Extension Proposal for Drying of Single Droplets at High Temperatures

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Summary

This proposal builds from the work done in the first three years of the project and seeks to maximize its value, and impact, for industries that are developing spray dried materials and formulations. To do this it will focus on three areas: 1> establishing a best practice work process for prediction of product morphology from laboratory experiments and material characterization. It will include experimental work on the influence of temperature history on morphology and an evaluation of quantitative prediction by validating versus as large a scale dryer as possible. 2> Assessment, evaluation, and where possible development, of material property characterization techniques which are capable of making measurements at boiling conditions i.e. high temperature and low moisture content. 3> Extension of the material types investigated to crystallizing and colloidal systems.

Background and rationale

The final droplet morphology is due to the complex interaction between the droplet material, transport and thermodynamic properties and the drying history. The regime maps and models developed in the first phase of the project will give insights into the final particle morphology, the key drivers behind the morphology and how these might be altered to change morphologies. However, as the behaviour of the systems chosen in the first phase of the project has shown, the distinct phase behaviour of a material leads to regime maps which are material specific. The reapplicability of regime maps across other materials is therefore relatively limited.

Even for materials that can be clustered in terms of their phase behaviour, and for which models might be expected to provide reasonable predictions, the challenge in measuring material and thermodynamic properties to predict drying kinetics and morphologies *ab initio* makes this a complex and time consuming challenge. Consequently, when accessing new formulations or materials the effort required to characterize the phase behaviour and material properties will be significantly more than running drying experiments. That being the case if we want to learn about the predict morphology, estimate drying rates and predict dryer performance, rather than *ab initio* models, the most efficient product and process development process will be to use experimental techniques, interpreted through models.

The key opportunity therefore is how best to predict product properties and process performance for a high temperature system from small scale experiments; this is reflected in the first theme of the proposal outlined below. In addition, the time we have had to focus on measurement techniques has a been limit so there is the opportunity to take this further and to test systems for quantifying the material property evolution during drying. Work in this area will help refine models and to quantify mechanistic understanding. Where beneficial we will look to foster collaborations with experimental expertise and apparatus to help with measurement technique development

Finally, the work has focused on three systems HPMC, sodium silicate and sucrose which were chosen to be representative of the amorphous, skin forming/polymeric class of materials. The work over the next year is also likely to be primarily focused on this class of materials. There is therefore an interest in extending the work to other classes of material namely crystallizing systems and colloidal systems

Proposal

T the following three themes are proposed for a continuation of the project, the focus on each theme would be open for feedback and discussion:

1. **Best practice work process for the prediction of morphology**
   The first phase of the project has shown that mechanistic and qualitative understanding of morphology development can be obtained from filament drying. Work is underway to establish if drying models can capture the behaviour across the range of conditions tested , *e.g.* do the approaches in the models capture the physics of the system well enough to allow material properties parameters to be calibrated. Here we will build on this work and use it to propose and evaluate methodologies, combining experimental and modelling techniques, to estimate the morphology and intra-granular porosity for a product from a spray drier. These methodologies would range in accuracy from the more qualitative to the quantitative. The quantitative approaches would use CFD and/or zonal models to predict drying histories. Further single particle drying experiments are anticipated to look at the influence of the temperature history on the particle morphology, a potentially important factor for some systems.
   Testing and validation of the methodology would be done versus as large scale experiments as possible, at minimum the method would be tested versus a well characterized lab scale dryer.
   Challenges/Risks: 1> Validation: The challenge with attempting this for large scale dryers is typically the work required to establish the geometry and boundary conditions and validate the airflow model are considerable unless these have already been established. 2> The optimum method and accuracy of the methods are likely to be may be material dependent.

2. **Material characterization**
   The key challenge in material property characterization and measurement is the ability to do this at the temperatures and moisture contents seen during the droplet boiling events. These relatively extreme conditions are a challenge for both standard and advanced techniques. Consequently, existing techniques are not capable of making the measurements required. New methods or modifications to existing methods will therefore be identified, assessed and developed to measure material, transport and thermodynamic properties during the drying history of the droplets or at the equivalent conditions. A key aim will be to get these methods as simple and robust as possible and to provide tools for qualitative assessment as well as quantitative evaluation. A collaborative approach will be taken for this theme, with the aim of bringing in complementary expertise where synergies exist. A more detailed discussion of some

of the methods is appended to this document. *Challenges/risks:* The effort and cost involved in developing these techniques may be prohibitive, consequently a key milestone in the project will be the decision on which routes to take.

3. **Extension to other material classes**
   Extending the methods to suspension/ colloidal systems, and crystallizing systems (or others that are a priority for IFPRI) rather than the skin/polymer systems that have been the focus to date.

Draft work plan:

Year 1:

Theme 1: a) Establish influence of temperature history on morphology and drying behaviour of HPMC, silicate and sucrose; b) testing and evaluation of single drop models with aim of establishing right to succeed with methodologies; c) identification of initial development methodologies; d) scale-up system assessment and characterization e.g. atomization measurement, inlet temp checking etc;

Theme 2: a) Viscosity/elasticity technique review and assessment. b) Identification and establishment of collaborations; c) experimental rig development

Theme 3: No action

Year 2:

1: a) test system runs at scale; b) characterization of products; c) CFD/zonal model development d) comparison of predictions to results; e) methodology refinement

2: a) method development; b) validation of technique

3: System selection and test runs

Year 3:

1: a) testing of methodology on new material system; b) consolidation and write-up

2: a) characterization of key systems; b) consolidation and write-up

3: a) full characterization of target systems; b) development of regime maps and evaluation of modelling framework

Appendix 1: Material Property Measurement

The characterization of material properties, e.g. viscosity, elasticity, diffusivity, etc for the systems investigated is challenging as they need to be measured at or near boiling point and at low moisture content. Properties such as diffusivity and viscosity also span many orders of magnitude and are therefore challenging to measure. These temperature and conditions are out of the range of most of the techniques available at collaborators or potential collaborators (Reid, Bristol; Schutyser, Wageningen; Murray, Leeds) who have advanced methods for measuring viscosity and diffusivity at low moisture contents. Consequently to move forward, new techniques need to be developed. Potential techniques fall into two categories: in-situ techniques where the properties are measured, during a drying experiment or ex-situ techniques where the properties are measured using alternative apparatus.

In-situ techniques

The advantage of these techniques is that the materials are at the conditions of interest, all be it for a typically limited period of time, and the structures formed, and consequently their material properties, are those of relevance to the puffing droplets. Visco-mechanical properties can be potentially estimated by perturbing the system, and measuring its response. This could be via movement, oscillation e.g. in a Newtonian systems the surface tension and viscosity of a droplet can be estimated by oscillating a droplet; inflation using injected gas; or by passive measurement looking at the bubble expansion dynamics during drying or driven via an external heat source. The use of microwaves as an external heat source was evaluated during the first phase of the project, unfortunately it was found to be ineffective at heating droplets. However IR-lasers have potential and have been used in heat transfer studies on droplets

Diffusivity – this can be estimated from drying curves, if boiling does not occur, and it is also most value to the models in the period before boiling..

Ex-situ techniques

These techniques span well established techniques such as rotating rheometers and more complex systems/geometries such the study of emulsion systems. The challenges in these cases are: stopping the material boiling and drying, an establishing the same material phase and structure as would be seen in a dryer.

For materials that remain liquid like for a period under the conditions of interest, ‘standard’ rheological methods can be used. To prevent drying a closed system will be necessary, and to prevent boiling a pressurized system is required. For more solid like materials DMA methods may be possible, all be it with the same issues as the rheological experiments, but with the additional complexity of how to make the sample of the material to be tested.

More speculative techniques could involve the use of emulsions to stop drying. For example, an emulsion of the solution of interest in a silicone oil, could be made and the droplets allowed to dry slowly overtime via diffusion of water through the oil. The rheological properties of the material could then be evaluated by using a vacuum system and/or heat to drive bubble nucleation and growth.

Microscopy could be used to look at inflation dyanamics and models used to interpret and quantify the droplet characteristics. The applicability of this type of approach is likely to be material dependent.