Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Spray Dried Milk-Protein Stabilized Emulsions

with High Oil Content

A thesis presented in partial fulfilment of the

requirements for the degree of

Doctor of Philosophy

in

Food Technology

At
Riddet Institute, Massey University
Palmerston North
New Zealand

Amit Taneja

2016

MASSEY UNIVERSITY
TE KUNENGA KI PŪREHUROA
UNIVERSITY OF NEW ZEALAND

Abstract

This study explores the behaviour of oil droplets in milk protein-stabilized emulsions during spray drying. The impact of preheat treatment on the stability of oil droplets during drying in milk protein-stabilized emulsions in maltodextrin was also observed, using a variety of techniques such as particle size analysis, various microscopy techniques and sodium dodecyl sulphate polyacrylamide gel electrophoresis. In the last section of the study, the stability of the powdered emulsions was investigated against oxidative deterioration when soybean oil was replaced with fish oil in the emulsion formulation.

The results showed that spray drying and redispersion of the powdered emulsions in water (at similar total solids content) caused a shift in the droplet size distribution to larger values for all emulsions made using low concentration of whey protein isolate or sodium caseinate (0.5−2.0%, w/w w.b.), in comparison with their respective parent emulsions. However, the droplet size distribution was affected only very slightly by spray drying when the protein concentration was above 2.0% (w/w). This minimum concentration of protein that was required to produce emulsions that were stable during the spray drying process was 3.0% (w/w) for the emulsions prepared using aggregated milk protein products as compared with 2.0% (w/w) for the NaCas- and WPI-containing emulsions.

It was suggested that the amount of unadsorbed protein in the bulk phase of the parent emulsions play a crucial role in stabilizing the oil droplets during spray drying. When the surface of the oil droplet is saturated with protein molecules and the bulk phase of the emulsion has sufficient unadsorbed protein, the oil droplet is stable during drying. However, for emulsions with a low concentration of unadsorbed protein in the bulk phase (≤ 1.0% for WPI or NaCas emulsions), protein molecules could potentially migrate from the surface of the oil droplet to the air–water interface, causing "gaps" in the oil droplet interface and leading to coalescence and/or bridging flocculation.

Emulsions containing low levels of maltodextrin showed marked coalescence during spray drying and redispersion even at a WPI concentration of 10.0% (w/w). Above a critical concentration (12.0%, w/w), maltodextrin appeared to stabilize proteins at the interface and provide adequate rigidity to the matrix perhaps by forming a glass, under the drying conditions.

In whey protein-stabilized emulsions made with preheat treated protein solution (above 70ºC), a shift was observed in average droplet diameter towards the larger size range, because of droplet coalescence as a result of spray drying. This was thought to probably be a result of protein aggregation in emulsions, which adversely affected the ability of proteins to stabilize the emulsion droplets during spray drying and further emphasized the crucial role of monomeric whey proteins. A reduction in the non-adsorbed monomeric whey proteins as a result of preheat treatment led to oil droplet coalescence during drying. The stability of the emulsion made with pre-heat treated whey proteins was noticeably improved when NaCas was added to the emulsion either before or after the homogenization step. This improved stability was believed to be a result of the steric effect of caseins that prevented large-scale aggregation of whey proteins.

The stability of emulsions during drying as shown by the change in the average droplet diameter before and after drying showed a negative correlation with oxidative stability of these emulsion where soybean oil was replaced with fish oil. The protein content and preheat treatment also showed a positive impact on the oxidative stability of spray-dried emulsions.

Overall, the finding from this systematic study has advanced the understanding of the mechanisms of the stability of oil droplet during drying as well as the impact of emulsions components and processing conditions. This may help to design emulsion formulations and processes and extend the applications of milk-protein stabilized powdered emulsions with high oil content.

Acknowledgements

For me, the journey towards completing my PhD has been a very special one. I've received support and guidance from so many people during this time towards whom I'd like to express my deepest gratitude.

A special thank you goes to my supervisor, Dist. Professor Harjinder Singh, not only for his tremendous academic support, but also for giving me so many wonderful opportunities during the time I spent at the Riddet Institute. Harjinder truly has been an inspiration for me to work hard and back my abilities. I also had the pleasure of having many great discussions with Harjinder regarding my research and a few good discussions on cricket and how to fix my golf swing.

I am also very grateful Dist. Professor Paul Moughan for his continued encouragement throughout my studies. He has always inspired me to speak my mind no matter how unconventional it may sound.

I also thank, Professor Richard Archer, my co-supervisor, for always inspiring to be rigorous in my approach and providing critical evaluation during the planning of my experimental chapters.

A big thank you to Professor Jim Jones, my co-supervisor, for providing continued support and encouragement that was a driving force for me to keep pushing hard and continue my research with great enthusiasm.

Associate Professor Aiqian Ye has been the person that I go to anytime to discuss openly regarding my research. I appreciate the time that Aiqian made available for to meet and listen patiently to any of my concerns and give honest feedback. Thank you Aiqian for being so dedicated to your role as my co-supervisor.

I want to acknowledge the contributions of the following people

- Anant Dave for training me on electrophoretic equipment and techniques.
- Sophie Gallier and Jianyu Chen for showing me how to operate the Confocal Laser Scanning Microscope at the MMIC, Palmerston North.
- Dr. Carlos Montoya for helping with the densitometry software for PAGE scanned gels.
- Chris Hall and Janiene Gilliand for their support with particle size measurement.
- Dr. Peter Zhu for helping with the GC headspace propanal analysis and measurement with peroxide value.
- Dr. Vikas Mittal for his guidance with the use of sigmaplot statistical software.
- Professor Douglas Dalgliesh for spending time with me to discuss the effects of heating on whey proteins.
- Doug Hopcroft for his assistance with sample preparation and helping me with image analysis on the Scanning electron Microscope.
- Jianyu Chen for patiently working with me to develop a modified method for transmission electron microscopy of my powder samples.

I’ve spent a lot of time at the Riddet Institute and even though I am not there anymore, the people that I worked with have special place in my heart. Thank you to my Riddet colleagues Ansley, Terri, Fliss, Willi, John, Shane, Sharon, Janiene, Natascha, Nok, Jack, Maria, Guilaume, Ajit, Carlos and Chris (Teddy).

A sincere and a very special thank you to the people who never stop giving, Shantanu Das, Jinita Das, Anwesha Sarkar, Preet Mohinder Singh and Jaspreet Kaur.

My family has always been there for me and understood what my research meant to me. Thank you Nancy, Anushka, Pervez and Ritu Taneja for being there for me.

Finally, but by no means least, thanks to Nimmi, my better half, and my son Arjun for their unconditional and almost unbelievable support. They are the most important people in my world. I dedicate this thesis to them.

Contents

List of Figures

List of Tables

List of Publications

Taneja, A., & Singh, H. (2012). Challenges for the delivery of long-chain n-3 fatty acids in functional foods. *Annual review of food science and technology*, *3*, 105-123.

Taneja, A., Ye, A., Jones, J. R., Archer, R., & Singh, H. (2013). Behaviour of oil droplets during spray drying of milk-protein-stabilised oil-in-water emulsions. *International Dairy Journal*, *28*(1), 15-23.

Taneja, A., Ye, A., & Singh, H. (2015). Influence of protein concentration on the stability of oil-in-water emulsions formed with aggregated milk proteins during spray drying. *Dairy Science & Technology*, *95*(3), 279-293.