

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.

Shelf life of Goat Infant Formula Powder

A thesis presented in partial fulfilment of the requirements for the degree

of Master of Engineering

in

Chemical and Bioprocess Engineering

at Massey University, Palmerston North,

New Zealand.

Po-Han (Leo) Lai

B. Eng (Hons)

2015

Abstract

Oxidative rancidity was found to be a problem in goat milk infant formula powder. Oxidative rancidity results from the lipid oxidation processes, where oxygen reacts with unsaturated fatty acids from milk powder to produce lipid hydroperoxides and radicals, the primary oxidation products. These primary oxidation products are odourless; however, they are very reactive to breakdown into hydrocarbons, aldehydes and ketones. Aldehydes have low flavour threshold limits and are responsible for causing the rancid flavour in the milk powder.

Peroxide value (PV) is one of the most widely used tests for oxidative rancidity as it is a measure of the concentration of lipid hydroperoxides; however, it is difficult to provide a specific guideline relating PV to rancidity. A reliable test is needed to determine whether the goat milk infant formula powder is unacceptable due to oxidative rancidity to the consumer. It was found that oxygen was a useful parameter to monitor lipid oxidation. Oxygen is the main reactant in lipid oxidation, and the rate of oxygen consumption is a useful tool to track lipid oxidation. Hexanal was determined to be the main secondary oxidation product responsible for the off flavour of milk powder.

An experiment of accelerated storage trials for two infant formula products (Powder A and Powder B) was conducted by using a range of higher temperatures from 37°C to 57°C over a period of 12 to 24 weeks. Headspace oxygen and headspace hexanal of the milk powder in the glass vials were measured over the storage period. Sensory analysis was also conducted in parallel with the storage trial to provide a relationship between the sensory score and hexanal concentration, ultimately determining the unacceptable flavour threshold limit for hexanal concentration. The chemical kinetic constants were estimated by fitting a general n^{th} order reaction with an Arrhenius law model with the concentration of oxygen obtained experimentally. The model followed half order reaction for both products. The Arrhenius rate constant, k_0 , and activation energy, E , were found to be $7.8 \times 10^9 \text{ \%}^{0.5} \text{ week}^{-1}$ and 62.0 kJ mol^{-1} for Powder A and $1.34 \times 10^7 \text{ \%}^{0.5} \text{ week}^{-1}$ and $45.60 \text{ kJ mol}^{-1}$ for Powder B.

It was discovered that oxygen and hexanal were highly correlated with R^2 of 0.905 for Powder A and R^2 of 0.918 for Powder B when fitted exponentially. It was predicted that Powder A would be unacceptable after a storage time of 40 weeks, and 31 weeks for Powder B under 25°C storage temperature.

Data tables were generated to outline the different maximum storage times allowed with different storage temperatures and different initial storage oxygen concentration.

Acknowledgements

I would like to express my deepest appreciation to New Image Group Ltd., who provided me with this exciting project. In particular, I would like to thank Mr Todd Downie for all the support and help, supplying all the necessary information for this project.

I would like to express my gratitude to my Chief supervisor, Professor Tony Paterson, and supervisors Colin Brown and John Bronlund for sparing their time to provide me with useful guidance, stimulating suggestions and encouragement. Thank you for your constructive criticisms and professional advice. I appreciated the time and the effort you committed for our meetings.

My gratitude is extended to Ann-Marie Jackson, John Edwards and John Sykes for their assistance and all the technical support in using and maintaining the experimental equipment.

I would like to thank my parents for their support and encouragement throughout my entire project. Thank you dad and mum for the care packages you have sent me.

And last but not least, I thank God for His love and bountiful grace that always strengthen me. I am always reminded by this verse: 1 Peter 5:7 "Casting all your anxiety on Him because it matters to Him concerning you".

Table of Contents

Abstract.....	III
Acknowledgements.....	IV
List of Figures	IX
List of Tables	XI
Chapter 1 Introduction	12
1 Introduction	12
Chapter 2 Literature Review	13
2.0 Introduction	13
2.1 Physical form of milk fat	13
2.1.1 Phospholipids and Fatty acids compositions of milk Fats.....	14
2.1.2 Significance of Milk fat.....	15
2.2 Rancidity.....	15
2.3 Lipid Oxidation	16
2.3.1 Mechanism of lipid autoxidation reactions	16
2.3.2 Primary importance of Fatty acids.....	19
2.3.3 Oxidation Products.....	20
2.3.4 Factors affecting oxidation of lipids.....	21
2.3.4.1 Oxygen	21
2.3.4.2 Temperature	21
2.3.4.3 Light.....	21
2.3.4.4 Metals (pro-oxidants).....	22
2.3.4.5 Water activity.....	22
2.3.4.6 Degree of Saturation of lipids	23
2.4 Methods for measuring lipid oxidation	24
2.4.1 Peroxide Value (PV).....	24
2.4.2 Para-anisidine value	25
2.4.3 Totox value.....	26
2.4.4 Thiobarbituric acid (TBA)	26
2.4.5 Gas chromatography.....	27
2.4.6 Rancimat	28
2.5 Lipid oxidation versus sensory	29
2.5.1 Hydroperoxides concentration	31
2.5.2 Relationship between sensory test and chemical test	31

2.6	Lipolytic Rancidity	34
2.6.1	Enzyme	34
2.6.2	Lipoprotein Lipase	34
2.6.3	Lipases of psychrotrophic bacteria	35
2.6.4	Causes of lipolytic rancidity in milk and milk products	35
2.6.4.1	Induced lipolysis	35
2.6.4.2	Spontaneous Lipolysis	35
2.6.5	Effects of lipolysis in milk	36
2.6.6	Determination of Free Fatty Acids in milk products	36
2.7	Oxidative Rancidity versus Lipolytic Rancidity	37
2.8	Effects of packaging in the lipid oxidation	37
2.8.1	Bulk Density	38
2.9	Oxygen as an important parameter in lipid oxidation	39
2.10	Storage Trial	39
2.10.1	Methods combination	40
2.10.2	Sensory Test	40
2.11	Conclusion	40
	Chapter 3 Preliminary Experiment	42
3	Lipolytic Rancidity	42
3.1	Introduction	42
3.2	Method	42
3.2.1	Fat Extraction	42
3.2.2	Determination of fat acidity	43
3.3	Result	44
3.4	Discussion	44
3.5	Conclusion	45
	Chapter 4 Model Development	46
4	Introduction	46
4.1	Lipid oxidation Reaction	46
4.2	Rancidity development	47
4.2.1	FroPeroxide value	47
4.2.2	Oxygen Consumption	47
4.2.3	Hexanal Formation	48
4.2.4	Measurement of oxidation reaction and rancidity	49

4.3	Sensory Analysis.....	49
4.4	Reaction Kinetics.....	49
4.4.1	Reaction order	51
4.5	Conclusion.....	53
Chapter 5 Method Development.....		54
5	Introduction	54
5.1	Storage Test	54
5.1.1	Storage Conditions.....	54
5.2	Headspace analysis	56
5.2.1	Headspace Gas Chromatography.....	56
5.2.1.1	Static Headspace vs. Dynamic Headspace	56
5.2.2	Selection of the vial and sample volume	57
5.2.3	GC operational conditions	57
5.2.3.1	Standard calibration for GC.....	58
5.2.3.2	Gas Chromatography	59
5.3	Peroxide Value	60
5.4	Sensory Analysis.....	60
5.4.1	Experimental Design	60
5.5	Conclusion.....	62
Chapter 6 Results and Discussion		63
6	Introduction	63
6.1	Storage Trial	63
6.1.1	Particle Size of the powder	63
6.1.2	Fatty Acid Profile of the powder	64
6.2	Peroxide value.....	66
6.3	Oxygen Consumption.....	68
6.4	Hexanal	71
6.4.1	Hexanal Degradation.....	73
6.4.2	Additional Secondary and tertiary oxidation Products.....	76
6.5	Sensory.....	76
6.5.1	Trial two sensory results	81
6.5.2	Improvements to the sensory analysis	81
6.6	Reaction Kinetics.....	81
6.6.1	Prediction of oxygen Consumption.....	84

6.7	Relationship between Oxygen and Hexanal	85
6.8	Application of the kinetic model.....	87
6.8.1	Usefulness of the model	88
7	Conclusions and Suggestions for Future Work	90
7.1	Conclusions	90
7.2	Suggestions for future Works	91
8	References	92
	Nomenclature	97
9	Appendices.....	98
9.1	Raw data	98
9.2	Matlab [®] code to predict oxygen from given kinetic parameters and experimental data ...	103
9.2.1	Function file	105
9.2.2	Script file	105
9.3	Data table.....	107
9.3.1	Powder A.....	107
9.3.2	Powder B.....	109

List of Figures

Figure 2.3-1: Autooxidation mechanisms involving initiation, propagation and termination.	17
Figure 2.3-2: Oxidation curves for different types of food where the y-axis might represent a measurement of primary or secondary oxidation products. At values above the sensory cut-off line, trained panelists found the product unacceptably oxidised (Barden & Decker, 2013).	18
Figure 2.3-3: Mechanism of oleate autoxidation forming hydroperoxides Frankel <i>et al.</i> (1980).	20
Figure 2.3-4: Stability of foods as a function of water activity (Theodore P. Labuza & Dugan, 1971).	23
Figure 2.4-1: Concentration of PV in infant formula products over time in various temperatures (Romeu-Nadal et al., 2007).	24
Figure 2.4-2: Reaction between p-anisidine reagent and malonaldehyde (F. Shahidi & Wanasundara, 2002).	26
Figure 2.4-3: Reaction of 2 thiobarbituric acids (TBA) and malonaldehyde (MA) (Antolovich, Prenzler, Patsalides, McDonald, & Robards, 2002).	27
Figure 2.4-4: Chromatograms of volatile compounds in infant formula at 0 weeks (A) and after 4 weeks (B). Peaks numbered from 1 to 4 correspond to 1, propanal; 2, pentanal; 3, butyl acetate; 4, hexanal (Romeu-Nadal et al., 2004).	28
Figure 2.5-1: left: Relationship between PV and flavour acceptability of fish oil. Right: Relationship between the AV and acceptability of fish oil, where score of 1 is totally unacceptable (Jacobsen, 1999)	30
Figure 2.5-2: Concentration of oxidised milk versus the optical density of the TBA test from two types of milk (King, 1962).	32
Figure 2.5-3: Extent of reaction as a function of time (Theodore P. Labuza & Dugan, 1971)	33
Figure 2.6-1: Fatty acids, lipolysis, and goat flavour (Chilliard, Ferlay, Rouel, & Lamberet, 2003).	34
Figure 3.2-1: Experimental set up for Soxhlet extraction.	43
Figure 3.2-2: Fat acidity titration set up.	43
Figure 4.1-1: Lipid oxidation pathway of the lipids.....	47
Figure 5.1-1: Milk powder stored in the glass vial with rubber septum and fully sealed aluminium cap.	55
Figure 5.2-1: Diagram of the headspace analysis.	56
Figure 5.2-2: Hexanal standard curve.	58
Figure 5.2-3: Oxygen Standard curve.....	59
Figure 5.2-4: Chromatogram of oxygen peak (right) and air peak (left).....	59
Figure 5.2-5: Chromatogram of hexanal peak and unknown peaks developed through the storage period.	60
Figure 6.2-1: First trial of the PV result of Powder A and Powder B (A1 and B1).	66
Figure 6.2-2: Peroxide value of A2.	67
Figure 6.2-3: Peroxide value of B2.	68
Figure 6.3-1: Headspace oxygen concentration throughout the storage period of the first trial result.	68
Figure 6.3-2: Headspace oxygen concentration throughout the storage period of the second trial result.	70
Figure 6.3-3: Comparison of the oxygen concentration over the storage period between first and second trials of Powder B.	70
Figure 6.3-4: Comparison of the oxygen concentration over the storage period between first and second trials of Powder A.	71

Figure 6.4-1: Chromatogram of the hexanal peak obtained from GC-MS.....	72
Figure 6.4-2: Experimental results of the development of hexanal over the storage period for the first trial of Powder A and Powder B (A1 and B1).....	72
Figure 6.4-3: Experimental results of the development of hexanal over the storage period for the second trial of Powder A and Powder B (A2 and b2).....	73
Figure 6.4-4: The formation of hydroperoxides from linoleic acid oxidation.....	74
Figure 6.4-5: Formation of hexanal from the degradation of lipid hydroperoxide.	74
Figure 6.4-6: Chromatogram in week 0 of the storage period showing only the oxygen peak.	75
Figure 6.4-7: Chromatogram showing the carbon dioxide peak, carbon monoxide peak and oxygen peak in week 5 at a storage temperature of 57°C.	76
Figure 6.5-1: Sensory score for the first trial of Powder A.	77
Figure 6.5-2: Sensory score for the first trial of Powder B.....	78
Figure 6.5-3: ANOVA of sensory scores between three storage temperatures of Powder A1 and Powder B1 in the storage period.	80
Figure 6.6-1: Fitted profile of the half order kinetic model compared with the experimental data of the oxygen consumption from headspace analysis of Powder A1 (first trial).	82
Figure 6.6-2: Fitted profile of the half order kinetic model compared with the experimental data of the oxygen consumption from headspace analysis of Powder B1 (first trial).	82
Figure 6.6-3: Fitted profile of the half order kinetic model compared with the experimental data of the oxygen consumption from headspace analysis of Powder A (second trial).	83
Figure 6.6-4: Fitted profile of the half order kinetic model compared with the experimental data of the oxygen consumption from headspace analysis of Powder B (second trial).	83
Figure 6.6-5: Prediction of headspace oxygen consumption under storage temperature of 25°C for Powder A1 and A2 kinetic data.....	84
Figure 6.6-6: Prediction of headspace oxygen consumption under storage temperature of 25°C Powder B1 and B2 kinetic data.	84
Figure 6.7-1: The relationship between the production of hexanal and the consumption of oxygen, expressed as a change in oxygen content for Powder A (Trial 1+Trial 2).	86
Figure 6.7-2: The relationship between the production of hexanal and the consumption of oxygen, expressed as a change in oxygen content for Powder B (Trial 1 only).	86
Figure 6.8-1: Predicted oxygen consumption as a function of time for Powder A at 25°C and 20.9% O ₂	87
Figure 6.8-2: Predicted oxygen consumption as a function of time for Powder B at 25°C and 20.9% O ₂	88

List of Tables

Table 2.1-1: Milk lipid content from some species (Christie, 1978).	14
Table 2.1-2: Composition of phospholipids in milk from different species (Fox, 1995).	14
Table 2.1-3: Fatty acids in milk triglycerides or total lipids from various species (Fox, 1995)	15
Table 2.3-1: Major fatty acids found in foods.....	19
Table 2.5-1: Correlation coefficient between 1/FTV and all chemical tests for measuring the intensity of oxidised flavour (Lillard & Day, 1961).....	31
Table 2.5-2: Relationship between sensory evaluation and intensity of oxidised off-flavour and optical density readings of milk (Clark & Bodyfelt, 2009).....	32
Table 2.5-3: Olfactory Perception Thresholds of various flavour compounds isolated from dairy foods (ppm) (Theodore P. Labuza & Dugan, 1971).....	33
Table 2.6-1: Concentrations of C4 to C-12 free fatty acids (FFA) in rancid milk (Fox, 1995).	36
Table 2.8-1: Degree of protection required by different foods and beverages (assuming 1 year shelf life at 25°C) (Salame, 1974).....	38
Table 3.3-1: Fat acidity of the goat milk powder (New Image Group Ltd) obtained from titration.	44
Table 4.2-1: The specific breakdown of unsaturated fatty acids to primary oxidation product hydroperoxides and secondary oxidation product aldehydes.	49
Table 5.4-1: The sensory score for comparison between the control and the sample.	61
Table 6.1-1: Size distribution of the milk powder for each product.....	64
Table 6.1-2: Fatty acid profile analysis of the powder g/100g powder.	65
Table 6.5-1: Sensory score corresponding to the hexanal concentration for the first trial of Powder A.	78
Table 6.5-2: Sensory score corresponding to the hexanal concentration for the first trial of Powder B	79
Table 6.8-1: Maximum storage time (in weeks) under certain storage temperature and initial storage oxygen concentration for Powder A.	89
Table 6.8-2: Maximum storage time (in weeks) under certain storage temperature and initial storage oxygen concentration for Powder B.	89
Table 9-1: Raw data for trial one Powder A and Powder B stored under 37°C.	98
Table 9-2: Raw data for trial one Powder A and Powder B stored under 47°C.	99
Table 9-3: Raw data for trial one Powder A and Powder B stored under 57°C.	100
Table 9-4: Raw data for trial two Powder A and Powder B stored under 47°C.	101
Table 9-5: Raw data for trial two Powder A and Powder B stored under 57°C.	102
Table 9-6: Sensory scores raw data for both A1 & B1.	103
Table 9-7: Concentration of oxygen consumption (%) of Powder A with the storage period under different storage temperatures at initial oxygen concentration of 20.5%. With maximum 15% consumption oxygen allowed.	107
Table 9-8: Oxygen consumption concentration (%) under various initial oxygen concentrations.....	108
Table 9-9: Concentration of oxygen consumption (%) of Powder B with the storage period under different storage temperatures at initial oxygen concentration of 20.5%. With maximum 15% consumption oxygen allowed.	109
Table 9-10: Oxygen consumption concentration (%) under various initial oxygen concentrations... ..	110