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Synopsis Of

An experimental investigation on heat and mass transfer characteristics during nozzle spray drying of active cathode material

A Thesis

To be submitted by

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Of

DOCTOR OF PHILOSOPHY

1 Abstract

Spray drying technique is used to produce dry powder by rapid evaporation of atomized solution or slurry under a hot gaseous ambient. Due to the improved particle shape, size, and quick drying of the solution, the technique has attracted significant interest. Depending on the product, spray drying can be performed either in continuous or intermittent mode. Under continuous mode, the chamber temperature continuously decreases, and the chamber tends to achieve an equilibrium temperature gradient. The wet-bulb temperature of the carrier gas at the chamber exit may fall below the temperature of the dried particles, which may lead to the re-hydration of dried particles and the collapse of the entire process. During intermittent drying the feed solution is sprayed intermittently and the chamber can regain its temperature during the non-spray period. Though, there is a large amount of research work available with respect to the characteristics of the end-dried product, research work related to heat and mass transfer characteristics during the process is minimal. It is needless to mention that the overall performance of the process and the quality of the dried product depends on the mechanism of heat and mass transfer.

The thesis comprises numerical and experimental investigation of the heat and mass transfer behavior of precursor for $\mathrm{Na_2Fe_{0.6}Mn_{0.4}PO_4F/C}$ electrode powder for sodium-ion batteries during intermittent drying process using a full cone nozzle spray with a co-current carrier drying medium. The research output also comprises design correlation for Nusselt number and Sherwood number. Though there are many sub processes present to refine the raw powder, which is spray-dried, to the final form, this thesis mainly focuses on the drying behavior of raw electrode powder.

The Eulerian-Lagrangian method is used to assess the spray drying numerically. Since both the air and the droplet flow are in one direction, the flow can be treated as 2D axisymmetric with the assumption of minimal 3D swirls. The boundary conditions with Particle Source In cell (PSI-cell) model is used to solve the transfer of heat, mass, and momentum between the continuous and dispersed phase. The Discrete Phase Modeling(DPM) is performed by solving the continuous phase calculations while keeping the number of discrete phase interactions with the continuous phase. The test fluids chosen are $\mathrm{Na_2Fe_{0.6}Mn_{0.4}PO_4F/C}$ precursor, saline solution, and precursor for LFP with the co-current hot carrier gases for the former two as air and the latter an inert gas respectively.

The experimental investigation on heat and mass transfer characteristics during the synthesis of $\mathrm{Na_2Fe_{0.6}Mn_{0.4}PO_4F/C}$ and mannitol solution using intermittent spray drying is carried out in a custom-made spray dryer. The nozzle orifice diameter, spray duration and spray pressure are operating parameters of the process that are respectively varied between 0.2 and 0.4 mm at 10 and 40 seconds, and 4 and 7 bar. Under considered operating conditions, the volumetric heat transfer coefficient varied between 1.5 and 3.5 $\mathrm{kW/m^3K}$ and Nusselt number range between 66 to 151. The volumetric mass transfer coefficient ranges between 2.5 and 5.0 $\mathrm{s^{-1}}$ and the Sherwood number range from 45 to 106. Additionally with $\mathrm{Na_2Fe_{0.6}Mn_{0.4}PO_4F/C}$ precursor, Mannitol is also used in experimental investigation. The correlation for the Nusselt number and Sherwood number that relate the flow characteristics and thermophysical properties of the carrier gas and precursor fluid is developed in terms of the Ohnesorge and Reynolds numbers.

2 Objectives

The research work is intended to investigate the heat and mass transfer characteristics during intermittent co-current spray drying of precursor of $\mathrm{Na_2Fe_{0.6}Mn_{0.4}PO_4F/C}$ cathode material .

The major objectives are as follows

(a) To investigate the spray patterns using patterns maps for a range of thermophysical properties of precursor, flow conditions and nozzle orifice sizes to decide the operating condition and nozzles that falls in the complete atomization regime

(b) To numerically analyze the spray drying process using Eulerian - Lagrangian approach to decide the dimensions of the custom-made spray drying apparatus. Apart from the precursor of $\mathrm{Na_2Fe_{0.6}Mn_{0.4}PO_4F/C}$, the precursor of LFP and saline solution is also considered as test fluids for numerical analysis.

(c) To develop a custom-made spray dryer with suitable instrumentation and controls.

(d) To experimentally investigate the heat and mass transfer characteristics during spray drying and to incorporate the intermittency of nozzle spray.

(e) To experimentally investigate the influence of pressure, precursor flow rate and nozzle size, on heat and mass transfer during the process.

(f) To develop correlations for Nusselt and Sherwood numbers, which correlate the thermophysical properties of the precursor and drying medium in terms of Re, Oh , spray pressure, nozzle size, and the spray duration. In order to cover the Reynolds number and Ohnesorge number range which was not practically achievable using precursor of $\mathrm{Na_2Fe_{0.6}Mn_{0.4}PO_4F/C}$, the data points of spray drying of Mannitol is considered.

3 Research gaps

From the repository of literature, it is observed that spray drying is explored with respect to products, focused on productivity(Jin and Chen (2009)), product characteristics(Yue *et al.* (2011);Son *et al.* (2014)), quality(Chen and Patel (2008);Dumoulin and Bimbenet (1998)). However, there is scope for research especially in the heat and mass transfer aspects. Following are the major aspects, which is open for research:

(a) One of the reported issues in the spray drying process is reducing productivity due to particles sticking to the wall. Hence it is essential to study the particle spreading in space to design the spray chamber for a particular nozzle and operating conditions.

(b) There is only a little studies available on the computational and experimental research on heat transfer and mass transfer during the spray drying process. Hence, there is a scope to analyze the process heat and mass transfer characteristics.

(c) Little research on the intermittent nature of the feed spray throughout the drying process. Intermittent airflow and heating are the topics of the study on intermittency.

(d) Only a few researchers have considered the volumetric approach for the heat transfer analysis of the spray dryer for different applications.

(e) A detailed correlation development is completely absent in the literature available and such correlations will be helpful in the design of spray dryers.

The above research gaps were identified through the literature survey, and have been addressed in the present research.

4 Most Important Contributions

4.1 Custom-made spray dryer

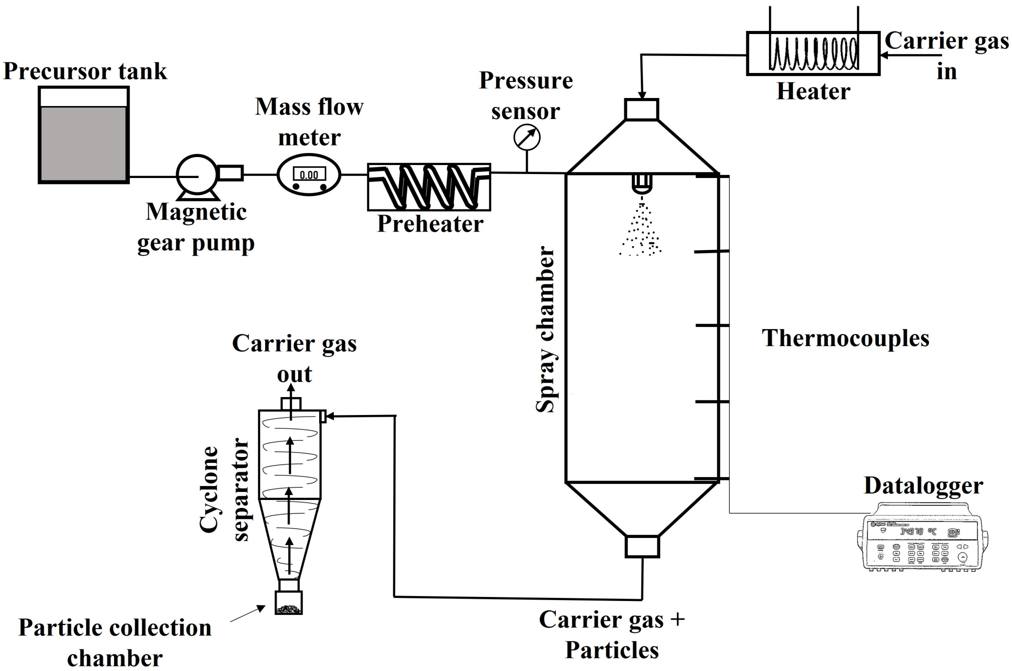


Figure 1: The schematic of the spray drier

To study the heat and mass transfer behavior during the spray drying of precursor a custom-made apparatus was constructed. Figure 1 depicts the schematic of a spray drying process. The setup is divided into the following circuits,

(a) Precursor flow circuit

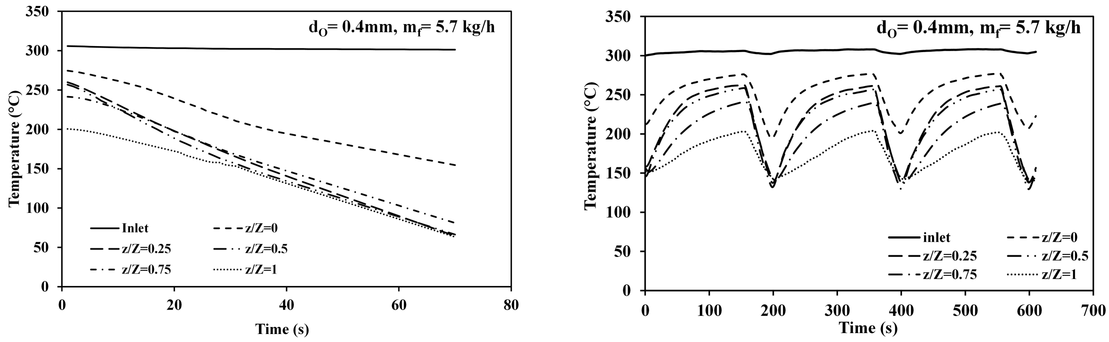
(b) Carrier gas circuit

(c) Spray chamber

(d) Particle collection circuit

The storage to the atomization of precursor in the system is the precursor flow circuit, where the nozzle atomizes the precursor pumped from the precursor tank. The carrier gas circuit constitutes the heating elements and allows the gas to enter the drying chamber. The spray chamber is also called the droplet drying circuit where the droplet and the drying medium meet together, and heat and mass transfer occurs. The dried particles are separated from the mixture leaving the spray chamber using the cyclone separator.

4.2 Continuous and intermittent spray drying



(a) Temperature of the chamber in the continuous drying process

(b) Temperature of the chamber in the intermittent drying process

Figure 2: Temperature profile of the spray chamber during continuous and intermittent drying

Figure 2a shows the chamber temperature during continuous spray drying at various locations in the axial direction (inlet and another five locations from the top to the bottom of the spray chamber [z/Z- Ratio between any axial location and the total height]). Prior to the initiation of the spray, the chamber initial minimum and maximum average temperatures are approximately 200 and 300°C, respectively. During the spray, the temperature drops at all the locations, and reaches low value at the outlet where the partial drying of the particles is possible. To overcome the difficulties present in the continuous drying process, an intermittent spray approach is considered. Figure 2b shows the temperature at axial locations of the spray chamber for an intermittent spray period of 40s and 5.7 kg/h precursor flow rate with nozzle of orifice diameter 0.4mm($d_O = 0.4\mathrm{mm}$) . During the spray period of 40s, the minimum and maximum temperatures of the chamber became 130 and 194°C and the cycle is repeated. As in the case of continuous spray drying, if the spray proceeds further, the outlet temperature will fall below the solvent saturation temperature, leading to the droplets rehydration and reducing the spray dryer effectiveness. The same is rectified by the adoption of the intermittent spray drying process.

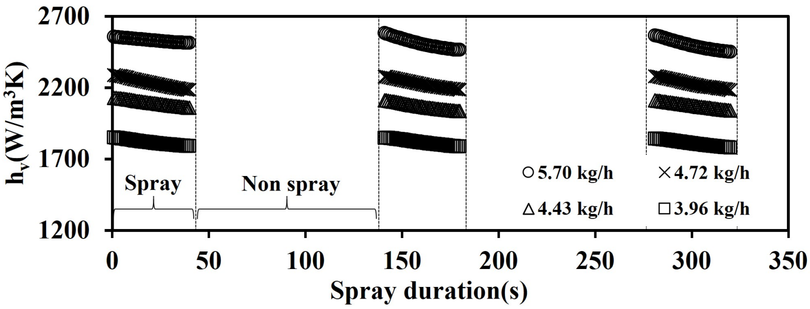


Figure 3: Volumetric heat transfer coefficient(h_v) during intermittent spray drying

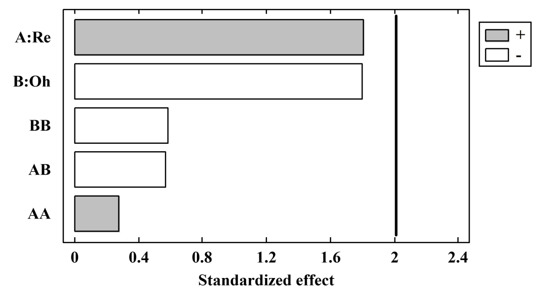
4.3 Volumetric heat transfer coefficient

Figure 3 shows the estimated volumetric average heat transfer coefficient during the spray and non-spray periods of the intermittent spray drying process. It is needless to mention that the surface area required to estimate surface heat transfer coefficient between the droplets and the drying gas is uncertain. Therefore, the volumetric heat transfer technique is employed for the study. The Figure 3 corresponds to m_f = 3.96 to 5.70 kg/h, P_f = 4 to 7 bar and the T_g to initiate spray is 300°C. The spray from the precursor nozzle is metered such that the spray ceases when the chamber outlet (z/Z=1) falls below the wet bulb temperature of the air. The spray duration is fixed to be 40s for the above-mentioned condition. During the spray, the maximum and minimum temperature in the chamber are 300°C and 230°C respectively, which corresponds to the inlet and exit of the chamber. For the spray period the estimated volumetric heat transfer coefficient at the beginning and the ending of spray period varies between 2.6 and 1.7 kW/m^3K respectively for the considered operating conditions.

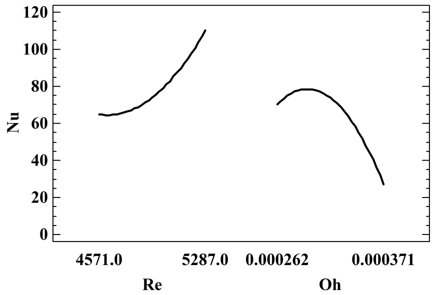
4.4 Influence of thermophysical properties and the operating conditions

The regression analysis is performed on the experimental data obtained during the investigation of the impact of the thermophysical properties of the fluids in terms of Oh and Re on the Nusselt and Sherwood numbers of the spray drying process.

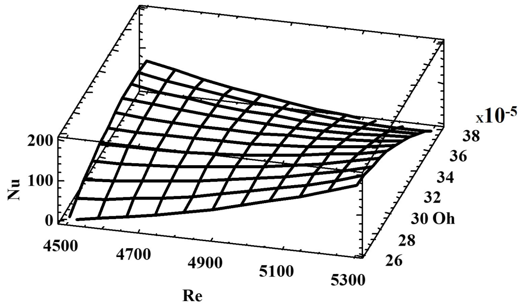
In terms of heat and mass transfer, the performance is enhanced by an increase in the Re. The Oh is identified as a significant, influential parameter with a negative effect on performance.



(a) The standardized effect of Re, Oh on Nu

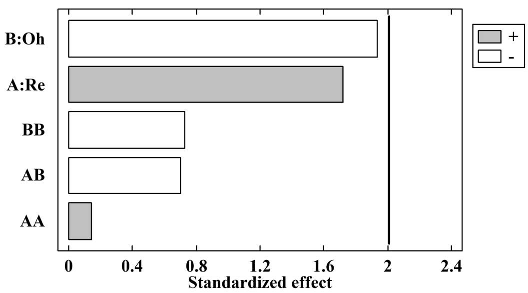


(b) Main effects plot of Re and Oh on Nu

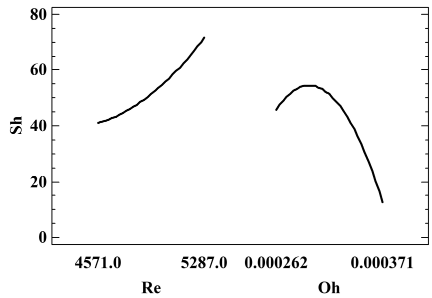


(c) Response surface of Nu against Re and Oh

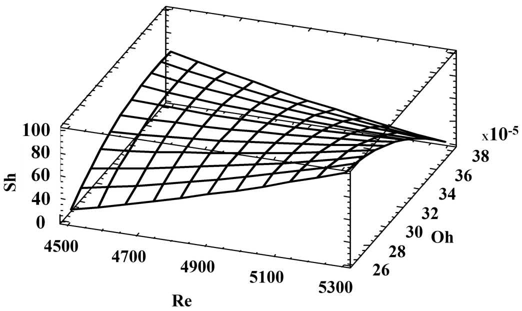
Figure 4: Effect of Re and Oh on the Nusselt number for $\mathrm{Na_2Fe_{0.6}Mn_{0.4}PO_4F/C}$



(a) Main effects plot of Re and Oh on Sh



(b) Main effects plot of Re and Oh on Sh



(c) Response surface of Sh against Re and Oh

Figure 5: Effect of Re and Oh on the Sherwood number of $\mathrm{Na_2Fe_{0.6}Mn_{0.4}PO_4F/C}$

5 Conclusions

The major conclusions of the heat and mass transfer study of the spray drying process as follows:

(a) With the help of spray pattern map analysis, the nozzle size and other primary operating conditions are chosen such that the spray lies at the complete atomization regime.

(b) The experimental analysis is carried out using the custom-made spray dryer. The $Na_2Fe_{0.6}Mn_{0.4}PO_4F/C$ precursor and mannitol are spray-dried with an intermittent drying technique, which comprises the spray intermittency. The volumetric heat transfer coefficient is considered as the variable to analyze the performance of the spray dryer.

(c) The volumetric heat transfer coefficient of the spray drying process range between 0.8 to 3.5 $\mathrm{kW/m^3K}$, and the Nusselt number range between 66 and 151, when operated with the considered operating conditions and the intermittent spray approach.

(d) The volumetric mass transfer coefficient of the process is calculated using the Lewis relation and found to be varying from 2.5 to 5 $\mathrm{s^{-1}}$ and the Sherwood number range from 45 to 106, for the considered operating conditions.

(e) Correlations are evolved for heat and mass transfer in terms of Nusselt number and Sherwood number by relating Reynolds and Ohnesorge numbers.

(f) The response surface analysis examines the impact of different operating conditions. In the process, heat and mass transfer were strongly affected by Re and Oh of the process.

(g) Correlations have been developed to predict the Nusselt number(Nu) and Sherwood number(Sh) for combined experimental values of $Na_2Fe_{0.6}Mn_{0.4}PO_4F/C$ and Mannitol solution. The deviation between the experimental and predicted Nu and Sh is $\pm 20\%$. The deviation is further reduced to $\pm 10\%$ when removing outliers in the experimental data.

$$Nu = A_1 - A_2(Re) - A_3(Oh) + A_4(Re^2) + A_5(Re)(Oh) - A_6(Oh^2) \quad (1)$$

Where,

$A_1 = 3489.58$; $A_2 = 1.49254$; $A_3 = 1377.04$; $A_4 = 0.000162586$;
$A_5 = 0.377802$; $A_6 = 2402.05$;

The correlation for the Sherwood number is,

$$Sh = B_1 - B_2(Re) - B_3(Oh) + B_4(Re^2) + B_5(Re)(Oh) - B_6(Oh^2) \quad (2)$$

Where,

$B_1 = 2370.97$; $B_2 = 1.0175$; $B_3 = 656.943$; $B_4 = 0.000111237$;
$B_5 = 0.250455$; $B_6 = 2810.01$;

5.1 Scope for future study

(a) The custom-made setup can be modified to analyze the process as a counter-current and cross-flow drying process along with reducing and controlling the intermittency in microseconds.

(b) The custom-made setup can be automated entirely and modified with different atomization mechanisms.

6 Organization of the Thesis

The proposed outline of the thesis is as follows:

(a) Chapter 1: Introduction
   1.1 Spray drying
   1.2 Continuous and intermittent drying process
   1.3 Spray pattern maps
   1.4 Useful terminologies

(b) Chapter 2: Literature survey
   2.1 Applications of spray drying
   2.2 Battery electrode manufacturing
   2.3 Other drying methods
   2.4 Literature on spray drying
   2.5 Objectives
   2.6 Methodology

(c) Chapter 3: Numerical investigation and results
   3.1 Pattern map analysis
   3.2 Energy, momentum, and mass transfer equations
   3.3 Computational domain
   3.4 Boundary conditions
   3.5 Operating conditions
   3.6 Grid dependency test
   3.7 Model validation
   3.8 Results and discussion of numerical analysis
   3.9 Conclusions

(d) Chapter 4: Experimental investigation
   4.1 Spray drying apparatus
   4.2 Instrumentation

(e) Chapter 5: Results and discussion
   5.1 Volumetric heat transfer coefficient
   5.2 Precursor preparation and operating conditions
   5.3 Intermittent drying of precursor of $Na_2Fe_{0.6}Mn_{0.4}PO_4F/C$
   5.4 Elemental analysis

5.5 Heat and mass transfer analysis of the process using mannitol solution
5.6 Heat transfer during intermittent spray drying
5.7 Conclusions

(f) Chapter 6: Correlation development
6.1 Correlations of Nu and Sh for precursor of $Na_2Fe_{0.6}Mn_{0.4}PO_4F/C$
6.2 Correlations of Nu and Sh for Mannitol
6.3 General equations for Nusselt and Sherwood numbers

(g) Chapter 7: Conclusions and future scope
7.1 Theoretical investigation – Spray pattern
7.2 Theoretical investigation – Numerical study
7.3 Experimental investigation and correlation development – Intermittent drying

6.1 Nomenclature

CFD	Computational Fluid Dynamics
DPM	Discrete Phase Modeling
LFP	Lithium Ferrous Phosphate
LMTD	Logarithmic Mean Temperature Difference, °C
Re	Reynolds number
Oh	Ohnesorge number
Nu	Nusselt number
Sh	Sherwood number
z/Z	Dimensionless axial position
d_O	Nozzle orifice diameter, mm
m_f	Precursor flow rate, kg/h
P_f	Pumping pressure, bar
T_g	Carrier gas temperature, °C
h_v	Volumetric heat transfer coefficient, W/m^3K

7 List of Publications

7.1 Journals

1. Rajasekar, K., Raja, B. An investigation on heat and mass transfer characteristics during spray drying of saline water. *Sādhanā, Springer* 47, 90 (2022), doi.org/10.1007/s12046-022-01863-w.

2. Rajasekar, K., Raja, B. Investigation on Heat and Mass Transfer in Spray Drying Process. *Journal of Engineering Thermophysics*. 30, 433–448 (2021), doi.org/10.1134/S1810232821030085.

3. Rajasekar, K., Raja, B. Experimental investigation on volumetric heat transfer coefficient during intermittent spray drying of mannitol solution. *Drying Technology* (Under review).

4. Rajasekar, K., Raja, B. An investigation on heat and mass transfer characteristics during spray drying synthesis of $Na_2Fe_{0.6}Mn_{0.4}PO_4F/C$ cathode material for sodium-ion batteries. *Applied Thermal Engineering* (Under review).

7.2 Conferences

1. Rajasekar. K, Raja. B, "Investigation of flow pattern of spray from solid cone Nozzle", *(FMFP 2020) International conference of Fluid Mechanics and fluid Power, 2020*, IIT Guwahati.

2. Rajasekar. K, Raja. B, "Numerical Investigation of pure single water droplet using Eulerian-Lagrangian Approach", *(ICAME 2020) International Conference on Advances in Mechanical and Industrial engineering, 2020*, KIIT Bhubaneshwar.

3.Pothi Raj. R, Rajasekar. K, Raja. B, "Heat transfer analysis of water spray drying – A Numerical Approach", *(FUC 2021) Fluids Under Confinement, 2021*, IIT Kharagpur.

4. Pothi Raj. R, Rajasekar. K, Raja. B, "Numerical Investigation on heat transfer characteristics during spray evaporation of water",*ISHMT- ASTFE Heat and Mass Transfer conference (IHMTC 2021), 2021*, IIT Madras, 1145-1149, DOI: 10.1615/IHMTC-2021.1740

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2. **Dumoulin, E.** and **J. J. Bimbenet** (1998). *Spray drying and quality changes*, 209–232. Springer US, Boston, MA. ISBN 978-1-4613-0311-4. doi:10.1007/978-1-4613-0311-4-10.

3. **Fletcher, C. A.** (2012). *Computational techniques for fluid dynamics: Specific techniques for different flow categories*. Springer Science & Business Media.

4. **Jin, Y.** and **X. D. Chen** (2009). Numerical study of the drying process of different sized particles in an industrial-scale spray dryer. *Drying Technology*, **27**(3), 371–381, doi:10.1080/07373930802682957.

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6. **Son, M. Y.**, **J.-K. Lee**, and **Y. C. Kang** (2014). Fabrication and electrochemical performance of 0.6 li2mno3-0.4 li (ni1/3co1/3mn1/3) o2 microspheres by two-step spray-drying process. *Scientific reports*, **4**(1), 1–7.

7. **Vehring, R.** (2008). Pharmaceutical particle engineering via spray drying. *Pharmaceutical research*, **25**(5), 999–1022.

8. **Versteeg, H.** and **W. Malalasekera** (1995). *An introduction to Computational Fluid Dynamics Longman Group Ltd*.

9. **Vertruyen, B.**, **N. Eshraghi**, **C. Piffet**, **J. Bodart**, **A. Mahmoud**, and **F. Boschini** (2018). Spray-drying of electrode materials for lithium-and sodium-ion batteries. *Materials*, **11**(7), 1076.

10. **Yue, P.**, **Z. Wang**, **W. Peng**, **L. Li**, **W. Chen**, **H. Guo**, and **X. Li** (2011). Spray-drying synthesized lini0.6co0.2mn0.2o2 and its electrochemical performance as cathode materials for lithium ion batteries. *Powder Technology*, **214**(3), 279–282. ISSN 0032-5910, doi:https://doi.org/10.1016/j.powtec.2011.08.022.