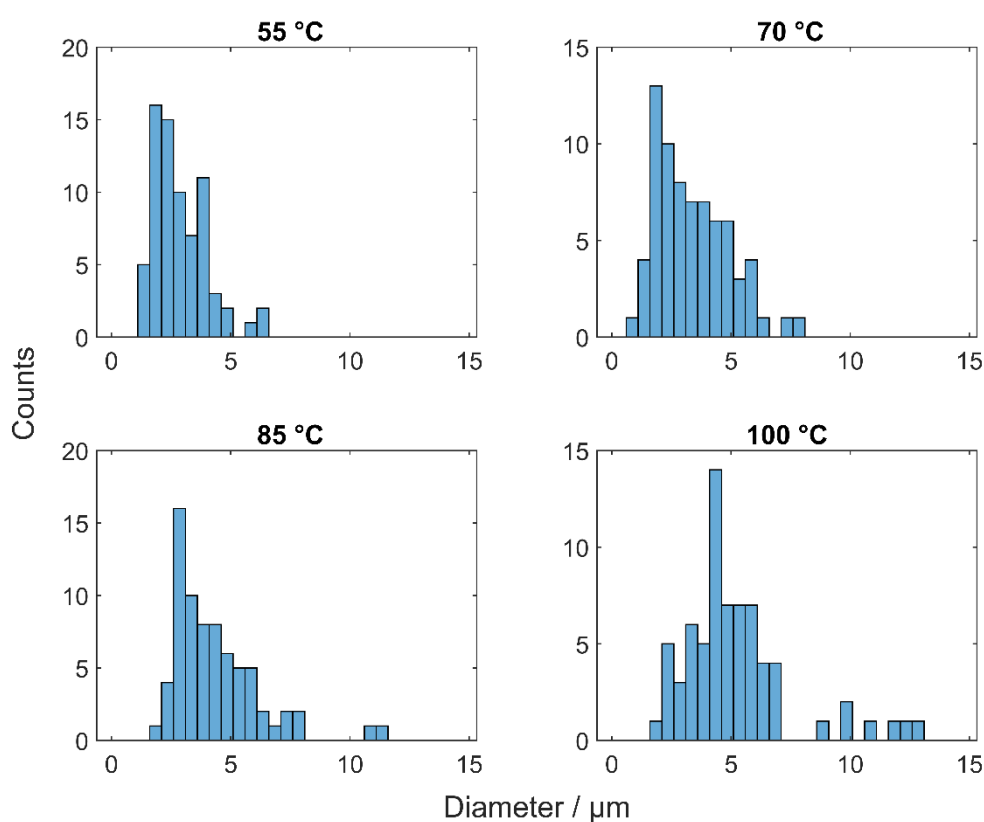


Figure 88: Histograms showing the dependence of visually inspected diameter of paracetamol/CAB spray dried microparticles on drying temperature

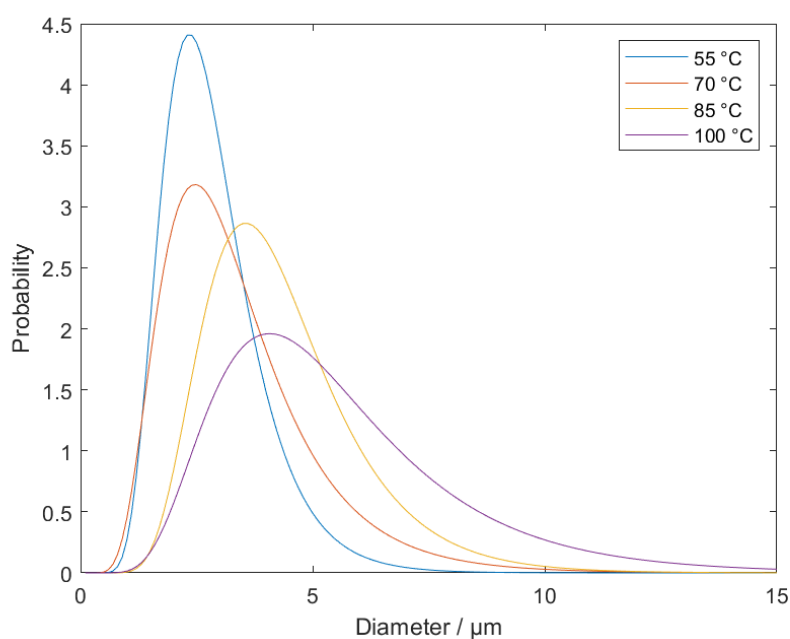


Figure 89: Lognormal distributions fitted to the particle size distributions for paracetamol/CAB microparticle spray dried at various inlet temperatures.

Table 32: Summary of paracetamol/CAB microparticle size analysis

$T_{in} / ^\circ\text{C}$	Mean / μm	d10 / μm	d50 / μm	d90 / μm
55	2.85	1.73	2.60	4.14
70	3.38	1.68	3.09	5.54
85	4.35	2.67	3.81	6.47
100	5.53	2.91	4.78	9.90

It is evident from the histograms in Figure 88 that the spray dried samples exhibited average particle sizes within the expected range of – 1-10 micron, consistent with the literature data on spray dried nitramines summarised by Table 3. Moreover, there is an apparent skew of the sizes to higher values with increasing inlet temperature that is much more evident in Figure 89. Examination of the lognormal fitted data shows a distinct broadening of the particle size distribution with increased inlet temperature with concurrent particle

size increase. While the distributions for samples prepared using 55 and 70 °C inlet temperatures have almost identical peak positions, the actual values of the mean particle size and d50 show a distinct increase with temperature. Note that the mean diameter was calculated using Equation 37, in which μ and σ are the representative parameters of the lognormal distribution, obtained using the lognfit function in MatLab.

$$\text{Mean} = \exp\left(\mu + \frac{\sigma^2}{2}\right) \quad (37)$$

PXRD phase analysis was conducted for the RDX samples, showing recrystallisation in the α polymorph resulting from all drying temperatures. This result was consistent with the literature reports on the topic – which have not showed any evidence that spray drying RDX produces metastable states [139,140,143,144,147]. It should be noted that the RDX/CAB composite materials showed a significant raise of amorphous background signal relative to spray dried pure RDX. No scaling was applied to the data presented in Figure 90.

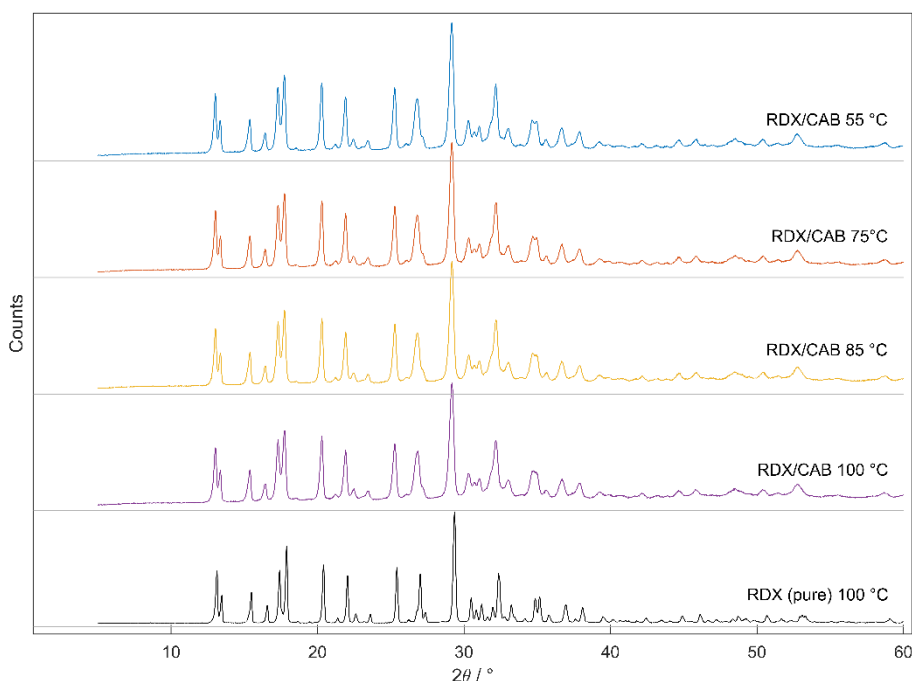


Figure 90: Stacked diffraction patterns for spray dried RDX/CAB composite compared to the diffraction pattern of spray dried pure RDX showing a significant difference peak resolution and amorphous background signal (grey lines indicate 0 count x-axis for each trace). All samples exhibited the stable alpha phase regardless of production parameters.

Inclusion of CAB binder in the spray drying process appeared to significantly broaden the peaks, which as previously discussed, can result either from crystallite size reduction or increased crystal strain. To further investigate the origin of this broadening the microstrain and crystallite size were calculated using Williamson-Hall analysis. Williamson-Hall plots for RDX/CAB prepared at 55, 70, 85 and 100 °C are shown in Figure 91, Figure 92, Figure 93 and Figure 94 respectively. Due to the poor resolution of peaks, particularly at high diffraction angles, a more stringent criteria for peak fit error was applied to the selection of points evaluated. Williamson-Hall analysis was conducted only on peaks for which the fit error was lower than 5 %. While this data handling approach results in a significant portion of the data being excluded from analysis, the excluded data points corresponded to the same overlapped peaks in each sample. Results are summarised in Table 33.

The impact sensitiveness of each RDX/CAB composite was investigated by Rotter tests, following the full 50 shot Bruceton ladder analysis detailed by the EMTAP manual of tests [176]. Despite material production in nominally dry conditions the samples were dried *in vacuo* prior to testing. Results are shown in Table 33 as Fofl values.

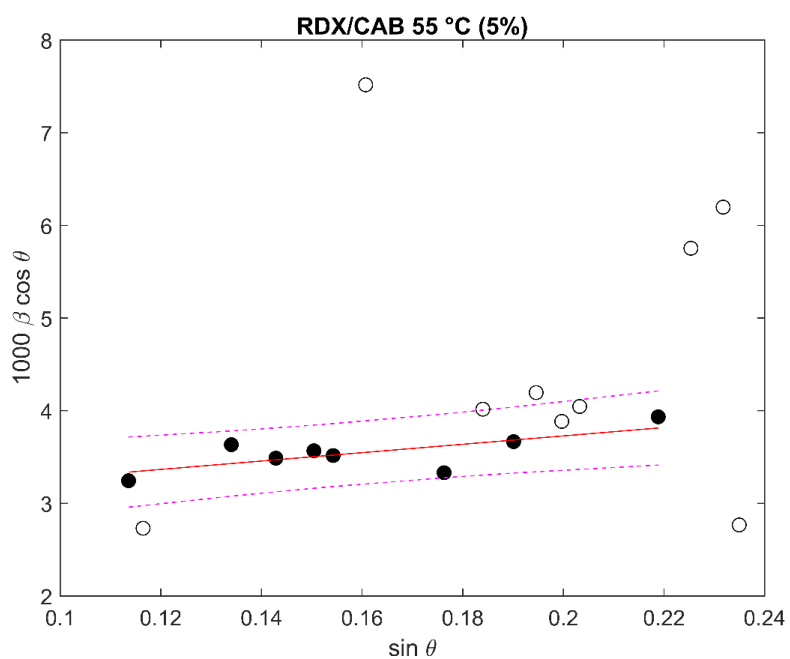


Figure 91: Williamson-Hall plot for RDX/CAB prepared using an inlet temperature of 55 °C. Hollow circles correspond to high error data. Linear regression of the accurate data (black circles) is represented by the red line with 95 % confidence bounds represented by the dashed purple lines.

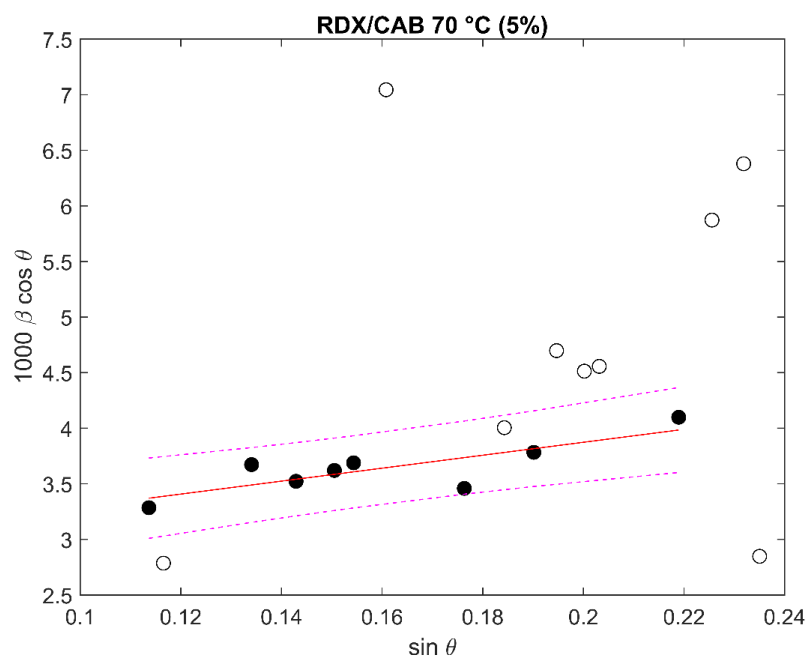


Figure 92: Williamson-Hall plot for RDX/CAB prepared using an inlet temperature of 70 °C. Hollow circles correspond to high error data. Linear regression of the accurate data (black circles) is represented by the red line with 95 % confidence bounds represented by the dashed purple lines.

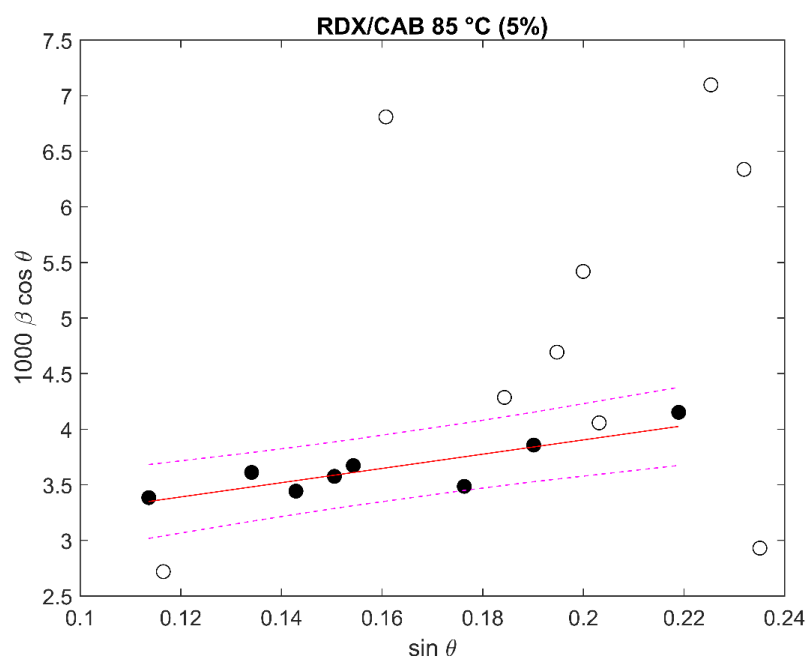


Figure 93: Williamson-Hall plot for RDX/CAB prepared using an inlet temperature of 85 °C. Hollow circles correspond to high error data. Linear regression of the accurate data (black circles) is represented by the red line with 95 % confidence bounds represented by the dashed purple lines.

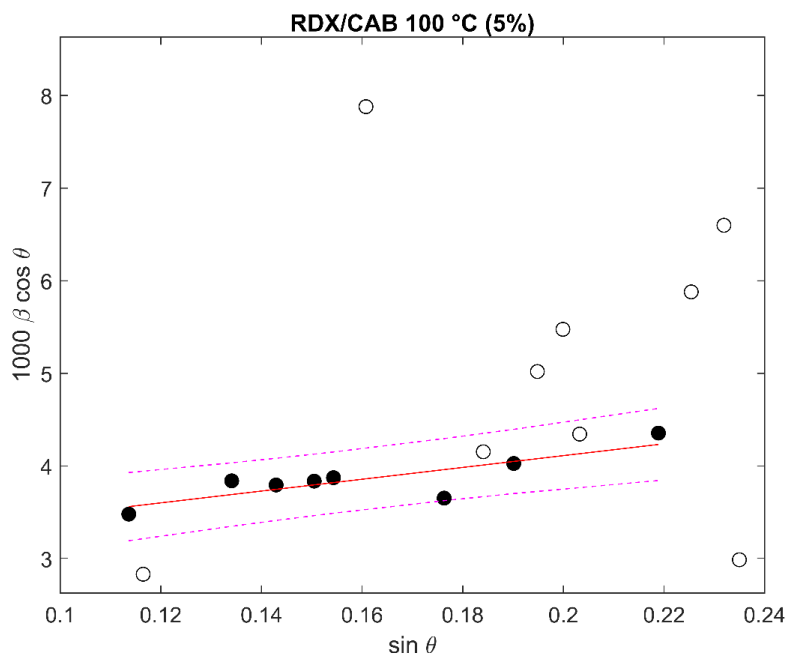


Figure 94: Williamson-Hall plot for RDX/CAB prepared using an inlet temperature of 100 °C. Hollow circles correspond to high error data. Linear regression of the accurate data (black circles) is represented by the red line with 95 % confidence bounds represented by the dashed purple lines.

Table 33: Summary of Williamson-Hall and Rotter testing results for spray dried RDX/CAB samples compared to spray dried pure RDX.

Sample	1000 x $C\epsilon$ (a.u.)	1000 x Error (a.u.)	L (nm)	Error (nm)	F of I (a.u.)
RDX/CAB 55 °C	4.5	1.8	49.1	5.1	102.0
RDX/CAB 70 °C	5.8	1.7	51.2	5.3	97.5
RDX/CAB 85 °C	6.4	1.6	52.9	5.2	97.6
RDX/CAB 100 °C	6.4	1.8	48.9	4.9	94.7
Spray dried RDX	2.8	1.1	71.9	7.7	77.3

Results of the Williamson-Hall analysis of RDX/CAB composites are presented in Table 33. All values exhibited high error margins, making the following discussion of trends dubious without further refinement of the raw data. There appears to be a dependence of crystallite microstrain on drying conditions as evidenced by the increase of microstrain with inlet temperature across the range of 55 – 85 °C. Similarly, within this range, the crystallite size was also positively correlated to inlet temperature. Deviation from trends was observed in the 100 °C sample, since the drying gas exhaust temperature for this sample was 52 – 58 °C it is highly likely that the drying conditions were too extreme for this process to be considered spray drying. It is likely that temperatures within the droplet exceeded the wet-bulb temperature, and so the process is far more comparable to a spray flash evaporation (SFE) process. SFE, while an excellent tool for preparing micronized and nanometric powders, including energetic materials, lacks the inherent morphological control of spray drying [141,193]. . The figure of insensitivity values (Fol) show a clear reduction of sensitivity towards impact for all samples prepared with CAB binder, as expected for any energetic material when phlegmatized with a binder [139]. More interestingly, there is a definite trend towards lower impact sensitivity for materials prepared with lower inlet temperatures.

5.5.3 Discussion

RDX/CAB microparticles were prepared by spray drying in a series of runs in which all process parameters except temperature were kept constant. This work used cellulose acetate butyrate (CAB) instead of poly vinyl acetate (PVAc) despite the latter being common to a significant portion of spray dried nitramine literature. This choice was made because use of CAB in energetic formulations [22,194] is significantly more widespread than PVAc [195]. While polymer nature is reportedly used to control the morphology of spray dried microparticles [149] there is more inherent potential for morphological control afforded by the multitude of spray drying process parameters [83,196,197]. The droplet evaporation rate, governed predominantly by the inlet temperature and solvent volatility, demonstrates the most significant influence on particle morphology. As such, the inlet temperature of the drying gas was set at four different levels (55, 70, 85, 100 °C) in an attempt to validate observations made by Sun *et al.* who report that spray drying RDX at high temperatures invariably gave the best particle morphology, reasoning that the reduction of drying time resulted in fewer droplet collisions [147]. The temperature range chose spans all of the reported temperatures at which RDX and HMX composites have been spray dried. Due to restrictions energetic samples and the SEM, inert samples were prepared under identical experimental conditions aside from substitution of RDX for paracetamol

Literature reports on spray dried energetics can broadly be separated into those seeking to modify particle morphology using either process or formulation control [140,142,146,147,149], and those that focus on the benefit of spray drying as a means of either mixing nitramines with hard to disperse nanometric aluminium or a means of reducing the shock sensitiveness of the material [139,143,144]. The latter group are often limited in the scope of morphological discussion. This section sought gain an understanding of how the morphology, dictated by spray drying parameters, would influence the hazard sensitiveness.

While it was initially expected that the higher supersaturation generated during the high drying temperature experiments would cause a higher nucleation rate,

thus leading to a negative correlation of coherence length with temperature this was not the case. The interpretation proposed for the observed positive correlation between coherence length and drying temperature is that the formation of hollow spheres at high drying temperature resulted in solvent entrapment thus promoting crystal growth. Such a growth profile was reported for RDX/PVAc spray dried at 55 °C [140], so it is likely that the effect is exaggerated with the higher temperatures used in this work.

Results of the Williamson-Hall analysis of RDX/CAB prepared with an inlet temperature of 100 °C appeared not to follow the aforementioned trends. This sample showed relatively high strain, but low average crystallite size. Since this run was unique in that the high inlet temperature resulted in outlet temperatures greater than the boiling point of acetone. It is highly likely that this resulted in significant deviation of droplet drying mechanics from the simple Fickian diffusion, involving mass transfer processes such as fluid jetting that may have prevented the formation of a homogenous shell. Incomplete formation of the shell, coupled with the high supersaturation under rapid solvent evaporation, would have promoted nucleation over crystal growth, resulting in smaller and more highly strained crystallite materials.

The work here showed that application of CAB coating such that dry particles were RDX/CAB composited in 90:10 ratio by weight resulted in significant reduction of sensitivity to impact, relative to the standard. Moreover, the sensitivity was shown to be controllable as a function of drying temperature. A dubious correlation was observed between the Williamson-Hall microstrain values and temperature, which while not significant within the error margins of the presented data could certainly warrant further investigation. It is hoped that through refinement of the data, the associated error values can be reduced allowing this relationship to be better understood.

5.6 Crystal habit modification of RDX using tailor made additives

5.6.1 Material preparation

The effect of five tailor made additives (TMAs) on the crystallisation of RDX was investigated as a function of TMA concentration. To assess the viability of the chosen TMAs, a preliminary experiment was conducted in which small quantities of RDX solution (0.1 mol.dm^{-3}) were doped with highly diluted TMA in small glass shell vials. For each RDX/TMA combination, five vials were prepared containing RDX/AcO solution (2 cm^3) to which TMA/AcO solution ($5 \mu\text{l}$, $c = 4 \times 10^{-2}$, 4×10^{-5} and $4 \times 10^{-8} \text{ mol.dm}^{-3}$) was added. The molar combinations of RDX/TMA were prepared in ratios such that the TMA was present at one part per thousand, one part per million and one part per billion moles of RDX. Upon addition of TMA solution, each vial was sealed individually with parafilm, the centre of which was pierced once with a needle to allow for solvent egress. The vials were left undisturbed for approximately a week, until all solvent had evaporated, after which time the parafilm was removed and the crystals were examined.

Preparation of solutions for spray drying was conducted in an identical manner, solutions

of RDX/TMA were prepared that assessed the effect of TMA concentrations at the part per thousand, part per million and part per billion molar ratio relative to RDX. Spray drying was conducted following the procedure detailed in Section 4.4.2 using the parameters shown in Table 34.

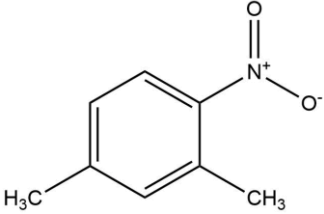
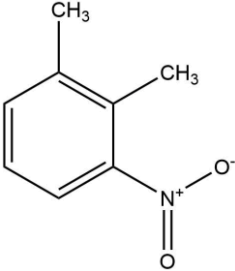
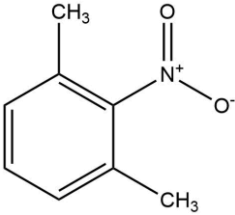
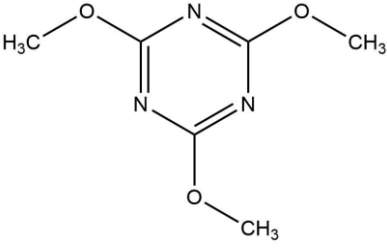
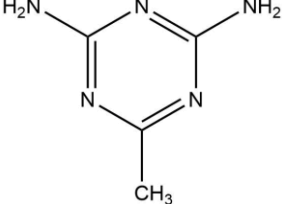
Since relatively few large crystals were prepared by the preliminary evaporative crystallisations a scale up experiment was conducted using AcO/H₂O solvent antisolvent crystallisation to prepare the samples. These experiments were conducted using a ratio of TMA to RDX of one part per thousand. The initial solution was prepared by dissolving RDX (2.2217 g, 0.010 mol) in acetone (100 cm^3) to give an initial concentration of (0.1 mol.dm^{-3}). An aliquot (10 cm^3 , 0.001 mol RDX) was taken using a volumetric pipette and transferred into a 250 cm^3

two necked round bottomed flask. Separately, solutions of each TMA in acetone were prepared at ($0.001 \text{ mol.dm}^{-3}$) in volumetric flasks from which aliquots (1cm^3) were transferred by micro syringe into the crystallisation vessel. The sealed crystallisation flask was then equilibrated (15°C , 30 min) with stirring provided by a two-paddle overhead stirrer, the shaft of which passed through a PTFE/Viton seal to prevent solvent loss. A tube was passed into the crystallisation flask via a ported and sealed stopper, with the tip of the tube being held above the level of the fluid. Water (50 cm^3) was passed through this tube under the action of a syringe pump operating at $100 \text{ cm}^3.\text{hr}^{-1}$. By the end of each 30 min crystallisation, a 1:5 solvent/antisolvent ratio was reached. Crystals were recovered immediately by vacuum filtration over a POR 3 sintered funnel. Residual moisture was removed by washing with cold denatured ethanol ($3 \times 10 \text{ cm}^3$). Yields were calculated based on the final mass once the crystals had been dried *in vacuo* overnight.

Table 34: RDX/TMA spray drying parameters.

Control measure	Value
Inlet temperature	90°C
Outlet temperature	50°C
Atomisation and drying gas	N_2
Feed flow rate	5 ml.min^{-1}
Nozzle pressure	8 bar
Nozzle diameter	1.4 mm
Gas flow rate	40 mm
Aspiration rate	100 %
Feedstock	RDX (0.1 M) TMA (10^{-4} , 10^{-7} , 10^{-10} M) in AcO 10cm^3
Cyclone	High performance

Table 35: The five TMAs used to modify RDX crystal growth

TMA number	IUPAC name	Structure
1	2,4-dimethyl-1-nitrobenzene	
2	1,2-dimethyl-3-nitrobenzene	
3	1,3-dimethyl-2-nitrobenzene	
4	2,4,6-trimethoxy-1,3,5-triazine	
5	6-methyl-1,3,5-triazine-2,4-diamine	

5.6.2 Results

The evaporative crystallisation samples were inspected visually, but no quantifiable measurements were made. The extent of the observation was to ensure that crystals formed as a result of all combinations. Since these nitrobenzene compounds were liquid at room temperature it was thought that some issues with oil or wax formation may occur. Since this was not the case, and since all samples appeared to prepare reasonably different crystals (within the small sample size), the investigation proceeded into spray drying the combinations as a means of scale up.

Observation of spray dried RDX/TMA composites using optical microscopy revealed no significant differences between samples. For two reasons, this result was unsurprising. As previously discussed, the sensitiveness of optical microscopy is severely limited when applied to particle of this size. Furthermore, the nature of spray drying, and its dependence on process parameters significantly negates the scope to which TMA's can affect the overall morphology of the composite microparticle. It was however expected that the morphology of the nanocrystals that compose the spray dried particle would be subject to modification of crystal growth by the introduction of TMA impurities. In the absence of TEM, the impact of TMA impurities on crystal habit were assessed by application of the Scherrer equation to PXRD line widths, following the procedure described in Section 0. The peaks to which Scherrer's equation was applied was taken from the works of Liu *et al.* and Ter Horst *et al.* who identify the (111), (200), (020), (002) and (210) planes as being the prevalent faces of RDX grown in a vacuum (simulated) and from acetone (static cooling crystallisation) respectively, an image of the latter crystal is shown below in Figure 95 [134,136].

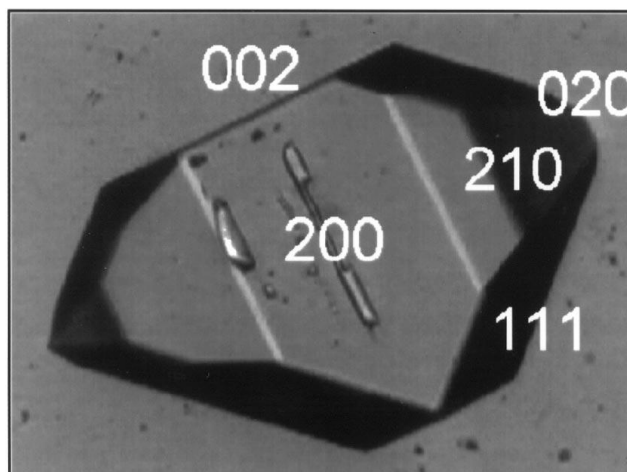


Figure 95: RDX grown from solution in acetone by cooling crystallisation with morphologically significant faces annotated [134]

A table of results is included in Appendix C.1. Errors were calculated by propagation of the associated peak fit error through the Scherrer equation. The magnitude of errors was generally very low since the peaks corresponding to the principle faces of the crystals were not overlapping. The sample containing 2,4,6-trimethoxy-1,3,5-triazine at 1 part per million had an unexpectedly high coherence length in the (020) plane, with accompanying high error value that could not be explained by specific investigation of the analysed peak.

To visualise the impact of TMA inclusion in the RDX spray drying process, the coherence lengths were plotted on radar charts. Within each chart, the axes boundaries are identical and correspond to coherence length along the state plane in nm. It was hoped that ready comparison of the three plots would be aided by preserving fixed axes boundaries for all of the plots, however this resulted in poor resolution of detail. The shaded blue area of each plot corresponds to the Scherrer lengths of the control RDX sample, prepared using the same spray drying conditions in the absence of any impurities. Charts were produced using the Spider_plot plugin for MatLab, written and maintained by Moses [198].

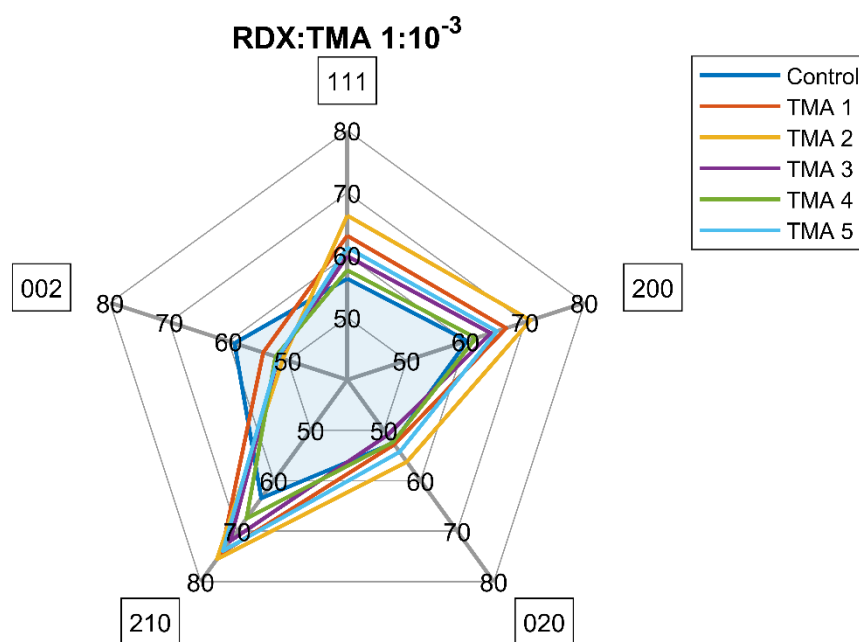


Figure 96: Radar plot of RDX Scherrer lengths with TMA impurity at 1 part per thousand RDX molecules

With TMA inclusion at the part per thousand level a significant modification of crystal habit was observed. The relative coherence lengths of the (111), (200) and (020) lattice planes were relatively unchanged, however differences in magnitude were notably present. TMA inclusion resulted in significant reduction of the (002) plane coherence length and increased coherence length of the (210). Since the crystals were prepared from solution in acetone, it can be assumed that the basic morphology should follow that presented by ter Horst *et al.*, and so it expected that this reduction of the (002) face and promotion of the (210) face may increase the sphericity of crystals within the spray dried composite particle [134].

Doping of RDX composites with lower concentrations of TMA (at the part per million and part per billion levels) did not result in suppression of the (002) face. At both impurity levels, the most obvious effect of TMA introduction was a slight suppression of (020) coherence length. Since the (020) face is by far the smallest face visible on the static AcO grown crystals presented by ter Horst *et al.*, favoured growth of this plane as a result of TMA inclusion may lead to the

formation of more pointy crystals. Such features are typically undesirable in energetic formulations, due to their tendency to fracture when exposed to the high shear mixing techniques employed [125]. One anomaly was observed, TMA 4 (2,4,6-trimethoxy-1,3,5-triazine) appeared to cause a very significant increase of the (020) plane coherence length, however, the error associated with this value was of comparable magnitude to the value itself. Since no logical reason for such an anomalously high coherence length and error could be found for this datum, it was not excluded from the plot in Figure 97, but interpretation of it is avoided.

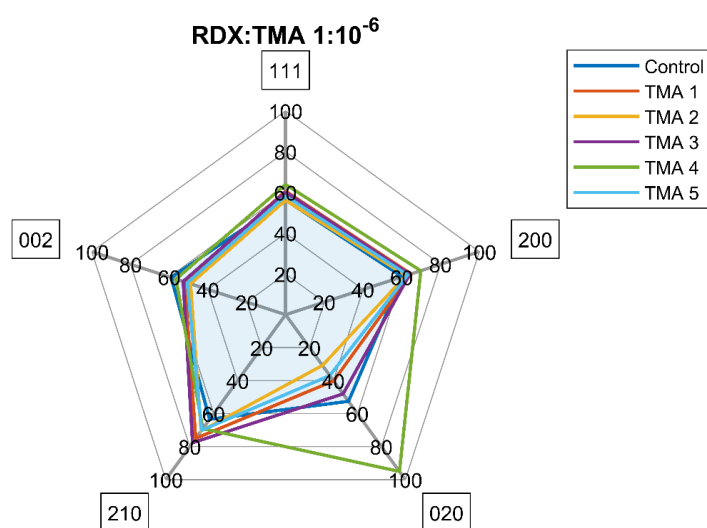


Figure 97: Radar plot of RDX Scherrer lengths with TMA impurity doped at 1 part per million RDX molecules

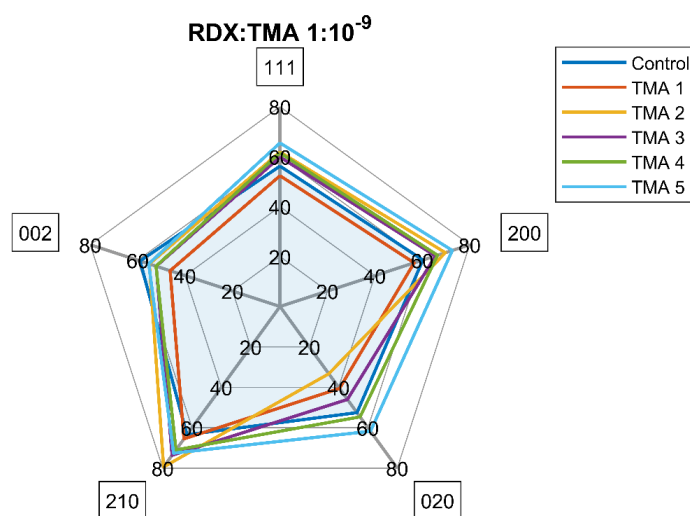


Figure 98: Radar plot of RDX Scherrer lengths with TMA impurities doped at 1 part per billion RDX molecules

Overall, a significant difference in the effect of TMA concentration was noted, with impurity levels at the part per thousand producing a dramatic effect on the coherence length of various major faces of crystals within a spray dried microparticles. Below this concentration, the differences in crystal habit as a result of TMA inclusion were negligible.

Having proven that the selected TMAs effectively modified the crystal habit of RDX when spray dried, a scaleup experiment was conducted to evaluate the effect of TMA presence in solvent-antisolvent crystallisation of RDX. Acetone was chosen as the solvent, for its high solubilising capacity for RDX, and water was used as the antisolvent. TMA doping was included only at the part per thousand level, following the observation of diminished effects in the spray drying experiment. The resultant crystals, viewed by optical microscopy showed significant differences in morphology, as can be seen in Figure 99. The presence of 2,4-dimethyl-1-nitrobenzene and 1,2-dimethyl-3-nitrobenzene caused significant reduction of particle size. Despite being structurally similar to the two aforementioned TMAs, 1,3-dimethyl-2-nitrobenzene doping resulted in the formation of significantly larger crystals than those formed in the presence of the other two dimethyl nitrobenzene isomers, with slightly irregular morphologies and poorly defined vertices between lattice planes. Addition of 2,4,6-trimethoxy-1,3,5-triazine to the crystallisation of RDX significantly increased the prevalence of secondary growth. Crystals prepared from this combination showed a mixture of defined and rounded plane edges. The inclusion of 6-methyl-1,3,5-triazine-2,4-diamine in RDX crystallisation produced the widest array of interesting results. Extensive crystal secondary growth, facial elongation and significant growth modification around a fault were all observed in this sample. A more extensive array of micrographs, for each sample, is presented in Appendix C.2.

Shape analysis of the antisolvent precipitated RDX/TMA samples, following the procedure optical microscope image analysis procedure outlined in Section 4.2.1 produced values for the and aspect ratio of each particle. These values

are represented as box plots of circularity and aspect ratio in Figure 100 and Figure 101 respectively. Statistical analysis, using one-way analysis of variance (ANOVA) tests, showed that differences in mean values of circularity and angle of repose were significant. Results of the ANOVA tests are presented in Table 36. The mean values of circularity and aspect ratio are presented alongside the measured angle of repose for each sample in Table 37.

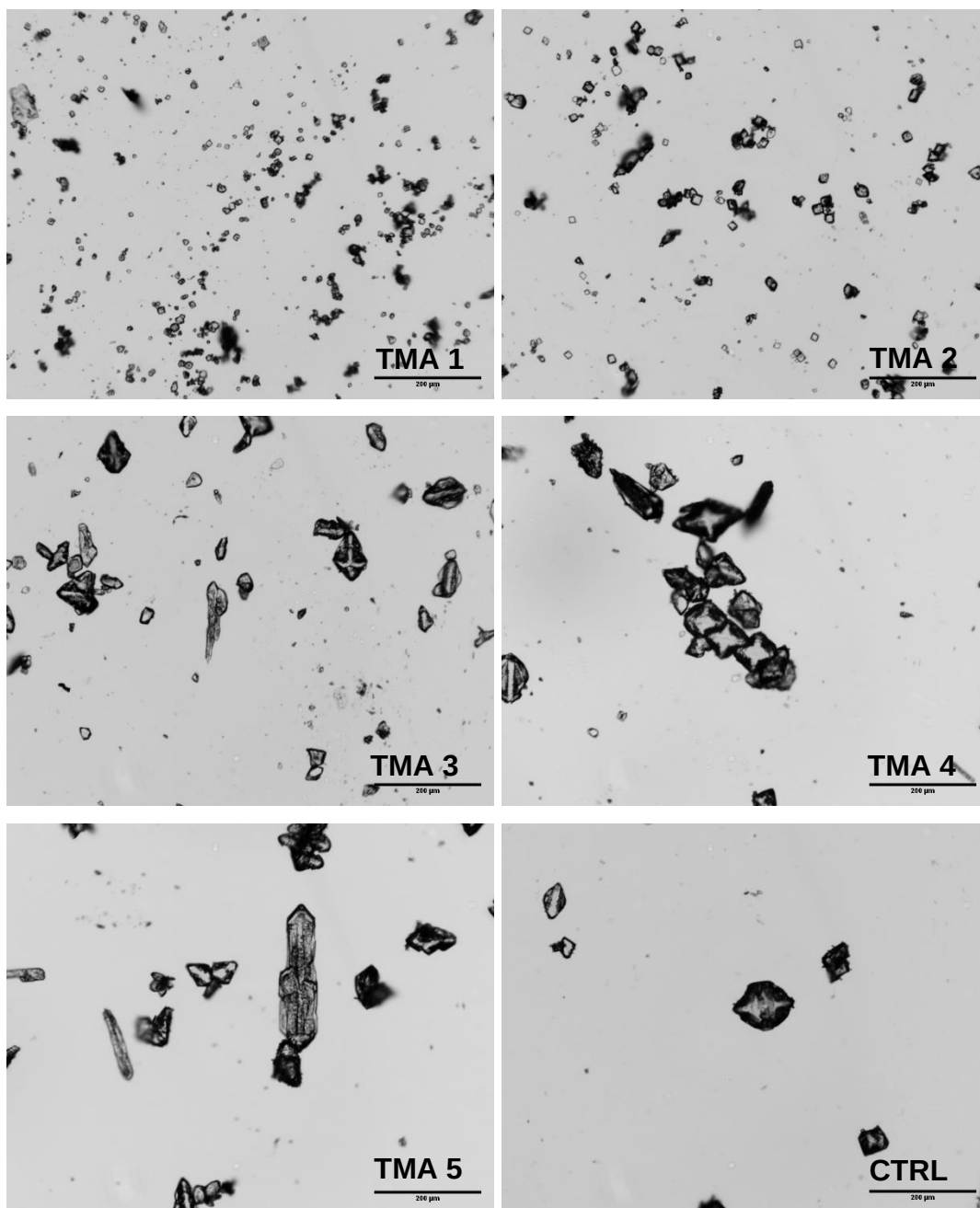


Figure 99: Optical micrographs of RDX prepared by solvent antisolvent precipitation in the presence of TMAs. Scale bar 200 μm .

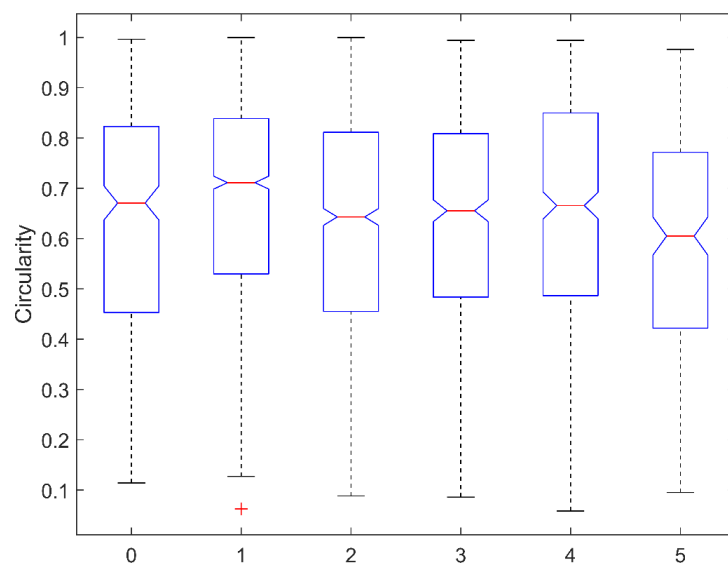


Figure 100: Box plot of circularity for each TMA doped sample showing overall deviation from circularity in all samples, with the lowest median value corresponding to the sample containing 6-methyl-1,3,5-triazine-2,4-diamine.

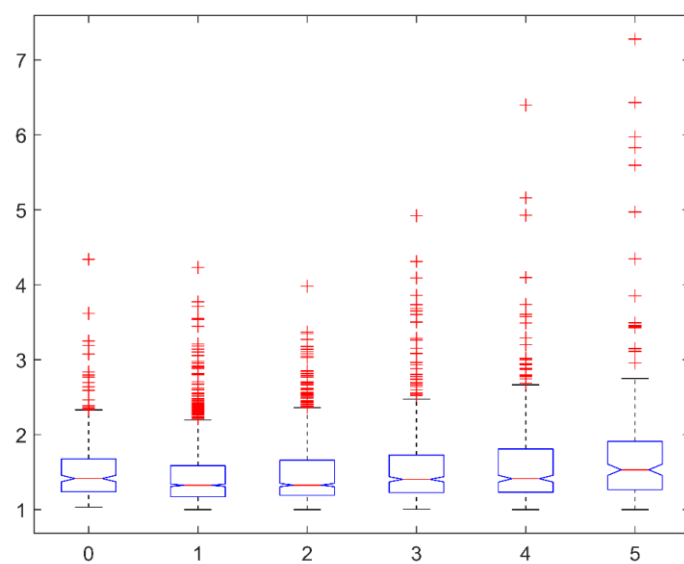


Figure 101: Box plot of crystal aspect ratio for each TMA doped sample showing overall deviation from squareness in all samples, with the highest aspect ratios corresponding to the sample containing 6-methyl-1,3,5-triazine-2,4-diamine.

Table 36: Summary of ANOVA results for circularity and aspect ratio consistently showing statistically relevant differences in both the means of each shape representation value.

Circularity ANOVA					
Source	SS	df	MS	F	Prob>F
Groups	28.746	5	5.74927	22.96	8.89034x10 ⁻²³
Error	953.363	3807	0.25042		
Total	982.109	3812			

Aspect ratio ANOVA					
Source	SS	df	MS	F	Prob>F
Groups	2.635	5	0.52704	11.03	1.43821x10 ⁻¹⁰
Error	194.731	4075	0.04779		
Total	197.366	4080			

Table 37: Summary of mean circularity and aspect ratio values for antisolvent precipitated RDX/TMA samples.

	TMA	Mean Circularity	Mean AR	Angle of repose (°)
[1]	2,4-dimethyl-1-nitrobenzene	0.74286	1.4456	48.3 ± 2.1
[2]	1,2-dimethyl-3-nitrobenzene	0.68732	1.4962	49.6 ± 1.2
[3]	1,3-dimethyl-2-nitrobenzene	0.74677	1.5715	42.7 ± 2.7
[4]	2,4,6-trimethoxy-1,3,5-triazine	0.72697	1.6082	42.9 ± 4.6
[5]	6-methyl-1,3,5-triazine-2,4-diamine	0.67786	1.8152	44.6 ± 6.1
	Control	0.72847	1.5440	41.9 ± 3.2

5.6.3 Discussion

Spray dried RDX/TMA showed significant modification of crystal habit when impurities were present at concentrations of 1 part per thousand, particularly in reduction of (002) coherence length and extension of (210) coherence lengths. It is expected that this shift would result in an overall more spherical crystal shape. However, these values were obtained by application of Scherrer's equation to powder XRD peak widths, and as such are inherently averaged over the entire sample and the impact of significant outliers cannot be eliminated from the results of this technique. Concentrations of impurity below 1 part per thousand presented significantly less modification of crystal habit, being constrained to slight reduction of the (020) plane coherence length. Since this face has been shown by ter Horst *et al*, to be the smallest face of RDX grown by evaporation from acetone, it is probable that the extent of TMA effect on these samples is a sharpening of this vertex, resulting in crystal morphologies resembling those grown by evaporation from γ -butyrolactone [134].

In the RDX/TMA antisolvent crystallisations, TMAs 1 and 2 (2,4-dimethyl-1-nitrobenzene and 1,2-dimethyl-3-nitrobenzene respectively) produced crystals with much lower particle sizes than the other runs. The obviously lower diameters of these particles, relative all other samples in this experiment, may be a result of either nucleation promotion or equilibrium solubility change [48]. Since the TMAs are both relatively polar liquid under standard conditions, it is not possible to say by which mechanism the crystallisation of RDX is impacted. These crystals showed significantly larger planar faces, reminiscent of the large (200) faces observed when RDX is grown from solution in cyclohexanone [134]. The coherence length of (200) plane was notably higher in spray dried samples containing these TMAs.

Interestingly, the third nitrobenzene containing TMA, 1,3-dimethyl-2-nitrobenzene, did not cause a significant size reduction of the crystals relative to the control. It is thought that the electron donation from two methyl ring substituents the nitro group substantially reduced the partial charges of this polar moiety thereby reducing any dipolar interaction energies.

Antisolvent RDX/TMA samples doped with 2,4,6-trimethoxy-1,3,5-triazine and 6-methyl-1,3,5-triazine-2,4-diamine both exhibited some crystals with the morphology expected for RDX prepared from solution in acetone, however, there was also significant elongation of some crystals. Crystal elongation was particularly extensive in 1,3,5-triazine-2,4-diamine doped samples, the only species capable of donating hydrogen bonds. This would be consistent with a higher interaction energy, and subsequently more work being required to remove these species from a face.

The attempt to correlate flow characteristics (angle of repose) with crystal morphology was partially successful. Samples containing TMAs 1 and 2 presented with particularly small crystal sizes and this was reflected in the high measured angle of repose. For the remaining samples, there appeared to be good correlation between reduced elongation and improved flow characteristics.

6 Conclusions

Sonocrystallisation of AP produced remarkably different results depending on whether the sonication was applied indirectly in a pulsed sequence, or directly in a constant operation mode. Pulsed sonication enhanced the growth of slow crystallised AP, producing larger crystals with better edge definition than crystallisations in the absence of sonication. Constant sonication on the other hand, as expected, led to a massive increase in the rate of nucleation and the resultant particles were an order of magnitude smaller than crystals prepared under the same conditions without sonication. Unlike with the pulsed sonication, constant sonication appears to have produced near spherical particles with very few defined faces. Despite the dramatic reduction of particle size caused by constant sonication, the angle of repose values (and implied flowability) of these samples was remarkably similar to significantly larger AP crystals. This can be attributed to the significantly improved sphericity of the former, relative to the somewhat uncontrollable morphologies generated by rapid cooling crystallisation of AP in the absence of sonication.

Most of the literature optimisations of AP cooling crystallisation suggests that the smallest and roundest particles are generated with maximised agitation rates, the results found here generally support this. However, only very marginal differences in particle size could be obtained from variation of the agitation rate between 400 - 1200 RPM. The mode of agitation appears to offer significantly more scope for size modification. For magnetically stirred samples increasing the mass and size of the magnetic stirrer bar produced resulted in a significant reduction of particle size and increased rounding of particles. Whereas overhead stirring generally led to much larger, more sphericalised particles.

Despite the expectation that optimisation of spray drying process parameters would have a pronounced effect on both particle size and size distribution, the obtainable differences were marginal and fit poorly into the factorial model. Attempted validation of the spray drier optimisation models using RDX highlighted the issues with this oversimplified approach to particle engineering.

And while there were notable similarities in the dependence of particle size on atomisation performance, the models are insufficiently accurate to make predictions.

A reliable, negative correlation between particle size and angle of repose was observed as expected. The scope for flowability modification through size enlargement was shown to be extremely limited using a two fluid nozzle, and further work might seek the advantages of wider particle sizes offered by rotary and ultrasonic atomisation. Other correlations were noted and interpreted but bore little weight due to poor data fit and low impact. Flowability was also linked to the degree of agglomeration in the spray dried powder, which was in turn rationalised with respect to microparticle surface roughness and central void space. Significant modification of powder flowability was achieved using known glidants, showing comparable angle of repose values to ammonium perchlorate crystals two orders of magnitude larger. While issues were encountered with adhesion of the glidant to microparticle, these could readily be offset by reformulation with a small quantity of binder content. Ideally the binder should be of low molecular mass to ensure good separation of the proposed three phases (solute, binder and glidant) by Peclet number.

Despite the process controls of the B-290 spray drier offering limited scope for particle size modification, it was demonstrated that the morphology of particles could be modified by adjustments to the rate of drying, as expected [80,88,157,158]. Particle density and morphological uniformity were maximised at the lowest drying temperatures used, in contrast to the suggestions of Sun *et al.*, [147] and it is put forth that their observations may be the result of systematic issues with the spray drier used.

Reduction of nitramine shock and impact sensitivity is a significant driving force behind much of the interest in spray drying nitramines. And so far, there have been numerous reports that show its benefits. However, the majority of these reports attribute the reduction of sensitivity to either reduction of crystallite size or improved crystal quality as a result of the spray drying process [139,140]. Herein it has been demonstrated that the impact sensitiveness of uncoated

spray dried RDX was higher than standard RDX, and only showed improvements when microencapsulated with a binder. It was then demonstrated the impact sensitiveness of spray dried RDX/CAB composites could be controlled through variation of the drying temperature - with lower temperatures, and thus lower supersaturation rates, producing less impact sensitive powders.

These last two points produce an interesting question, whether the reduction of impact sensitiveness was a result of the particle morphology differences or whether it was the result of crystal quality differences. While it is not definitive proof, the correlation between reduced Williamson-Hall microstrain and reduced impact sensitiveness, indicates that the improvements can not solely be attributed to the morphological differences between composites, and must indeed stem at least in part from improved crystal quality.

Finally, the potential of five aromatic species to selectively inhibit growth of specific lattice planes of RDX was assessed in spray drying and antisolvent crystallisations. The Scherrer equation was used to assess relative coherence lengths of the key morphological lattice planes of RDX in spray dried samples and significant differences in relative coherence lengths were noted upon TMA inclusion. TMA inclusion in antisolvent crystallisations of RDX (AcO/H₂O) likewise resulted in a range of observable morphological deviations. While the impact of TMA inclusion in spray dried materials produced no macroscopic differences in powder flow behaviour, the modified particle size and elongation produced by TMA inclusion into antisolvent precipitated RDX was shown to correlate with angle of repose measurements.

7 Future work

Completing a PhD is not possible without abandoning a seemingly endless number of untravelled investigative paths, some of which are harder to leave behind than others.

The poor quality of the paracetamol spray drying optimisation is an example of the latter. While it is certainly true that future work could focus on refining this model, with better particle size data and more accurate representations of the powder flow (obtainable from SEM and powder rheometry respectively), the general result was that spray drying pure materials renders them as highly cohesive micronized substances. Despite this being ideal in some applications, such as improving the solubility kinetics of poorly soluble pharmaceuticals, it's virtually useless for our printing system.

Instead, future work should focus on the reformulation of spray dried materials to optimise flow, making careful note of the potential influence that the formulation has on the impact sensitiveness. While discussing reformulations, it must be mentioned that the impact sensitiveness values of the RDX/CAB spray dried composites were obtained at relatively low room temperatures (16-18°C). Crucially, this is below the glass transition temperature of CAB. An investigation of the effect of plasticisation of RDX/CAB microparticles, regarding hazard sensitiveness and printed mechanical performance would be most intriguing.

The discussion of RDX/CAB microparticle morphology relied heavily on inert simulation using paracetamol/CAB particles prepared under identical conditions. However, for total assurance that the observed trends are genuinely transferable it would be ideal to image the energetic samples directly. Similarly, it would be very interesting to compare the trends observed in microstrain and impact sensitiveness, to the NQR broadening in these samples.

Spray drying RDX has been shown, both here and in the literature, to reliably provide the stable α polymorph. Whereas spray drying HMX has been shown to

generate at least four different polymorphs, and relatively little work has been conducted to gain control over which polymorph forms.

A vast array of ammonium perchlorate samples were prepared and characterised in the scaled up cooling crystallisations, and while the activation energies for decomposition were found and used to make inference about the relative stabilities of crystal forms, it would be nice to build the context of this data with relevant burn rate tests. Similarly, static flow characteristics of AP, RDX and paracetamol have all been extensively studied though this work, but these have yet to be applied to the printing system.

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APPENDICES

Appendix A Characterisation methods

A.1 Williamson Hall Plots

Requires that data be separated into two files, corresponding to the data fitted, and not fitted. Fitted peaks must correspond to the correct d_{hkl} spacing for a peak, exposed to $\text{CuK}\alpha$, and not be a result of shouldering due to $\text{CuK}\beta$ diffraction. Moreover, should peaks were not fitted when the total FWHM error exceeded specific values.

```
data = readmatrix("70_filtered.xlsx"); % Input data in form of three columns 1: 2theta or
position, 2 left fwhm, 3 right fwhm
data2 = readmatrix("70_void.xlsx"); % Input anomalous data (note that the anomalies were
defined where FWHM error was > 20% of value)
% d = readtable("Class4_WH_Peaks.xlsx"); % Purely to help find relevant columns
w = data(:,1); % w = 2theta (degrees)
c = 0.9*0.154; % c = kLmabda
B = (data(:,2)+data(:,3)).*pi/180; % B = FWHM (sum of FWHM left and right) in radians
bINS = (10^(-4)*tand(w/2).^2+0.0005*(tand(w/2))).*pi/180; % bIRF = instrumental broadening in
radians
l = c ./((B-bINS).*cosd(w/2)); % Scherrer's equation (note B and b are in radians, w is in
degrees hence cosd is used)
X = sind(w/2); %Calculate x coordinates
Y = (B - bINS).*cosd(w/2).*1000; %Calculate y coordinates
out(:,1) = X; %Save coordiantes in matrix named out
out(:,2) = Y;

w2 = data2(:,1); % w = 2theta (degrees)
c2 = 0.9*0.154; % c = kLmabda
B2 = (data2(:,2)+data2(:,3)).*pi/180; % B = FWHM (sum of FWHM left and right) in radians
bINS2 = (10^(-4)*tand(w2/2).^2+0.0005*(tand(w2/2)+0.0651)).*pi/180; % bIRF = instrumental
broadening in radians
l2 = c2 ./((B2-bINS2).*cosd(w2/2)); % Scherrer's equation (note B and b are in radians, w is
in degrees hence cosd is used)
X2 = sind(w2/2);
Y2 = (B2 - bINS2).*cosd(w2/2).*1000;

[p,S] = polyfit(X,Y,1); % p returns 2 coefficients fitting r = a_1 * x + a_2
[f1, delta] = polyval(p,X,S); % compute a new vector r that has matching datapoints in x

figure
plot(X,Y,'ko','MarkerFaceColor','k'); %Plot data as black circles
hold on
plot(X,f1,'r-'); % Plot linear fit
plot(X,f1+2*delta,'m--',X,f1-2*delta,'m--') % Error bars at 2*stddev (95% confidence limits)
plot(X2,Y2,'ko'); % Plot anomalies as hollow circles
hold off
%xticks ([0.10 0.15 0.20 0.25 0.30])
%xlim([0.1 0.30])
yticks([0 2 4 6 8 10 12])
%ylim ([1.0 3.0])
xlabel 'sin \theta';
ylabel '1000 \beta cos \theta';
title 'PA/CAB 70 °C'
Strain = p(1) %Gradient (Strain value) x 1000
Length = 0.9*0.154*1000/ p(2) %Length in nm

out % Prints the data coordinates (x,y), copy them from workspace, for use in in regression
fitting (I used excel since its easier to get the fit error than matlab)
```

A.2 Digital image angle of repose fitting

Angle of repose, automated angle fitting script – requires use of 2D image cropped to contain only the edge of the powder investigated, therefore each image must be analysed on both sides to remove any systematic error resulting from misalignment of the horizontal axis.

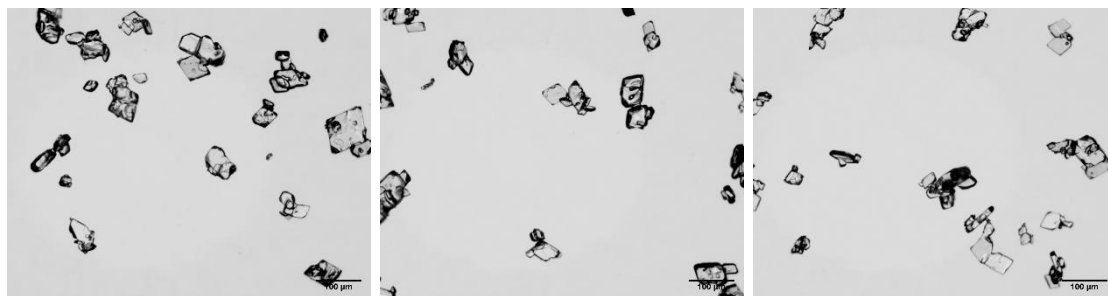
```
%% Image import
% Import and show the loaded file at position 1.
filename = "1200 RPM Sonicated.jpg"
%function [Angle_of_Repose] = imageAnalysis
I = imread(filename);
subplot(2,2,1);
imshow(I);
title (filename)
% Convert loaded file to binarized logical
J = imbinarize(I);
% Extract the first slice to leave a 2D matrix of logical data
J_xy = J(:, :, 1);
% Show binarized image at position 2.
subplot(2,2,2), imshow(J_xy);
title 'Make binary'
% Find edges in binary file J using sobel method with 0.5 threshold limit
E = edge(J_xy, 'sobel', 0.5);
% subplot(2,2,3), imshow(E);
% title Edge
G = flip (E,1);
%% Curve fitting (note inversion of y axis)
% CREDIT to Image Analyst https://www.mathworks.com/matlabcentral/answers/140830-calculate-equation-of-a-curve-from-an-image
% Retrieve the matrix position (row and column indices) of the edge in matrix E
[rows, columns] = find (G);
% Fit a linear equation
coefficients = polyfit(columns, rows, 1); % Gets coefficients of the formula.
% Fit a curve to 500 points in the range that x has.
fittedX = linspace(min(columns), max(columns), 500);
% Now get the y values.
fittedY = polyval(coefficients, fittedX);
% Plot the original points in red:
subplot(2,2,3);
plot(columns, rows, 'r+', 'LineWidth', 2, 'MarkerSize', 2);
hold on;
% Overlay the fitting in blue.
plot(fittedX, fittedY, 'b-', 'linewidth', 1);
grid on;
xlabel('X pixels', 'FontSize', 8);
ylabel('Y pixels', 'FontSize', 8);
xticks('')
yticks('')
xlim ([0 800])
hold off;
title 'Find and fit boundary'
coefficients;
%% Conversion of gradient to angle of repose (degrees) assuming x y vectors = 1
m = coefficients(1,1);
c = coefficients(1,2);
Angle_of_Repose = atan(m)
%% Plot the fitted angle of repose line over the original image
[rows2, columns2] = find (E);
% Fit a linear equation
coefficients2 = polyfit(columns2, rows2, 1); % Gets coefficients of the formula.
% Fit a curve to 500 points in the range that x has.
fittedX2 = linspace(min(columns2), max(columns2), 500);
% Now get the y values.
fittedY = polyval(coefficients2, fittedX2);
subplot(2,2,4)
figure2 = imshow(I);
hold on
plot (fittedX,fittedY, 'r-', 'LineWidth', 2)
title ("AoR = " + Angle_of_Repose + "°")
```

Appendix B Small batch AP cooling crystallisations (100 µm scale bar)

B.1 10g magnetic stirring

B.1.1 No modification

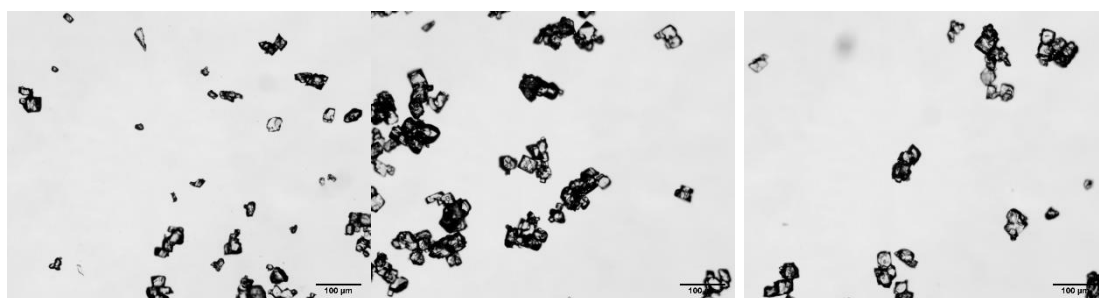
10g 400RPM



10g 800RPM



10 g 1200RPM

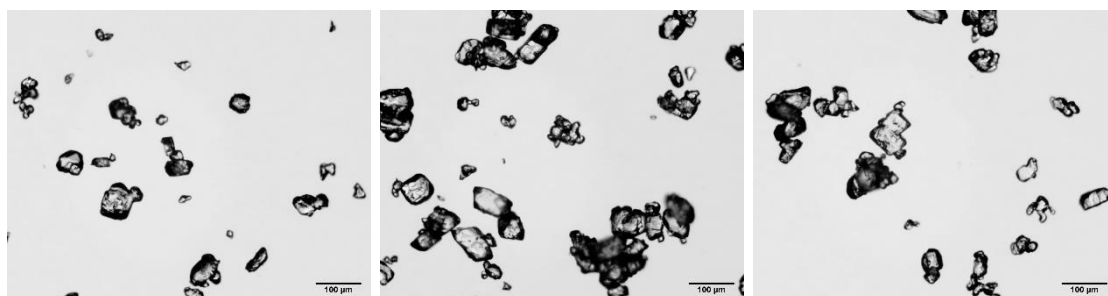


B.1.2 10g magnetic stirring + equilibration

10g 400 RPM + 24 hr equilibration



10 g 800 RPM + 24 hr equilibration

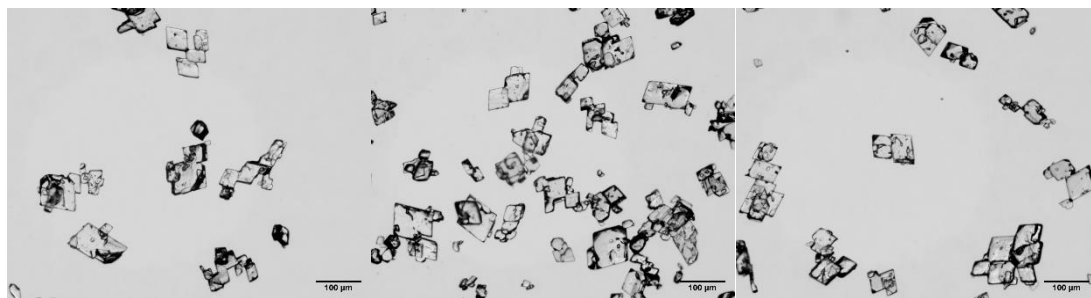


10g 1200RPM + 24 hr equilibration



B.1.3 10 g magnetic stirring + pulsed sonication

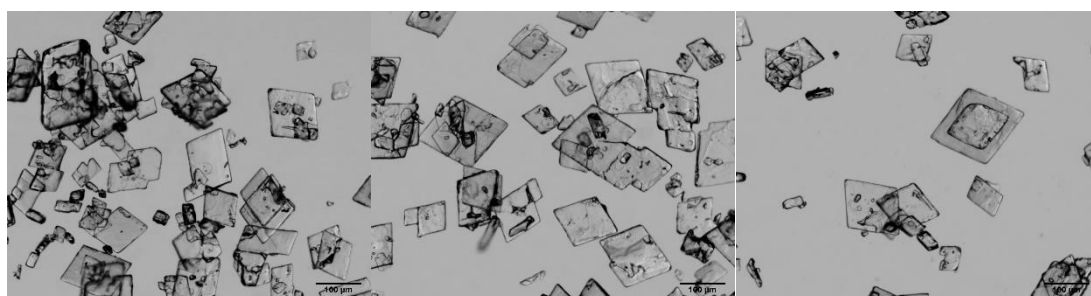
10g 400RPM + pulsed sonication



10g 800RPM + pulsed sonication



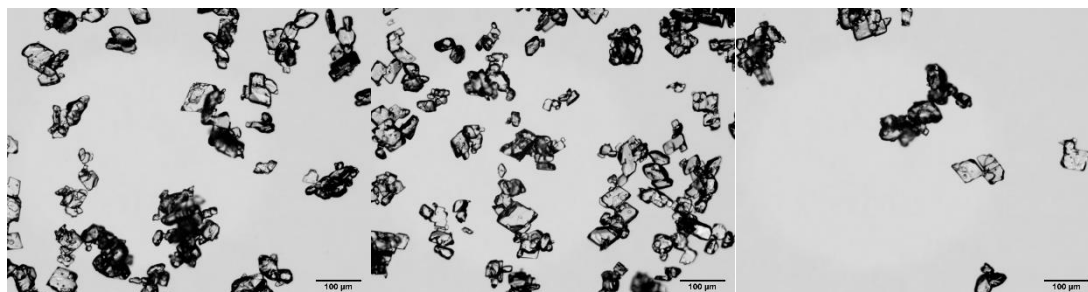
10g 1200 RPM + pulsed sonication



B.2 40g magnetic stirring

B.2.1 No modification

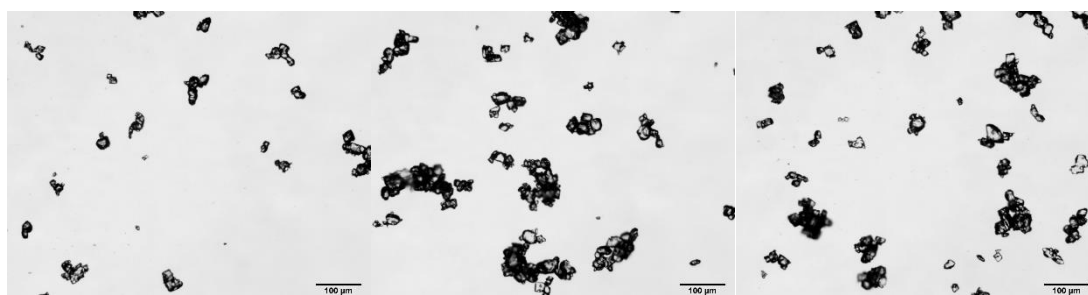
40g 400RPM



40g 800 RPM

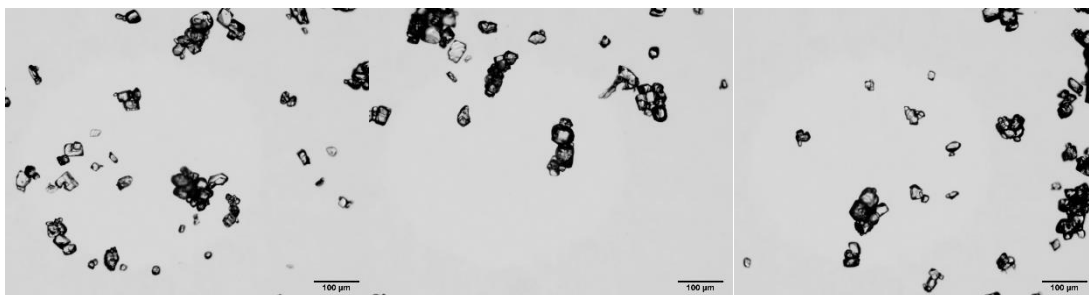


40g 1200 RPM



B.2.2 40 g magnetic stirring + Equilibration

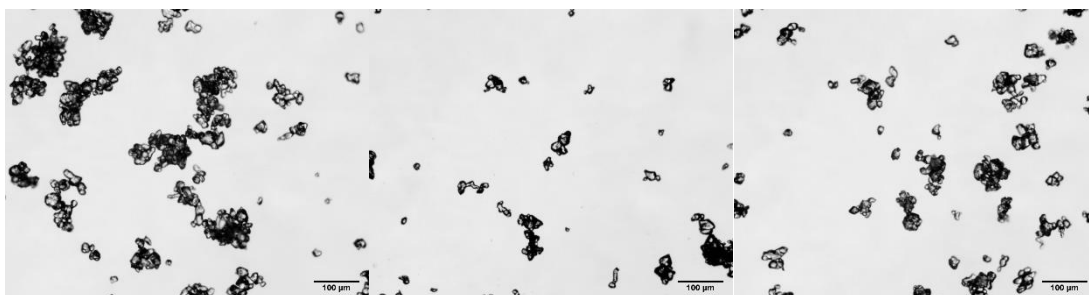
40g 400 RPM + 24 hr equilibration



40g 800 RPM + 24 hr equilibration

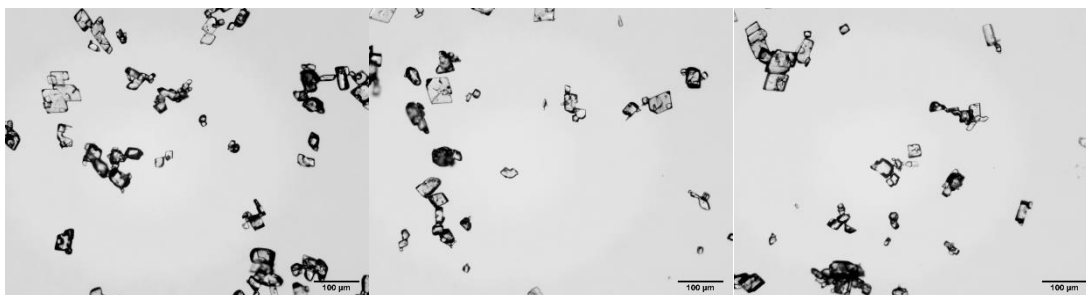


40g 1200 RPM + 24 hr equilibration

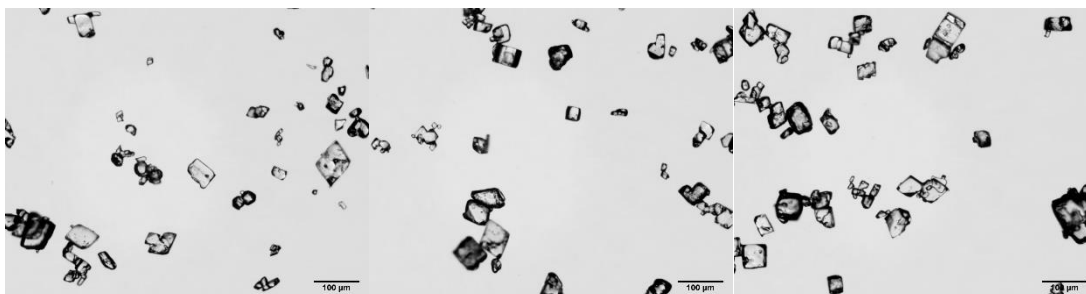


B.2.3 40 g magnetic stirring + pulsed sonication

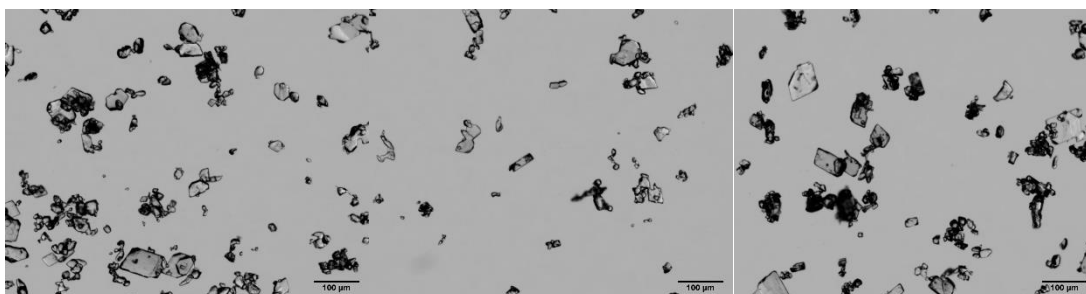
40g 400RPM + pulsed sonication



40g 800 RPM + pulsed sonication



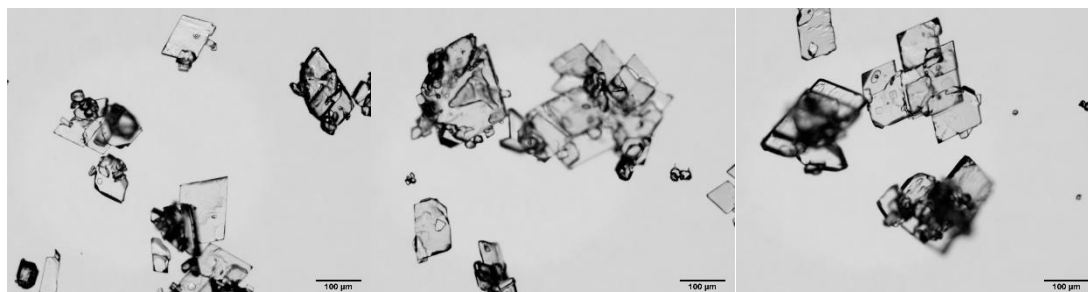
40g 1200 RPM + pulsed sonication



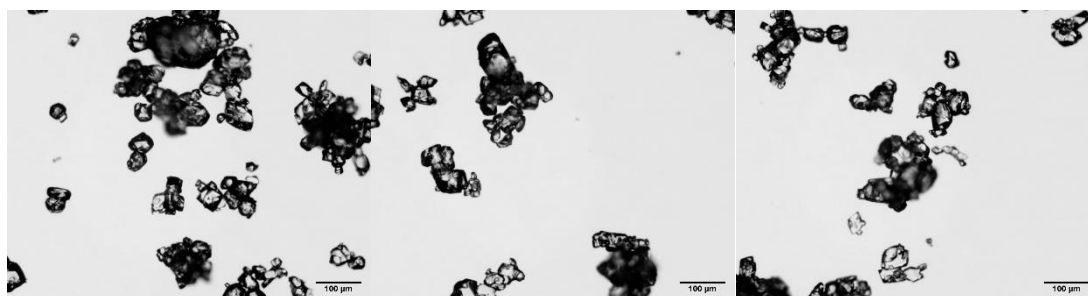
B.3 Overhead stirring

B.3.1 No modification

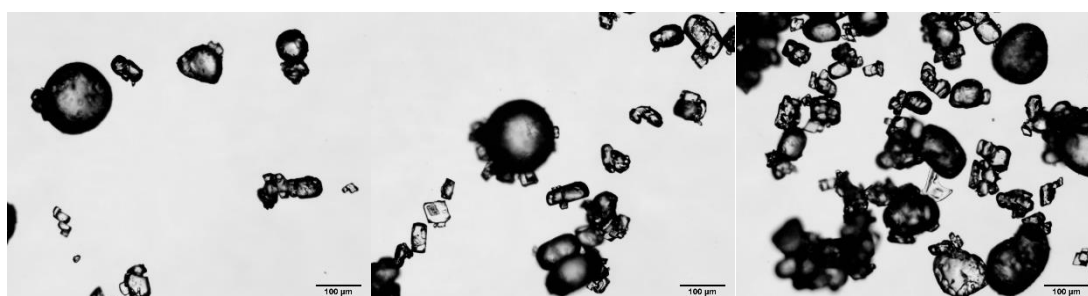
Overhead stirring 400 RPM



Overhead stirring 800 RPM

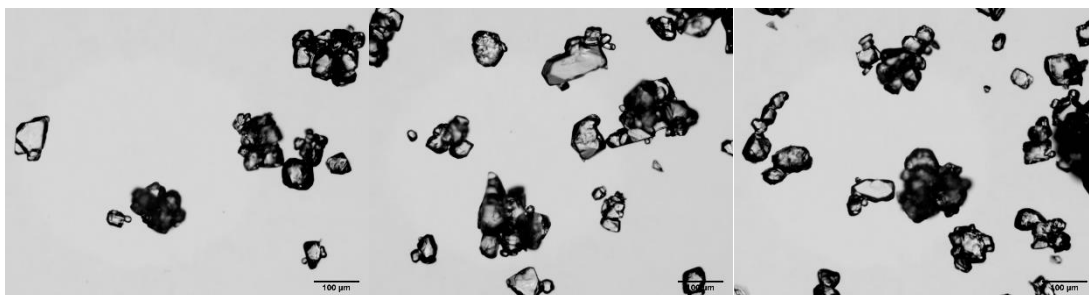


Overhead stirring 1200 RPM

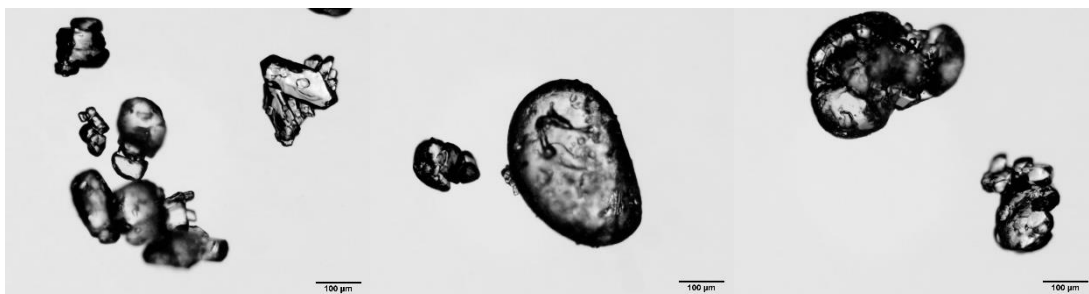


B.3.2 Overhead stirring + equilibration

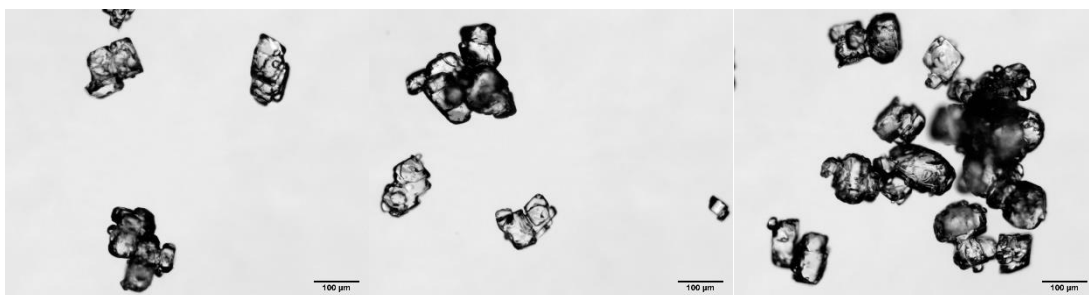
Overhead stirring 400 RPM + 24 hr equilibration



Overhead stirring 800 RPM + 24 hr equilibration



Overhead stirring 1200 RPM + 24 hr equilibration



B.3.3 Overhead stirring + pulsed sonication

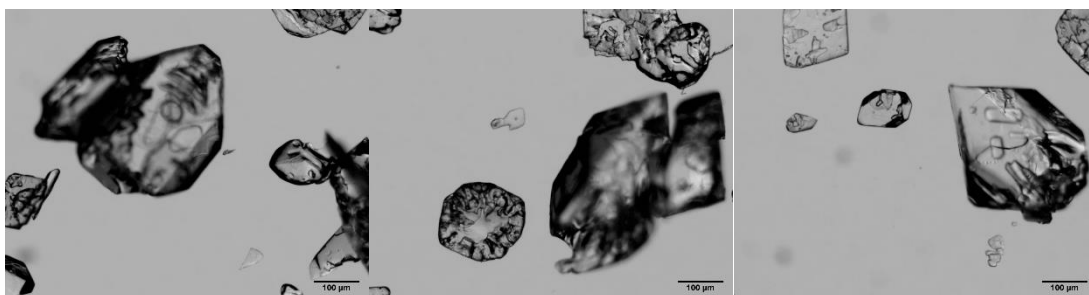
Overhead stirring 400 RPM + pulsed sonication



Overhead stirring 800 RPM + pulsed sonication



Overhead stirring 1200 RPM + pulsed sonication



Appendix C Spray dried paracetamol

C.1 Correlations between flow and powder properties

Dependant	Independent	Intercept	Error	Grad	Error	R2	p-value
Hausner ratio	Diameter	1.57	0.06	-0.006	0.005	0.108	0.214
Angle of repose	Diameter	61	3	-0.7	0.2	0.388	0.010
Hausner ratio	Span	1.7	0.3	-0.1	0.1	0.047	0.418
Angle of repose	Span	60	20	-7	9	0.042	0.444
Hausner ratio	Density	4	3	-2	2	0.077	0.298
Angle of repose	Density	300	150	-200	100	0.168	0.115

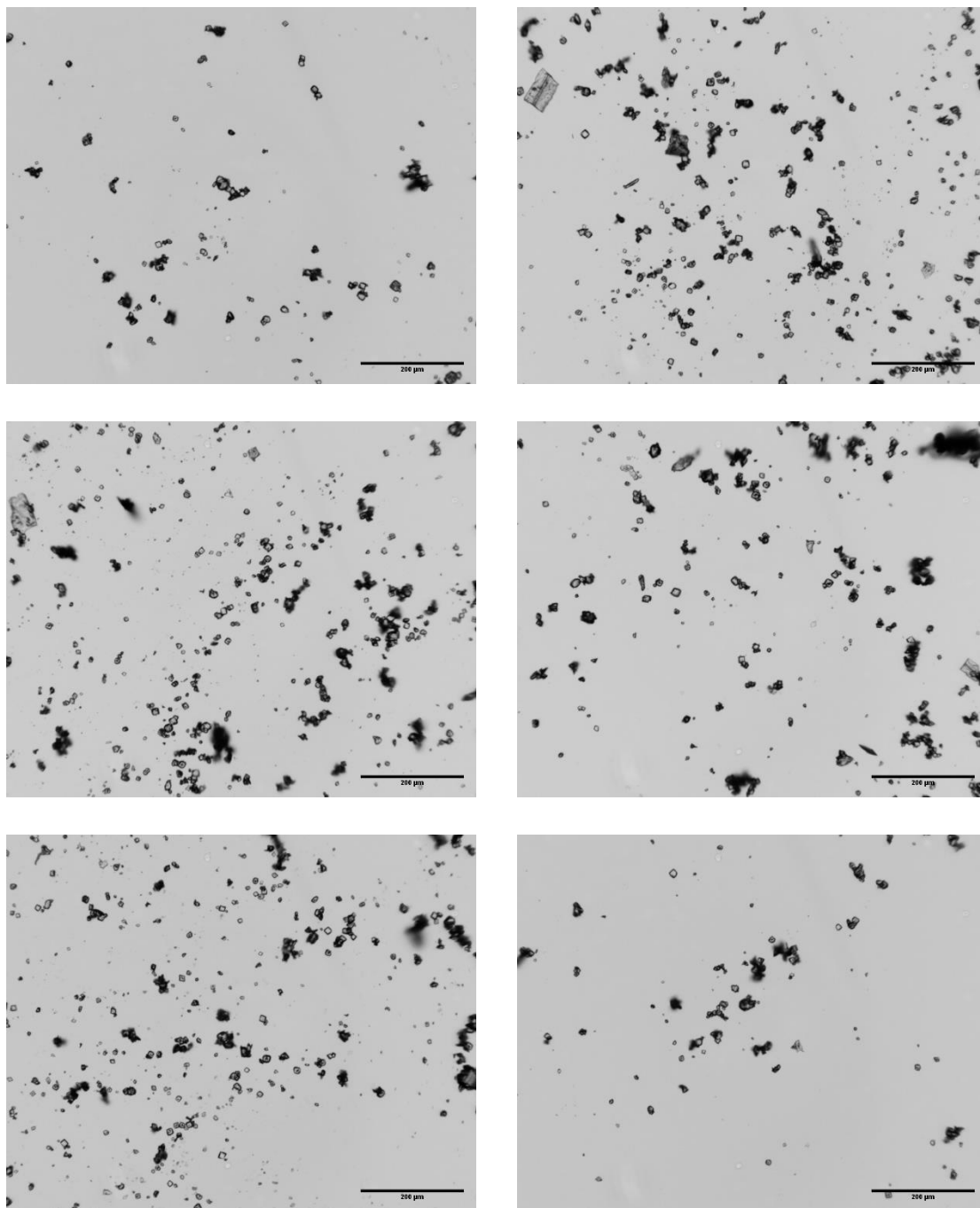
Appendix D RDX/TMA

D.1 Spray dried RDX Scherrer lengths summary table

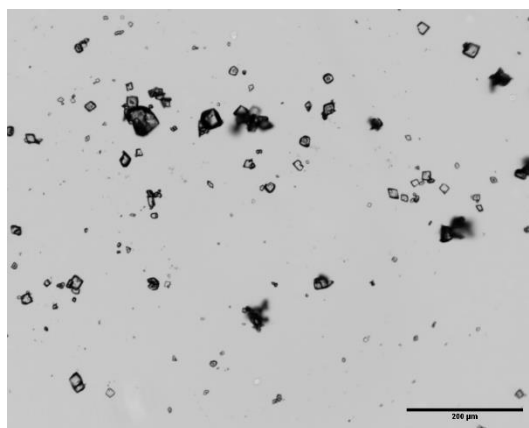
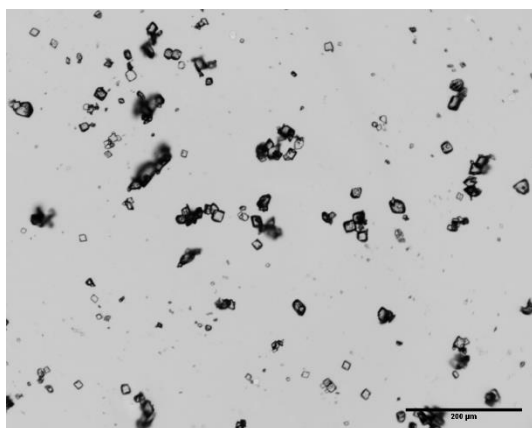
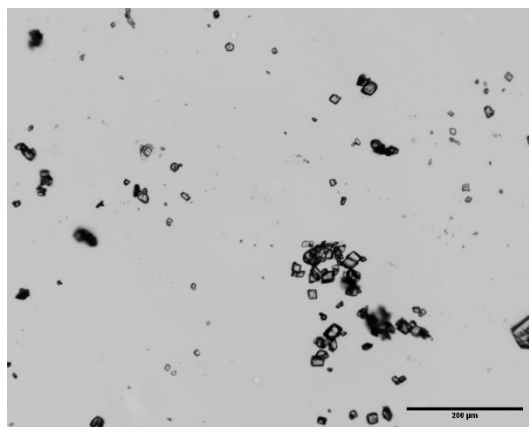
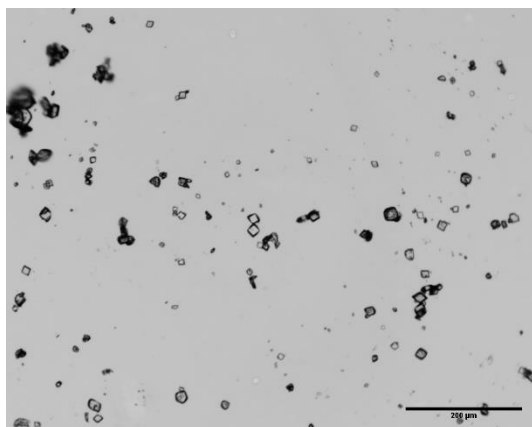
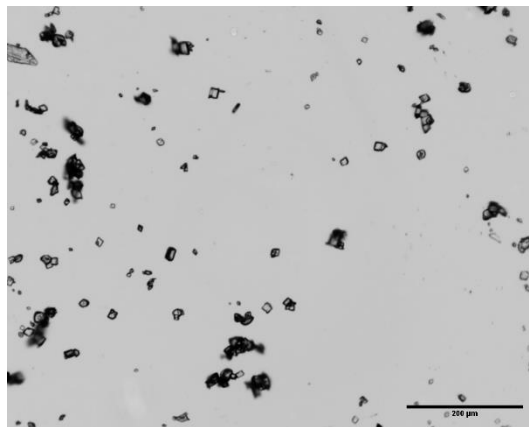
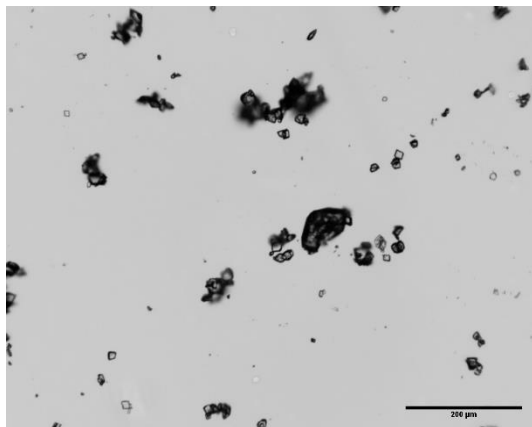
TMA	pp	Plane	2 θ (°)	Length (nm)	Error (nm)	TMA	Pp	Plane	2 θ (°)	Length (nm)	Error (nm)
1	T	111	13.06	63.12	3.1	3	B	111	13.07	59.84	2.6
1	T	200	13.39	66.81	5.2	3	B	200	13.40	65.52	4.0
1	T	020	15.25	52.83	15.5	3	B	020	15.24	46.01	22.3
1	T	210	15.42	74.36	7.5	3	B	210	15.42	73.63	15.2
1	T	002	16.47	54.17	3.3	3	B	002	16.47	52.19	2.6
1	M	111	13.05	60.64	2.1	4	T	111	13.06	57.59	2.4
1	M	200	13.38	64.71	4.0	4	T	200	13.40	61.71	3.9
1	M	020	15.25	40.14	19.2	4	T	020	15.25	52.41	12.5
1	M	210	15.41	75.03	15.7	4	T	210	15.42	67.50	6.2
1	M	002	16.47	52.08	2.6	4	T	002	16.47	52.10	2.6
1	B	111	13.08	52.37	1.7	4	M	111	13.05	63.89	4.6
1	B	200	13.42	56.56	3.6	4	M	200	13.38	69.77	8.4
1	B	020	15.27	40.59	18.1	4	M	020	15.25	95.08	67.3
1	B	210	15.44	65.51	13.7	4	M	210	15.40	69.12	8.7
1	B	002	16.49	46.33	1.8	4	M	002	16.44	56.58	9.3
2	T	111	13.04	66.35	5.4	4	B	111	13.06	61.48	2.7
2	T	200	13.37	70.90	8.5	4	B	200	13.39	66.41	4.4
2	T	020	15.15	56.26	25.6	4	B	020	15.24	54.63	25.1
2	T	210	15.41	75.56	10.0	4	B	210	15.42	70.98	15.4
2	T	002	16.45	50.83	6.3	4	B	002	16.47	52.27	3.2
2	M	111	13.08	56.14	2.7	5	T	111	13.05	61.22	2.5
2	M	200	13.41	62.13	4.3	5	T	200	13.39	65.24	5.2
2	M	020	15.27	30.78	4.4	5	T	020	15.24	54.30	16.7
2	M	210	15.42	70.55	6.9	5	T	210	15.41	73.92	8.8
2	M	002	16.47	49.06	2.5	5	T	002	16.45	51.68	3.7
2	B	111	13.06	61.88	2.2	5	M	111	13.06	58.24	2.2
2	B	200	13.39	69.74	3.9	5	M	200	13.40	63.06	3.5
2	B	020	15.24	33.31	4.4	5	M	020	15.25	36.93	14.5
2	B	210	15.41	79.42	6.9	5	M	210	15.42	70.09	9.9
2	B	002	16.46	55.09	3.0	5	M	002	16.47	50.73	2.6
3	T	111	13.07	59.84	2.2	5	B	111	13.04	65.49	3.3
3	T	200	13.40	64.23	4.2	5	B	200	13.38	72.65	6.8
3	T	020	15.26	50.96	28.1	5	B	020	15.24	61.74	26.2
3	T	210	15.42	71.99	19.4	5	B	210	15.40	72.60	9.2
3	T	002	16.47	51.67	3.1	5	B	002	16.46	55.35	4.9
3	M	111	13.05	60.17	2.8						
3	M	200	13.39	64.09	4.3						
3	M	020	15.26	48.02	20.8						
3	M	210	15.41	77.69	21.2						
3	M	002	16.46	52.83	2.9						

D.2 Solvent antisolvent TMA doped RDX crystallisation images (200 μm scale bar)

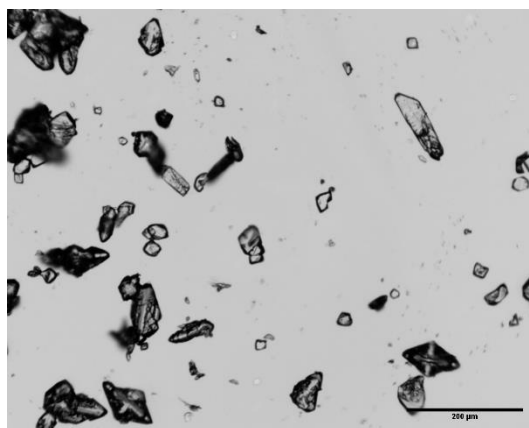
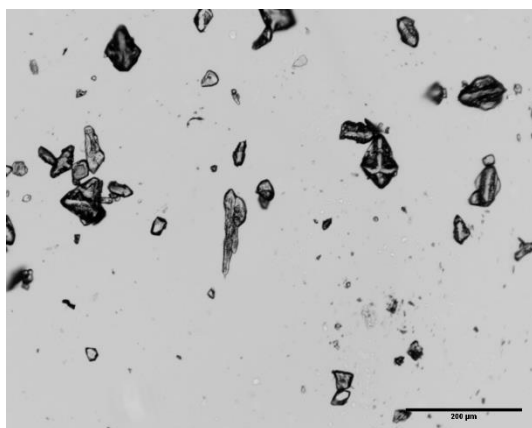
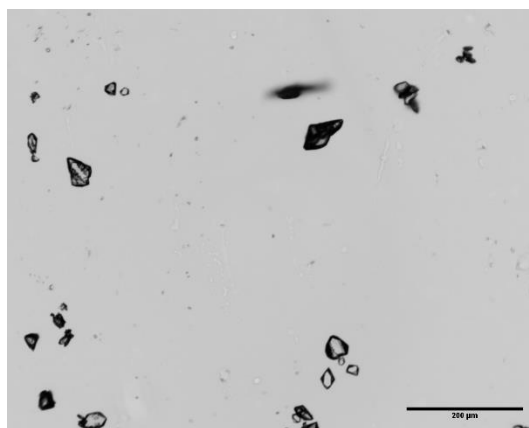
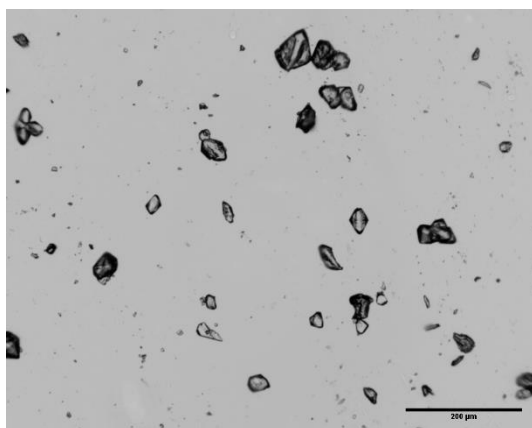
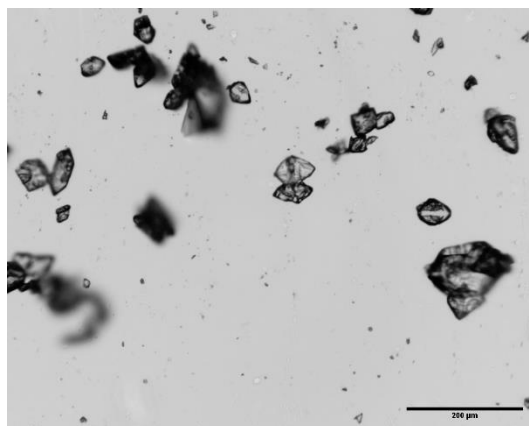
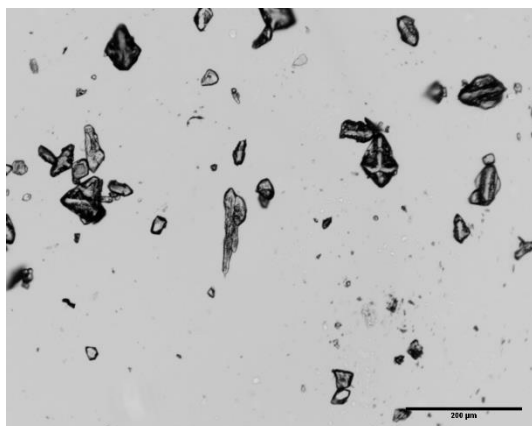
D.2.1 TMA 1: 2,4-dimethyl-1-nitrobenzene



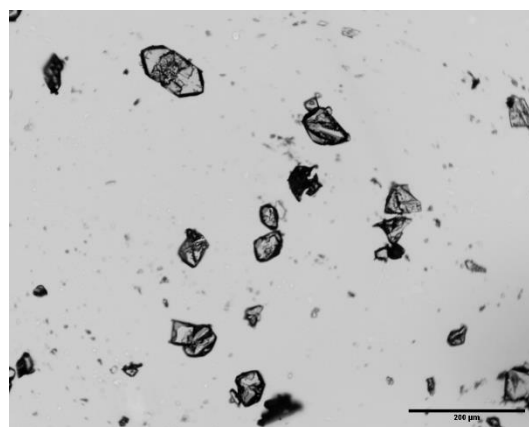
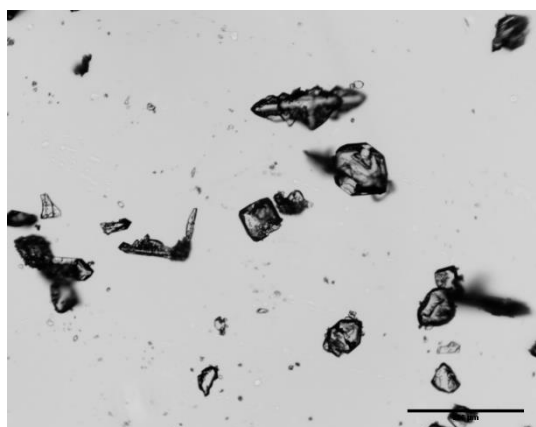
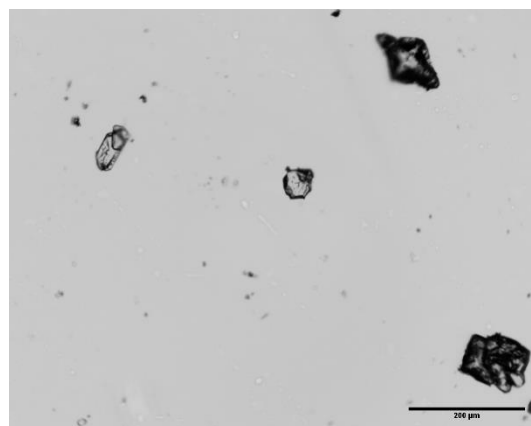
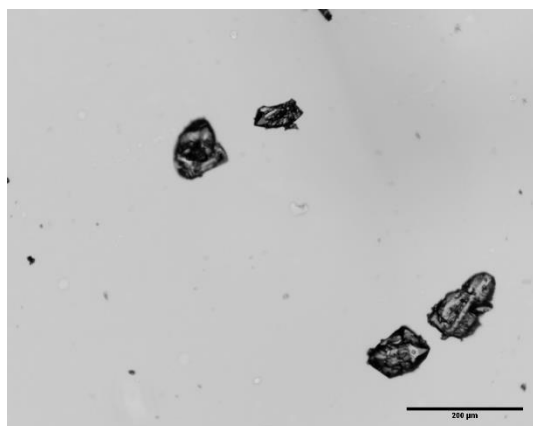
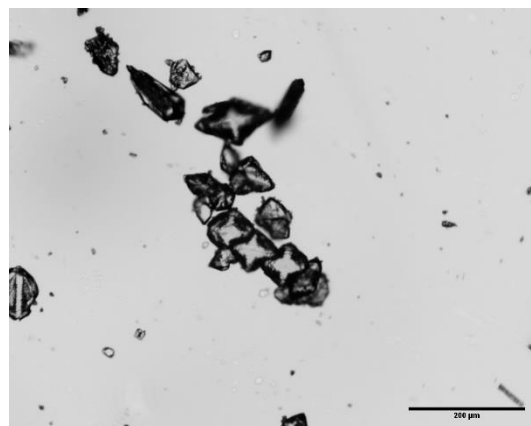
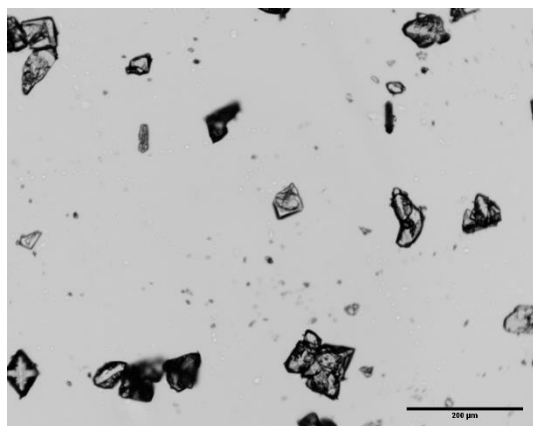
D.2.2 TMA 2: 1,2-dimethyl-3-nitrobenzene



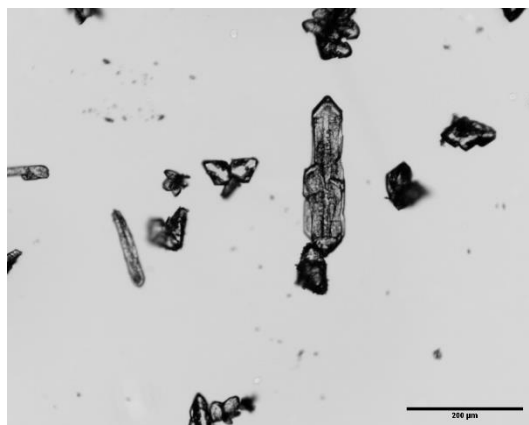
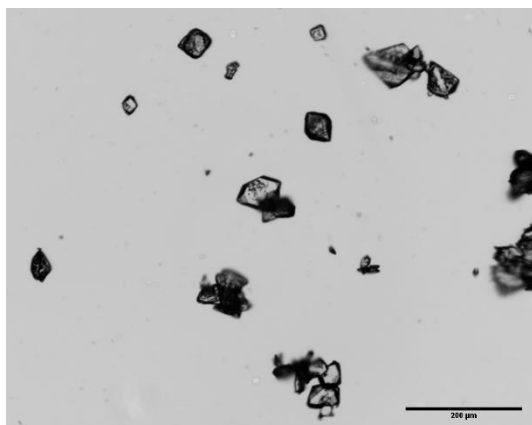
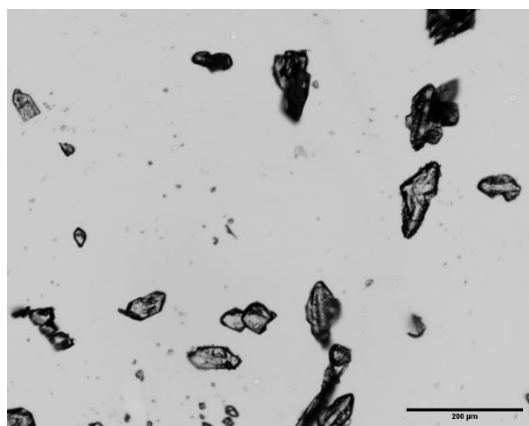
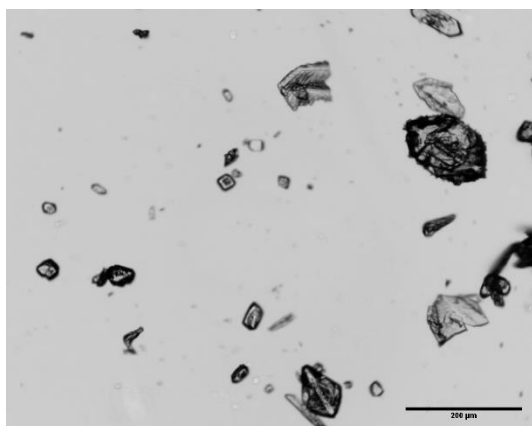
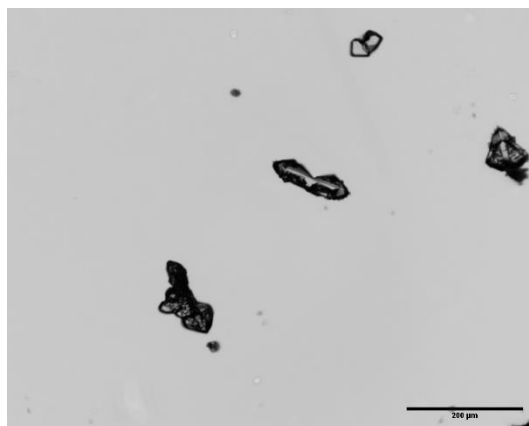
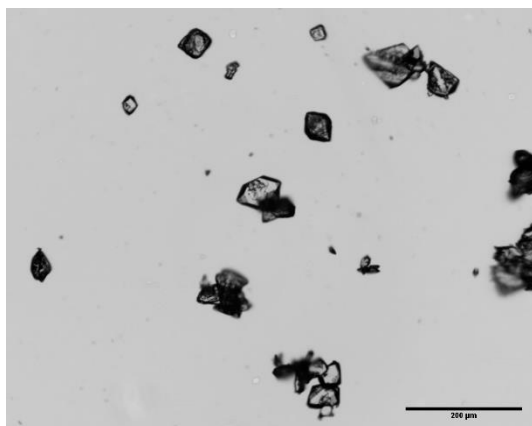
D.2.3 TMA 3: 1,3-dimethyl-2-nitrobenzene



D.2.4 TMA4: 2,4,6-trimethoxy-1,3,5-triazine



D.2.5 TMA 5: 6-methyl-1,3,5-triazine-2,4-diamine



D.2.6 Pure RDX

