

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 Development of a Chemical Analogue  
of Thermal Destruction of Bacterial Spores

A Thesis Presented in Partial Fulfilment  
of the Requirements for the Degree of

Doctor of Philosophy

at Massey University

Gordon John Kitch Packer

1967

MASSEY UNIVERSITY



1061258282

### SUMMARY

A study has been made of methods in which chemical reactions are used to evaluate the total lethal effect of heat on the bacterial population in a sealed container of food material. The chemical reaction technique has also enabled a study to be made of the effect that the movement of the material within the container has on the lethality of the applied heat.

The relationship between the extent of a chemical reaction and the degree of destruction of bacterial spores is shown to depend both on the activation energies and decimal reduction times of the chemical and bacterial systems, and on the "heat penetration" characteristics of the material being processed.

Acid hydrolysis of sucrose, in buffered solution, was chosen as the model chemical reaction systems. It was used in the experimental study of two types of process, one with cans stationary, as in ordinary commercial batch retorts, and the other with the cans rotated "~~and over and~~" as in some commercial agitating batch retorts and continuous cooker-coolers.

The effect of convection on the extent of sucrose hydrolysis has been investigated. By combining records of can temperature with data on the rate of sucrose hydrolysis, the final concentration of sucrose has been calculated for a range of processes. These calculated values have been compared with those actually obtained in the can.

Theoretical considerations show that the effect of heat on bacterial and chemical systems as calculated from temperatures measured at points fixed with respect to the container, is not necessarily the same as that actually obtained in the container if convection takes place during the process. Simple convection models have been used to relate the extent of sucrose hydrolysis calculated from the temperature data, to that actually obtained in the can. These convection models show that the temperature at the geometrical centre of the can could be considered typical of the whole can for both static and agitated can processes.

The degrees of destruction of two micro-organisms with different "heat-resistances" have also been calculated from the can temperature data. These have enabled relationships between the sucrose hydrolysis and the spore destruction to be established. The effects of the various processing factors on these relationships, and on the rate of heat transfer to the can have been studied. The factors investigated were processing pressure and length of process, for static can and agitated can runs, and type and speed of rotation for agitated can runs only. The processing pressure in the agitated can runs, and the length of the process in both agitated and static can runs do not appear to have significant effects, but the effects of all other factors studied are significant.

The concept of equivalent time difference, which arises from the relationship between the extent of a chemical reaction and the degree of spore destruction has been defined and examined. Model temperature vs time curves for a greater range of processes and can sizes than that used in the experiments have been calculated using heat transfer rate data based on the agitated can runs, and the dependence of the equivalent time difference on the type of process and on the size of can is discussed.

Multiple reaction systems in which measurements of the extents of several chemical reactions, each with different activation energies, are used to estimate the degree of destruction of spores have been investigated. The model temperature vs time curves, derived for the analysis of the equivalent time difference concept, were used with data on the rates of the sucrose hydrolysis reaction, which has an activation energy of 22.35 kcal/mole, and on the rates of two hypothetical reactions with activation energies of 30 and 45 kcal/mole. Estimation of the degree of spore destruction using reactions in pairs or in groups of three is discussed.

If a pair of reactions is used, a knowledge of rates of heat transfer to the can is required for satisfactory estimation of the lethal effect of heat. If three reactions are used, the lethality of the process can be estimated without heat transfer rate data.



Errors arising in the estimation of the lethal effect of heat on bacterial spores using chemical reactions singly, in pairs, or in groups of three are discussed. The ~~maximum~~ errors in the lethality of the process as estimated using the various chemical reaction techniques were found to be less than one quarter of those arising from the same sources in traditional process calculation methods, in quite a number of instances much less. It is also shown that uncertainties arising from the necessary experimental measurements can be evaluated much more readily with a chemical reaction technique, especially the three reaction system, than they can in other methods of process evaluation.

## ACKNOWLEDGEMENTS

The author wishes to record his gratitude to the following;

Professor R. L. Earle, his supervisor, for his guidance and continual encouragement;

Mrs S. F. Rabone, and Miss M. Ward, who typed the draft and final copies respectively of this thesis, which, with its numerous equations and formulae has been far from straightforward;

The Dairy Production and Marketing Board for financial assistance during the early stages of the work; and

Mr William H. Terry of William H. Terry and Co., Ltd., Wellington, for assistance with the costs of preparation of this thesis.

The author also wishes to thank his parents for their encouragement throughout, and their financial help, especially during the later stages of the work.

---

## TABLE OF CONTENTS

<u>INTRODUCTION</u>	1
<u>THE DEVELOPMENT OF CANNING EQUIPMENT AND PROCESSING METHODS</u>	2
<u>MICROBIOLOGICAL DEVELOPMENT IN CANNING PRACTICE</u>	4
<u>DEVELOPMENT OF CALCULATION METHODS OF PROCESS EVALUATION</u>	5
(a) Basic Bacteriological Data	5
(1) Heat Resistance Determination Methods	5
(ii) Heat Resistance Data Interpretation	9
(b) Basic Heat Penetration Data	13
(1) Experimental Temperature Measurement Methods	14
(ii) Experimental Heating Curves and Heating Curve Parameters	18
(iii) Application of Heat Transfer Theory to Heating Curves	20
(c) Process Calculation	25
(1) Bases of Process Calculation	25
(ii) Techniques of Process Calculation	29
(iii) Non-mathematical Methods of Process Evaluation	35
<u>THE PRESENT WORK</u>	36
<u>ADDENDUM</u>	36
 <u>DEVELOPMENT OF THE CHEMICAL ANALOGUE OF SPORE DESTRUCTION</u>	 38
<u>INTRODUCTION</u>	39
<u>Development of the Investigation</u>	39
<u>Development of the Chemical Analogue Concept</u>	39
<u>Experimental Plan</u>	40
<u>DEVELOPMENT OF BASIC CHEMICAL ANALOGUE THEORY</u>	40
<u>Nomenclature</u>	40
<u>Definition of Terms and Integrals</u>	41
<u>Spore Destruction Estimation from Chemical Reaction (I)</u>	42
(a) Integration of lethal rate with respect to time at a single point	42
(b) Integration with respect to volume	43

DEVELOPMENT OF BASIC CHEMICAL ANALOGUE THEORY - cont.

<u>Spore Destruction Estimation from Chemical Reaction (II)</u>	44
(a) Integration of lethal rate with respect to time at a single point	44
(i) The $\theta$ vs $E_A$ function for a general process	45
(ii) The $\theta$ vs $E_A$ function for processes of known or assumed form	47
1. The $\theta$ vs $E_A$ function	47
2. Number of parameters for standard heat penetration curves	48
(iii) The $\theta_{bact}$ vs ( $\theta_{chem}(1)$ , $\theta_{chem}(2)$ ) function	50
(b) Integration of $\theta$ with respect to volume	51
(i) General unknown $\theta_{bact} : v$ and $\theta_{chem} : v$ distributions.	51
(ii) Known $\theta_{bact} : v$ and $\theta_{chem} : v$ distributions: development of convection models.	54
1. Stationary can	54
2. Agitated can	58

CHEMICAL ANALOGUE EXPERIMENTS 59INTRODUCTION 60Aim of the Project 60Resume of the work 60EXPERIMENTAL WORK 60Chemical System Development 60

(a) The ideal system	60
(b) Selection of the chemical system	61
(i) Kinetic characteristics of sucrose hydrolysis	61
(ii) Analytical characteristics of sucrose hydrolysis	62
1. Analysis	62
2. Effect of temperature	62
3. Mutarotation	62
(iii) Stability of the system	63

Chemical System Development cont.

(c) Measurement technique	65
(d) Rate of hydrolysis determination	67
(i) Low temperatures	67
(ii) High temperatures	67
(e) Calculation of the specific rate vs temperature tables	69
(i) Unbuffered sucrose : 0.00101 NHECI, 0.750 M sucrose	69
(ii) Buffered sucrose solution : pH 3.5	70

Temperature Measurement

	72
(a) Instruments	72
(b) Calibration of thermocouple wire	74
(c) Thermocouple circuits	74
(i) Can thermocouple junctions	74
(ii) Stationary can circuits	76
(iii) Rotating can circuits	80
(d) Sources of error in temperature measurement	83
(i) Conduction errors in thermocouples	83
(ii) Electrolytic errors	86

Processing Experiments

	88
(a) Equipment	88
(i) Steam supply	88
(ii) Experimental retort	88
1. Instrumentation	91
2. Steam supply	91
3. Compressed air supply	91
4. Cold water supply	91
5. Revolving crate drive	91
(b) Preparation of the retort for processing experiments	93
(i) Instruments	93
(ii) Wiring and filling of cans	93
(iii) Arrangement of retort thermocouples	95
(iv) Closing	95

Processing Experiments cont.

(c) Process cycle	95
(1) Holding period	96
(ii) Cooling period	96
(iii) Sampling	96
(d) Processing experiments	96
(1) Sucrose hydrolysis rate determination	96
1. Hydrolysis rate determination at 212°F	97
2. Rate of hydrolysis determination at retort temperature	97
(ii) Static can runs	99
1. Temperature distribution runs	99
2. Sucrose hydrolysis runs	99
3. Sucrose, milk, and water comparison	99
(iii) Rotating can runs	99

CALCULATION METHODS 103Calculation Data 103

(a) Chemical reaction rate data	103
(b) Bacterial destruction rate data	103
(1) Lethal rate vs temperature : <u>B.stearothermophilus</u>	105
(ii) Lethal rate vs temperature : <u>B.subtilis</u>	105

Tabulation 105Plotting and Integration 107Calculation of Equivalent Retort Times 109

(a) Equivalent retort time from temperature data	109
(b) Equivalent retort time from sucrose hydrolysis data	109
(c) Calculation of $H_0$ from measurement of sucrose hydrolysis in agitated tubes	110

RESULTS AND DISCUSSION 112Static Cans 112

(a) Temperature distribution runs	112
(1) Convection pattern	112
(ii) Heat transfer calculations	114

Static Cans cont.

(b) Sucrose hydrolysis runs	116
(i) Equivalent point determination	116
(ii) Equivalent retort time correlation ( $\theta_{\text{bact}}$ vs $\theta_{\text{chem}}$ )	124
(iii) Equivalent time differences	126
(c) Milk, water, and sucrose solution comparison	128

Agitated Cans

(a) Temperature distribution runs	130
(b) Sucrose hydrolysis runs	133
(i) Heat transfer coefficients	133
1. Calculation of overall heat transfer coefficients	133
2. Comparison of agitated can and static can overall heat transfer coefficients	136
(ii) Comparison of calculated and measured sucrose hydrolysis equivalent retort times	137
(iii) Bacterial equivalent retort times and equivalent time differences	139
1. Effect of type of organism (B)	145
2. Effect of speed of rotation (S)	147
3. Effect of type of rotation (R)	148
4. Effect of length of process (T)	149

Equivalent Time Difference Analysis 151

(a) The specific rate difference function	152
(b) Calculation of the model can temperature vs time curves	157
(i) The model processes	157
(ii) Rates of heat transfer to the model cans	157
(iii) Method of calculation of the temperature vs time curves for the model cans	158
(c) Equivalent time differences for the model cans	160
(i) Effect of type of organism on equivalent time difference	161
(ii) Effect of can size and type of process on equivalent time difference	164
1. Effect of total length of heating and cooling periods	167
2. Effect of can size : square process	167

	xi
3. Effect of can size : non-square process	168
4. Effect of length of process	169
(d) Application of equivalent time difference analysis conclusions to real processes	170

<u>FURTHER DEVELOPMENT OF THE CHEMICAL ANALOGUE</u>	173
---	-----

<u>INTRODUCTION</u>	174
---------------------	-----

<u>MULTIPLE REACTION SYSTEMS</u>	174
----------------------------------	-----

<u>Temperature vs Time Curves of Best Fit</u>	174
---	-----

<u>Method</u>	176
---------------	-----

(a) Two reaction systems	177
(i) Temperature vs time curves of best fit	177
(ii) Equivalent time difference correlations	181
(b) Three reaction systems	182
(i) Types of best fit curves	182
1. Type I curve of best fit	185
2. Type II curve of best fit	187
(ii) Comparison of the two types of best fit curve as methods of calculation of spore destruction	189
1. The best fit curves	193
2. Equivalent time differences and equivalent retort times	195
(iii) Modification of the analogue	196
(iv) Error in equivalent retort time due to error in measurement of retort temperature	199
(v) Integration with respect to volume	201

<u>CONCLUSIONS AND POTENTIAL APPLICATIONS OF THE CHEMICAL ANALOGUE</u>	205
--	-----

<u>CONCLUSIONS</u>	206
--------------------	-----

<u>Theoretical Considerations</u>	206
-----------------------------------	-----

<u>The Experiments</u>	207
------------------------	-----

(a) Static cans	207
(b) Agitated cans	208



CONCLUSIONS cont.

<u>Analysis of the Equivalent Time Difference Concept</u>	209
<u>Multiple Reaction Systems</u>	210
<u>General Conclusions</u>	212

POTENTIAL APPLICATIONS OF THE CHEMICAL ANALOGUE

(a) Method for checking process calculation assumptions	213
(b) Evaluation of new or modified processes	213
(c) Trouble shooting and control techniques	213
(d) Evaluation of the effect of heat on vitamin losses etc.	214
(e) Evaluation of the effect of heat in continuous flow systems	214
(f) Low temperature applications	214

SYMBOLS AND DEFINITIONS, REFERENCES, AND APPENDICES

SYMBOLS AND DEFINITIONS

REFERENCES

APPENDICES

I	Comparison of Mass Average Survival Ratios, Calculated using Fixed Point and Moving Element Temperature Data	236
II	Calculation of Equivalent Retort Time for Linear Processes	242
III A	Calculation of pR vs A Table	244
III B	Inversion of 0.750 M Sucrose : pR vs A Table	246
IV	Calculation of the Acetic acid - Sodium acetate Buffer	247
V	Specific Sucrose Hydrolysis Rate vs Temperature Table	250
VI A	Solution of the Equation for Heating of the Thermocouple Junction by Conduction along the Wire	251
VI B	Calculation of Heat Conduction Error in the Thermocouple Wire	259
VII	Lethal Rate vs Temperature Tables for <u>B.stearothermophilus</u> and <u>B.subtilis</u>	262
VIII	Sucrose Hydrolysis - $E_A:30$ Reaction : Specific Rate Difference vs Temperature Table	263
	Sucrose Hydrolysis - $E_A:45$ Reaction : Specific Rate Difference vs Temperature Table	264

APPENDICES cont.

IX	Calculation of Equivalent Retort Times for Linear Semi-logarithmic Processes	265
X	Coefficients $a$ , $b$ , $\Delta a$ and $\Delta b$ for Calculation of Parameters for Type I Curve of Best Fit	269
XI	Nomenclature of Can Sizes	270

---