

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.

Development of a functional model for tomato paste rheology

A thesis presented in partial fulfilment of the requirements for the degree of
Master of Food Technology

at Massey University,
Manawatu,
New Zealand.

Noorul Faridatul Akmal

2017

Abstract

Tomato paste is a seasonal product, processed for retail or packed aseptically in bulk to use as a raw ingredient for manufacturing many other tomato based products such as sauces, ketchup, and soups. Paste is added to formulated food products to provide flavour, tomato solids, and viscosity. Viscosity is mostly imparted by the insoluble solids but there is a contribution from the soluble solids in the tomato paste. Because the composition and physical nature of tomato solids varies with processing methods, tomato variety and maturity, the functional properties of tomato pastes can also be highly variable. The objective of this study was to develop methodologies that could be used to characterise tomato paste batches in such a way that the functionality of the paste is predictable. Ideally rheological functionality should be predictable from compositional information and characterisation should require a minimum of measurement effort.

This work explored how paste composition impacted on paste rheology and found that much of the variation in flow properties of tomato concentrates can be explained by appropriate characterisation of the water insoluble and soluble solids levels in the paste. Serum contributes to the flow behaviour of tomato paste due to the presence of soluble solids in the serum. In particular, it was found that it was primarily sugars that cause this effect, potentially by enhancing the pectin-pectin interactions in the WIS components of the paste. In this work it was found that there were measurable differences in serum viscosity between pastes, however good overall model predictions could be achieved without considering the serum phase beyond the soluble solids concentration.

The Herschel-Bulkley model was found to be the most appropriate model to describe the flow behaviour of tomato paste. Herschel Bulkley parameters could then be linked to the insoluble and soluble solids levels in the paste. For some pastes the model could be fitted with just one paste specific parameter plus four other generally fitted constants (which apply to any paste). When applied to other pastes however, at least one of the other parameters was also required to be paste specific. These parameters relate the yield stress and the flow behaviour index to the water insoluble solids content. Because these two parameters need to be fitted for individual pastes, it is thought that they are influenced by the particle size and shape and/or their composition of the WIS fraction. For example elongated particles will orientate within a flow field with varying shear rates, thereby influencing the flow behaviour index.

There is potential to fit the two key paste specific parameters for a paste from a single flow curve. This could provide an industry implementable method to characterise tomato paste batches. Such a characterisation method would be useful for predicting flow behaviour under different processing conditions and how dilution during product formulation will affect viscosity. Future work should be carried out to extend this work to those aims.

Acknowledgments

A very special gratitude goes to New Zealand Ministry of Foreign Affairs and Trade for giving me the opportunity to study at Massey University under New Zealand Aid Programme. It is like a dream come true. I still remember the day I got the phone call informing that I have been granted to the New Zealand Asian Scholarship Awards, that day is still one of the best days in my life.

I would also like to express my eternal gratitude to my supervisor, Professor John Bronlund for his unwavering support and encouragement, and for helping me with the mathematical modelling, it is an art of analysing result and I am so glad that I am able to learn it from the expert. I want to thank also to my second supervisor, Dr Michael Parker who provided me with rheological advice.

Appreciation also goes out to Michelle Tamehana who helped me with the rheometer and provided me with technical support.

Margaret Low and Jacinta Gould from New Zealand High Commission in Malaysia and Sylvia Hooker, Jamie Hooper, and Dave Broderick from International Student Support Massey University, thank you very much for being so approachable and for assisting me a lot with immigration policies as international student.

For those who contributed to this thesis indirectly. Thanks to Shu, Ava, and Sarie for a cup of coffee over the weekend for all these years. A special thanks goes to Anynda who always offered me a help and night ride home from the lab when I needed one. Thank you also to my social netball team for making my life more interesting and help me to release the tense by throwing ball every Saturday morning.

To my mother, thank you very much for your unconditional love, for teaching me so much about perseverance. Love you infinity.

Table of Contents

Abstract	iii
Acknowledgements	v
Table of Contents	vii
Chapter 1 Introduction	1
Chapter 2 Literature Review	3
2.1 Introduction	3
2.2 Tomato fruit anatomy	3
2.3 Tomato fruit composition	3
2.3.1 Soluble solids	4
2.3.2 Water insoluble solids (WIS)	7
2.4 Changes in tomato fruit during ripening	12
2.5 Tomato product processing	15
2.5.1 Tomato products	15
2.5.2 Tomato paste processing steps	16
2.6 Factors effecting tomato paste rheology	19
2.6.1 Chemical properties (composition, concentration, and chemical structure)	19
2.6.2 Particle properties (size, size distribution, morphology, and deformability)	22
2.7 Tomato paste rheology	22
2.7.1 Newtonian and non-Newtonian fluid	23
2.7.2 Yield stress	24
2.7.3 Models to describe the non-Newtonian flow behaviour of tomato products ...	24
2.7.4 Instruments used to measure rheological properties of tomato concentrates .	27
2.7.5 Functional model of tomato products	29
2.8 Conclusions	32
Chapter 3 Evaluation of flow models for tomato paste production	33
3.1 Introduction	33
3.2 Materials	33
3.3 Methods	34

3.3.1	Total solids	34
3.3.2	Soluble solids (° Brix)	34
3.3.3	Water insoluble solids content	34
3.3.4	Pulp fraction	35
3.3.5	Flow behaviour	35
3.4	Results and discussion	35
3.4.1	Compositional characteristics	35
3.4.2	Flow behaviour of tomato paste	36
3.4.3	Flow behaviour model	37
3.4.4	Correlation between physicochemical properties of tomato paste and Herschel-Bulkley parameters	38
3.4.5	Effect of dilution on Herschel-Bulkley parameter	41
3.5	Conclusions	45
Chapter 4	The effect of the serum phase on tomato paste rheology.	47
4.1	Introduction	47
4.2	Materials	47
4.3	Methods	48
4.3.1	Preparation of pulp and serum fractions	48
4.3.2	Serum viscosity	49
4.3.3	Water insoluble solid (% WIS) determination	49
4.3.4	Reconstituted tomato paste prepared with its own serum (PS)	49
4.3.5	Variation of serum phase properties at fixed WIS content	49
4.3.6	Flow behaviour measurement	50
4.4	Results and discussion	50
4.4.1	Water insoluble solid (% WIS)	50
4.4.2	Effect of pulp preparation method on reconstituted tomato paste rheology ...	54
4.4.3	The contribution of serum on the flow behaviour of tomato paste	55
4.5	Conclusion	58
Chapter 5	Development of a model for predicting rheology	59
5.1	Introduction	59
5.2	Materials and Methods	59
5.3	Results and Discussion	62
5.3.1	Effect of %WIS and °Brix on flow behaviour data	62
5.3.2	Effect of %WIS and °Brix on Herschel-Bulkley parameters	64

5.4	Mathematical model development	67
5.4.1	Mathematical model Set 1 (Exponential model)	67
5.4.2	Mathematical model Set 2 (Power model)	67
5.5	Model fitting	67
5.6	Sensitivity analysis	68
5.7	Validation against blends of TP1 and TP4	80
5.7.1	Methods	80
5.7.2	Model fitting and performance	80
5.8	Validation against TP2, TP3 and TP5 at different dilutions	82
5.9	Conclusions	87
Conclusions and Recommendations		89
References		91

List of Tables

Table 2.1 - Composition of organic acids in fresh and processed tomato juice (Gould, 1992).....	5
Table 2.2 - Amino acid content of fresh and processed tomato juice (Gould, 1992).....	5
Table 2.3 - Carotenoids content in tomato fruit (Shi & LeMaguer, 2000).....	6
Table 2.4 - Minerals in normal ripe tomato fruit (Gould, 1992).....	6
Table 2.5 - Purified PME and PG activity in four different tomato varieties (Rodrigo et al., 2006).	11
Table 2.6 - USDA tomatoes classes (Barrett, Garcia & Wayne, 1998).	12
Table 2.7 - Definitions of processed tomato products (Hayes et al., 1998)	15
Table 2.8 - Effect of cultivar, maturity and growing season on tomato paste attributes (Garcia & Barrett, 2006).....	21
Table 2.9 - Relevant shear rate measurement ranges for viscometers and rheometers (Carrington & Langridge, 2005)	28
Table 2.10 - Instruments and measuring systems used to measure the steady flow behaviour of tomato products.....	30
Table 3-1 - General information of tomato paste used in this study	33
Table 3-2 Compositional properties of tomato paste.	36
Table 3-3 - Power law and Hershel Bulkley parameters for each tomato paste.....	38
Table 3-4 - Values of Herschel-Bulkley parameter reported by other researchers.....	39
Table 3-5 - °Brix, total solid content and Herschel-Bulkley parameters of tomato paste TP5 at different concentrations.....	41
Table 4.1 - Batch number and chemical properties of tomato paste TP1 and TP4.....	47
Table 4.2 - Reconstituted tomato paste using different continuous phase.....	49
Table 4.3 - Water insoluble solid content (WIS) of tomato pastes TP1 and TP4 obtained by the drying method.	50
Table 4.4 - Viscosity of tomato juice and reconstituted tomato juice (Whittenberger & Nutting, 1958)..	56
Table 4.5 - Concentration of metal ion in tomato paste, pulp and serum of tomato paste TP1.	57
Table 4.6 - pH of sample used in the study.	58
Table 5.1 - Composition of the washed pulp samples produced from Tomato pulps 1 and 4.....	60
Table 5.2 - Summary of target compositions for 25 different samples produced for TP1 and TP4	60
Table 5.3 - Values of model parameters for tomato concentrate TP1 and TP4 for exponential model. ...	67
Table 5.4 - Values of model parameters for tomato concentrate TP1 and TP4 for power model.....	67
Table 5.5 - Range of parameters value used in the sensitivity analysis (exponential model).....	68
Table 5.6 - Range of parameters value used in the sensitivity analysis (power model).....	73
Table 5.7 - Exponential model values obtained from common parameters n_{slope} , K_{slope} and σ_{oslope} and paste specific parameters K_b and σ_{ob}	74
Table 5.8 - Exponential model values obtained from common parameters n_{slope} , K_{slope} , σ_{oslope} and K_b and paste specific parameter σ_{ob}	77
Table 5.9 - Summary of blended paste compositions	80
Table 5.10 - Exponential model values obtained from common parameters n_{slope} , K_{slope} , σ_{oslope} and K_b and paste specific parameter σ_{ob}	80
Table 5.11 - Summary of model fits to TP2, TP3 and TP5 (common parameters indicated in italics)	83

List of Figures

Figure 2-1 - Tomato fruit anatomy.	3
Figure 2-2 - Total solids compositions of fresh tomato fruit (Davies and Hobson, 1981).	4
Figure 2-3 - Homogalacturonan primary structure (Ridley, O'Neill, and Mohnen, 2001).	8
Figure 2-4 - Rhamnogalacturonan I structure (Ridley, O'Neil and Mohnen, 2001).	9
Figure 2-5 - Calcium-pectin-crosslink as egg box model (Voragen, Coenen, Verhoef, and Schols, 2009). ..	10
Figure 2-6 - Schematic illustration of pectinmethylesterase (PME) and polygalacturonase (PG) activity upon homogalacturonan (Sila <i>et. al</i> , 2009).	11
Figure 2-7 - Pectin methylesterase (PME) activity during tomato ripening (Frenkel, et al., 1998).	13
Figure 2-8 - Polygalacturonase (PG) activity during tomato ripening (Eriksson et al., 2004).	14
Figure 2-9 - Sepharose CL-28-300 profiles of CDTA soluble pectin derived from Sunny tomato fruit alcohol insoluble solid (AIS) (Huber & O'Donoghue, 1993).	14
Figure 2-10 - Flow diagram for canned tomato paste production (Moresi & Liverotti, 1982).	18
Figure 2-11 - A schematic representation of the composition of plant-tissue-based food suspensions Moelants (2014).	19
Figure 2-12 - Newtonian fluid and time independent non-Newtonian fluid (Bourne, 2002).	23
Figure 2-13 - Linear relationship between shear stress and shear rate for shear thinning fluid obeying power law (Holdsworth, 1971).	24
Figure 3.1 - Plot of shear stress vs shear rate of tomato pastes including replicates.	36
Figure 3.2 - Correlation between Herschel-Bulkley parameters and compositional properties.	40
Figure 3.3 - Effect of dilution on Herschel-Bulkley parameters.	43
Figure 3.4 - Relationship between physicochemical properties of tomato concentrates and Herschel-Bulkley parameters.	44
Figure 4.1 - Schematic overview of tomato pulp fraction separation.	48
Figure 4.2 - Tomato paste model.	51
Figure 4.3 - Comparison of percentage of soluble solid determine using drying method with refractometer.	52
Figure 4.4 - Molar mass distributions of soluble polysaccharides in tomato serum. Elution times of pullulan standards are indicated to allow for a rough estimation of the molar masses (in Dalton) (Moelants et al. 2013).	53
Figure 4.5 - Shear rate versus shear stress curves of original tomato paste TP1 and reconstituted tomato paste with its own serum (PS). The data was plotted as the average of three replicates.	54
Figure 4.6 - Shear rate versus shear stress plots of reconstituted TP1 prepared with serum (PS) and water (PW). The data was plotted as the average of three replicates.	55
Figure 4.7 - Shear rate versus shear stress plot of reconstituted TP1 prepared with serum (PS), 18°Brix fructose solution (PF18), 28 °Brix fructose solution (PF28), matched calcium concentration (PC), excess calcium (PCX). The data are plotted as the average of three replicates.	57
Figure 5.1 - Relationship between physicochemical properties of tomato concentrates and Herschel-Bulkley parameters. (Figure 3.4 after %WIS data recalculation for adjusted °Brix).	61
Figure 5.2 - Shear stress versus shear rate data for reconstituted tomato concentrates at different % WIS and °Brix prepared from tomato pulps TP1 (A) and TP4 (B).	63
Figure 5.3 - Effect of % WIS (A) and °Brix (B) on Herschel-Bulkley parameters for tomato concentrates prepared from tomato pulp TP1.	65
Figure 5.4 - Effect of % WIS (A) and °Brix (B) on Herschel-Bulkley parameters for tomato concentrates prepared from tomato pulp TP4.	66
Figure 5.5 - Comparison of tomato concentrates viscosity obtained from experiment (***) and from fitting exponential model (____) for TP1.	69
Figure 5.6 - Comparison of tomato concentrate viscosity obtained from experiment (***) and from fitting exponential model (____) for TP4.	70

Figure 5.7 - Comparison of tomato concentrates viscosity obtained from experiment (***) and from fitting power model (____) for TP1.	71
Figure 5.8 - Comparison of tomato concentrates viscosity obtained from experiment (***) and from fitting power model (____) for TP4.	72
Figure 5.9 - Effect of parameter change on exponential model predictions. - Each parameter range was scaled from 0 to 1, corresponding to the range specified in Table 5.5.	73
Figure 5.10 - Effect of parameter change on power model predictions. - Each parameter range was scaled from 0 to 1, corresponding to the range specified in Table 5.6.	74
Figure 5.11 - Comparison of tomato concentrates viscosity obtained from experiment (***) and from fitting exponential model using combined parameters in Table 5.7 (____) for TP1.	75
Figure 5.12 - Comparison of tomato concentrates viscosity obtained from experiment (***) and from fitting exponential model using combined parameters in Table 5.7 (____) for TP4.	76
Figure 5.13 - Comparison of tomato concentrates viscosity obtained from experiment (***) and from fitting exponential model using combined parameters in Table 5.8 (____) for TP1.	78
Figure 5.14 - Comparison of tomato concentrates viscosity obtained from experiment (***) and from fitting exponential model using combined parameters in Table 5.8 (____) for TP4.	79
Figure 5.15 - Predicted and experimental viscosity for blends of TP1 and TP4 using parameters summarised in Table 5.10. Note that the four curves on each plot are for dilutions.	81
Figure 5.16 - Relationship between σ_{ob} and the proportion of TP1 and TP4 for blends.	82
Figure 5.17 - Model predictions for TP2, TP3 and TP5 when all parameters were paste specific.	84
Figure 5.18 - Model predictions for TP2, TP3 and TP5 when only σ_{ob} was paste specific.	85
Figure 5.19 - Model predictions for TP2, TP3 and TP5 when σ_{ob} and n_{slope} were paste specific.	86