

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.

THE KINETICS OF QUALITY DETERIORATION
IN LEMON JUICES AND CONCENTRATES
DURING STORAGE

A THESIS PRESENTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF TECHNOLOGY IN FOOD TECHNOLOGY
AT MASSEY UNIVERSITY

CHRISTINE MARIE L. SAMANIEGO

1984

ABSTRACT

The effects of initial dissolved oxygen content, temperature and total soluble solids content on the kinetics of the quality deterioration in lemon juices (9 °Brix) and concentrates (20-50 °Brix) during storage were determined.

The parameters used to measure quality loss were ascorbic acid retention, nonenzymic browning, and sensory quality. The suitability of furfural and hydroxymethylfurfural (HMF) as indices of quality deterioration was also investigated.

Ascorbic acid degradation and HMF formation were observed to follow a first-order reaction model while browning and furfural formation followed a zero-order model. Temperature dependence of the different reactions could be described by the linear and Arrhenius expressions over the temperature range of 10 to 36°C.

The initial dissolved oxygen content (0.41, 1.44 and 3.74 mg/L) did not significantly affect the rate of ascorbic acid degradation and furfural formation in single-strength lemon juice stored at 36°C. However, browning and HMF formation were significantly higher in the juice with 3.74 mg/L dissolved oxygen content than in the samples with the other two oxygen contents.

The total soluble solids concentration affected the rates of the different reactions but not to such a significant extent as the temperature effect. Ascorbic acid retention was observed to increase with an increase in soluble solids content.

The rate of the browning reaction generally increased with increases in soluble solids content for the 20 to 50 °Brix juice samples. The rate of furfural formation consistently increased with increases in soluble solids level at 36°C, but was not as consistent at 10 and 20°C.

The rate constants and activation energy values of the different reactions for the 9 °Brix juice were considerably higher than those for the 20 °Brix concentrate. These observations and the poor correlation obtained between ascorbic acid retention and browning, and between ascorbic acid retention and furfural formation for the higher Brix concentrates, suggested that different reactions or reaction mechanisms predominated in single-strength juice compared with concentrates.

Furfural could serve as an index of quality deterioration in single-strength lemon juice but not in concentrates (20-50 °Brix) due to its simultaneous formation and decomposition at these high soluble solids levels.

The sensory panel perceived significant changes in colour in the juices prior to changes in flavour. The browning reaction should thus be the main criterion in the determination of storage life.

Low temperature storage is essential for optimum storage stability. Over a 16-week storage period at 10°C, it is suggested that lemon juice be stored as a 50 °Brix concentrate. Some advantages of storing lemon juice at such high soluble solids levels are high retention of ascorbic acid and flavour properties, and reduction in storage and distribution costs. To extend the storage life of lemon juice concentrates beyond four months, storage temperatures lower than 10°C would be necessary so that the extent of browning would not reach unacceptable levels.

ACKNOWLEDGEMENTS

I wish to thank my supervisor, Dr Gordon Robertson for all the help, time and encouragement he provided during the course of this work.

Acknowledgement is extended to the New Zealand and the Philippine governments and to my company, the Food Terminal Inc. who made it possible for me to undertake my studies in this country.

Appreciation is also extended to Mr T. Gracie, Mrs M. Caldwell and Mrs M.C. Bewley for their technical assistance; to Mr T.S. Wong for his help in the computer work and for doing the illustrations of this thesis; to the post-graduate students and staff of the Faculty of Technology who were members of the sensory panel; to Noemi, Alfredo, Florante, Alberto and Chaturong for their help in conducting the experiments; and to Mrs V. Fieldsend for typing this thesis.

I am also grateful to my family for their continued support and interest throughout the entire degree course.

TABLE OF CONTENTS

	PAGE
ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
LIST OF TABLES	x
LIST OF FIGURES	xv
 CHAPTER 1: INTRODUCTION	 1
 CHAPTER 2: LITERATURE REVIEW	 3
2.1 Ascorbic Acid Degradation	3
2.2 Factors Affecting Ascorbic Acid Degradation and Nonenzymic Browning	8
2.2.1 Storage Time and Temperature	8
2.2.2 pH	12
2.2.3 Soluble Solids Content	12
2.2.4 Citric Acid	14
2.2.5 Oxygen	15
2.3 Kinetics of Ascorbic Acid Degradation and Nonenzymic Browning	16
2.3.1 Reaction Order	16
2.3.2 Reaction Rates	18
2.4 Sensory Quality of Citrus Juice During Storage	20
 CHAPTER 3: MATERIALS AND METHODS	 22
3.1 Materials	22
3.1.1 Lemon Juice	22
3.1.2 Calamansi Juice	22
3.1.3 Lemon Concentrate	23
3.2 Determination of Common Juice Parameters	23
3.2.1 Total Soluble Solids (TSS)	23
3.2.2 Titratable Acidity	23
3.2.3 Brix : Acid Ratio	24
3.2.4 pH	24

TABLE OF CONTENTS CONTINUED:

	PAGE
CHAPTER 3: CONTINUED	
3.3 Determination of Ascorbic Acid	24
3.3.1 Background	24
3.3.2 Procedure	25
3.3.3 Reliability of the Method	28
3.4 Determination of Furfural	28
3.4.1 Background	28
3.4.2 Procedure	29
3.4.3 Reliability of the Method	31
3.5 Determination of Hydroxymethylfurfural (HMF)	32
3.5.1 Background	32
3.5.2 Procedure	32
3.5.3 Reliability of the Method	33
3.6 Browning Measurements	34
3.6.1 Spectrophotometric Method	34
3.6.1.1 Background	34
3.6.1.2 Procedure	35
3.6.1.3 Reliability of the Method	35
3.6.2 Measurement with the use of the Neotec Du-Colorimeter	36
3.6.2.1 Background	36
3.6.2.2 Procedure	37
3.6.2.3 Reliability of the Method	38
3.7 Determination of Dissolved Oxygen	38
3.7.1 Background	38
3.7.2 Procedure	39
3.7.3 Reliability of the Method	39
3.8 Determination of Citric Acid	40
3.8.1 Background	40
3.8.2 Procedure	41
3.9 Sensory Evaluation	41
3.9.1 Background of the Magnitude Estimation Method	43
3.9.2 Background of the Descriptive Scoring Method	43

TABLE OF CONTENTS CONTINUED:

	PAGE
CHAPTER 3: CONTINUED	
3.9.3 Experimental Conditions and Procedure	45
3.9.4 Data Interpretation	47
CHAPTER 4: PRELIMINARY EXPERIMENTS	49
4.1 Quality Changes in Lemon Juice During Accelerated Temperature Storage (55°C): Objective Parameters	49
4.1.1 Introduction	49
4.1.2 Experimental	49
4.1.3 Results and Discussion	50
4.1.4 Conclusion	54
4.2 Quality Changes in Lemon Juice During Accelerated Temperature Storage (55°C): Sensory Parameters	55
4.2.1 Introduction	55
4.2.2 Experimental	55
4.2.3 Results and Discussion	56
4.2.4 Conclusion	60
4.3 Quality Changes in Lemon Juice During Accelerated Temperature Storage (55°C): Second Trial	60
4.3.1 Introduction	60
4.3.2 Experimental	60
4.3.3 Results and Discussion	61
4.3.4 Conclusion	67
4.4 Quality Changes in Calamansi Juice During Accelerated Temperature Storage (55°C)	68
4.4.1 Introduction	68
4.4.2 Experimental	68
4.4.3 Results and Discussion	69
4.4.4 Conclusion	72

TABLE OF CONTENTS: CONTINUED

	PAGE
CHAPTER 5: THE EFFECT OF INITIAL DISSOLVED OXYGEN CONTENT ON THE RATE OF QUALITY DETERIORATION IN LEMON JUICE DURING STORAGE	73
5.1 Introduction	73
5.2 Experimental	75
5.2.1 Experimental Conditions and Procedure	75
5.2.2 Data Analysis	76
5.3 Results and Discussion	77
5.3.1 Comparison of the Regression and Point-by-point Analyses	77
5.3.2 Dissolved Oxygen	81
5.3.3 Acidity and Total Soluble Solids	83
5.3.4 Ascorbic Acid	83
5.3.5 Browning	87
5.3.6 Furfural and Hydroxymethylfurfural (HMF)	91
5.4 Conclusion	91
CHAPTER 6: THE EFFECTS OF STORAGE TEMPERATURE AND TOTAL SOLUBLE SOLIDS CONTENT ON THE KINETICS OF QUALITY DETERIORATION IN LEMON JUICE	96
6.1 Introduction	96
6.2 Experimental	97
6.2.1 Experimental Conditions and Procedure	97
6.2.2 Data Analysis	99
6.3 Results and Discussion	100
6.3.1 Acidity and Total Soluble Solids	101
6.3.2 Ascorbic Acid	101
6.3.2.1 Effects of Temperature and Total Soluble Solids Content on Ascorbic Acid Retention	101
6.3.2.2 Kinetics of Ascorbic Acid Degradation	109

TABLE OF CONTENTS: CONTINUED

	PAGE
CHAPTER 6: CONTINUED	
6.3.3 Browning	121
6.3.3.1 Effects of Temperature and Total Soluble Solids Content on the Degree of Browning	121
6.3.3.2 Kinetics of the Browning Reaction	130
6.3.3.3 Predictive Model for Browning	139
6.3.4 Furfural	142
6.3.5 Sensory Evaluation	151
6.3.5.1 Flavour	151
6.3.5.2 Colour	158
6.3.6 Storage Life	164
6.3.6.1 Storage Life Determi- nation	164
6.3.6.2 Predictive Model for Storage Life	172
6.4 Conclusion	177
CHAPTER 7: SUMMARY AND CONCLUSIONS	180
BIBLIOGRAPHY	183
APPENDICES	197

LIST OF TABLES

TABLE		PAGE
2.1	Studies on the vitamin C retention in processed orange, tangerine, and grapefruit juices	9
3.1	Ascorbic acid content of fresh lemon juice	28
3.2	Furfural content of fresh lemon juice	31
3.3	HMF content of fresh lemon juice	34
3.4	Browning index of fresh lemon juice	36
3.5	Browning measurements of fresh lemon juice	38
3.6	Dissolved oxygen content (mg/L) of distilled water and lemon juice	40
4.1	Quality changes in lemon juice during storage (55°C)	50
4.2	Correlation coefficients among the quality parameters of lemon juice	52
4.3	Changes in flavour and colour of lemon juice during storage at 55°C	57
4.4	Correlation coefficients among the quality parameters of lemon juice	57
4.5	Quality changes in lemon juice during storage at 55°C	62

LIST OF TABLES: CONTINUED

TABLE	PAGE
4.6 Correlation coefficients among the different quality parameters measured in lemon juice stored at 55°C	66
4.7 Quality changes in calamansi juice during storage at 55°C	69
4.8 Correlation coefficients among the quality parameters of calamansi juice	71
5.1 Quality changes in lemon juice stored at 36°C	78
5.2 Results of the computations for zero- and first-order reactions based on regression analysis	79
5.3 Comparison of the regression and point-by-point method for determining rate constants	80
5.4 Changes in dissolved oxygen levels in lemon juice stored at 36°C	82
6.1 pH of lemon juice during storage	102
6.2 Titratable acidity (%) of lemon juice during storage	103
6.3 Total soluble solids content (°Bx) of lemon juice during storage	104
6.4 Ascorbic acid retention (%) in lemon juice during storage	105

TABLE OF CONTENTS: CONTINUED

TABLE		PAGE
6.5	Results of the computations for zero- and first-order reactions of ascorbic acid degradation based on regression analysis	110
6.6	Computed Arrhenius coefficients and Q_{10} values	112
6.7	Results of the regression analysis using the linear model	115
6.8	Errors in calculated rate constants caused by analytical errors	118
6.9A	Two-way Anova for the rates of ascorbic acid degradation in lemon juice and concentrates (9-50°Brix)	120
6.9B	Two-way Anova for the rates of ascorbic acid degradation in lemon juice concentrates (20-50 °Brix)	120
6.10	Browning (absorbance at 420 nm) in lemon juice during storage	122
6.11	Results of the computations for zero- and first-order reactions of browning based on regression analysis	132
6.12	E_a and Q_{10} values for grapefruit juice during thermal and concentration processes	134
6.13A	Two-way Anova for the reaction rates of browning in lemon juice and concentrates (9-50 °Brix)	138

TABLE OF CONTENTS: CONTINUED

TABLE	PAGE
6.13B Two-way Anova for the reaction rates of browning in lemon juice and concentrates (20-50 °Brix)	138
6.14 Furfural formation (mg/L) in lemon juice during storage	143
6.15 Results of computations for zero- and first-order reactions of furfural formation based on regression analysis	145
6.16A Two-way Anova for the rates of furfural formation in lemon juice and concentrates (9-50 °Brix)	150
6.16B Two-way Anova for the rates of furfural formation in lemon juice concentrates (20-50 °Brix)	150
6.17 Changes in the perceived levels of fresh lemon flavour in the lemonade samples	152
6.18 Off-flavour development in the lemonade samples	153
6.19 Summary of the results of studies that determined storage life of citrus juices based on flavour characteristics	155
6.20 Reported levels of furfural corresponding to significant changes in flavour	157

TABLE OF CONTENTS: CONTINUED

TABLE	PAGE
6.21 Changes in colour in the lemon juice samples during storage	159
6.22 Storage life in weeks of lemon juice and concentrates based on the browning reaction	165
6.23 Computed activation energy (E_a) and Q_{10} values for lemon juice and concentrates	169
6.24A Two-way Anova for storage life of lemon juice and concentrates (9-50 °Brix)	171
6.24B Two-way Anova for storage life of lemon juice concentrates (20-50 °Brix)	171
6.25 Predicted storage life in weeks of lemon juice and concentrates	174

LIST OF FIGURES

FIGURE		PAGE
2.1	Degradation of ascorbic acid	5
2.2	Possible ascorbic acid degradation pathways	7
2.3	Percent vitamin C retention (logarithmic scale) vs. months of storage at 4, 24, 32 and 37°C for canned single-strength orange juice	10
2.4	Changes in optical density of concentrated grapefruit juice	11
2.5	Effect of solids content on the rate of ascorbic acid degradation (predicted results)	13
2.6	Arrhenius plots of log k (mg of vitamin C loss/100 mL of juice per week) vs. reciprocal of absolute storage temperature. The grapefruit plot shows one linear profile, whereas the orange plot shows two distinct profiles.	19
3.1	Standard curve for ascorbic acid	27
3.2	Standard curve for citric acid	42
4.1	Quality changes in lemon juice during storage (55°C)	51
4.2	Quality changes in lemon juice during storage at 55°C	59
4.3	Quality changes in lemon juice during storage at 55°C	65

LIST OF FIGURES: CONTINUED

FIGURE		PAGE
4.4	Quality changes in calamansi juice during storage at 55°C	70
5.1	Changes in dissolved oxygen levels in lemon juice stored at 36°C	82
5.2	Ascorbic acid retention in lemon juice stored at 36°C, at three levels of initial dissolved oxygen (0.41, 1.44 and 3.74 mg/L)	84
5.3	Browning in lemon juice stored at 36°C, at three levels of initial dissolved oxygen (0.41, 1.44 and 3.74 mg/L)	88
5.4	Browning in lemon juice stored at 36°C, at three levels of initial dissolved oxygen (0.41, 1.44 and 3.74 mg/L)	89
5.5	Furfural formation in lemon juice stored at 36°C, at three levels of initial dissolved oxygen (0.41, 1.44 and 3.74 mg/L)	92
5.6	HMF formation in lemon juice stored at 36°C, at three levels of initial dissolved oxygen (0.41, 1.44 and 3.74 mg/L)	93
6.1	Ascorbic acid retention in lemon juices and concentrates during storage	106
6.2	Arrhenius plots for ascorbic acid degradation in 9°Bx and 20°Bx lemon juices	114

LIST OF FIGURES: CONTINUED

FIGURE		PAGE
6.3	Changes in the rate of ascorbic acid degradation with increases in soluble solids level at 20°C and 36°C	114
6.4	Browning in lemon juices and concentrates during storage	131
6.5	Arrhenius plots for the browning reaction in lemon juice and concentrates	135
6.6	Changes in the rate of browning with increases in soluble solids level at 10, 20 and 36°C	135
6.7	Activation energy (E_a) values for browning and furfural formation in lemon juice and concentrates	136
6.8	Plot of the predictive model (Equation 6-7) for browning, showing the actual k values and the predicted regression lines for the lemon juice concentrates at 10 to 36°C	141
6.9	Furfural formation in lemon juices and concentrates during storage	144
6.10	Changes in rate of furfural formation with increases in soluble solids level at 10, 20 and 36°C	148
6.11	Arrhenius plots for furfural formation in lemon juice and concentrates	148

LIST OF FIGURES: CONTINUED

FIGURE		PAGE
6.12	Samples of lemon juices and concentrates (9-50 °Brix) after three months storage at 10, 20 and 36°C	160
6.13	Changes in colour in lemon juices and concentrates during storage	162
6.14	Changes in storage life with increases in soluble solids level at 10, 20 and 36°C	165
6.15A	Storage life plots of lemon juice and concentrates, showing the Arrhenius relationship between the natural logarithm of storage life and the reciprocal of absolute temperature	167
6.15B	Storage life plots of lemon juice and concentrates, showing the linear relationship between the natural logarithm of storage life and temperature	167
6.16	Plot of the predictive model (Equation 6-12) for storage life, showing the obtained storage life values and the predicted regression lines for the lemon juice concentrates 10 to 36°C	173