Ernest Perez

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<u>Career history:</u>

2009 – present – Sr Engineer; Principal Engineer since 2018

NPTC/M Marysville, OH

- Thermal Process Establishment for pilot plant; Global markets -review thermal process specs for aseptic and retort processes
- Review, write and enforce technical standards and guidelines
- Technical assistance for Nestle markets CAPEX requests, insterility root cause, co-man assessments, new line commissioning

2007-2009 - Design Engineering Manager	NWNA, Coppell, TX
2003-2007 - Project Engineer	Gerber, Fort Smith, AR
'89-'92, '94-2001 – Production Supervisor & Aseptic Specialist	Nestle Nutrition, Eau Claire, WI
1992-1993 - Process Engineer	Nestle R&D Konolfingen, Switzerland
1988 – 1989 - Manufacturing Tech Services & Thermal Process Specialist	Nestlé Carnation, Los Angeles, CA

Education:

BS Food Process Engineering - Purdue University MS Food Science & Technology – University of California, Davis MBA – University of Wisconsin, Eau Claire

Hobbies and Interests: Family, Long Distance Running, NCAA Basketball

Market Technical Assistance:

Algeria, Argentina, Chile, Colombia, Costa Rica, Egypt, India, Indonesia, Mexico, Nicaragua, Netherlands, Peru, Thailand, Turkey, Venezuela, Vietnam







Kinetics of Microbial and Quality Factors in Thermal Processing

Institute of Food Thermal Process Specialists E. Perez February 28th, 2023



Fig. 6.62. Lines of equal degrees of denaturation drawn to demonstrate the temperature dependent changes in the rate constant

Why Discuss the Effect of Thermal Processing on Quality Attributes?



<u>Purpose</u>

Bring Awareness of the potential effect of thermal processing on food and beverage Quality attributes

<u>Importance</u>

- Thermal treatments have positive effects and may have *negative* effects
 - Loss of nutrients
 - Color and texture change
 - Formation of Unwanted Compounds

Expectation -

- 1. Be aware of different methods to quantify effects of thermal processes on food constituents
- 2. Be aware of effects of thermal processing on food & beverage quality indicators
- 3. Compare rates of reaction of microbial death kinetics to rates of nutrient degradation



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- Microbial Death Kinetics as starting basis
- Kinetic Models for Thermal Degradation of Nutrients and other Quality Indicator
- Compare Microbial Death Curves with Degradation of Food Components
- Nestle Thermokinetics App



Thermal Processing Definitions

- D_{Tref} Value Time it takes at <u>specified temperature</u> to kill 90% (1 log cycle) of a population of a specific Micro-organism.
- z Value The temperature change required to alter the D Value by a factor of 10.

Number of degrees of temperature required for the thermal death time curve (log F vs. T) to traverse one log cycle

- F Value Time for Equivalent microbe destruction (in minutes) at a given reference temperature.
- F₀ Equivalent microbe destruction in minutes at 121.1°C when z = 10°C (Used for C. botulinum)



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Thermal Processing Definitions – Graphic Representation of D_T Value



 D_T - value: Time in minutes at a specific temperature to reduce a population by 90%.

What is the D_T Value in this exmple?







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Thermal Processing Definition Graphic Representation of D Values at Different Temperatures



 $D_{120} > D_{128}$

D₁₂₀ = ~9.0 min D₁₂₈ = ~1.0 min

Decimal reduction (survivor curves) at different elevated temperatures



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Thermal Processing Definitions -Graphic Representation of z Value



 Z – value: the temperature increase required to cause a one log cycle reduction in the decimal reduction time

What is the z value in this example?



VS





Thermal resistance curve of a microbial population

D and z Values for Spore-Forming Bacteria

	Micro-organism	Approximate growth range (°C)	D-value range at 121°C (sec)	z-value range (°C)	Target D- value at 121°C ¹ (min)	Average z- value ² (°C)
	Geobacillus stearothermophilus	40-72	41-375	5.6-12	3.99	8.8
	Bacillus licheniformis	15-60	0.1-49	6.3-17.6	0.215	9.2
	Bacillus coagulans	25-65	1-94.8	8.1-24.1	.987	11.1
	Clostridium sporogenes	18-45	6-102	7.8-12.4	1.19	10
	Clostridium botulinum ³	3.3-48			0.21	10
	Bacillus pumilus	15-45	0.1-3.5	6.5-13.2	-	-
	Bacillus sporothermodurans	10-50	5-904	6.7-21.8	4.15	12.6
	Bacillus cereus	3-55	0.03-4	7.1-14.5	0.032	10.3



Thermal Processing Definitions -

Fo Value from General Method of Bigelow

Definition of Fo-value with constant Temperature

$$F_0(min) = \frac{t}{60} * 10^{(T-121.1)/z}$$

If, Temperature is dynamic

$$F_{\theta}(min) = \left(\frac{1}{60}\right) * \int_{t=0}^{t} 10^{(T-121.1)/z} dt$$

t = heating time, seconds

T = heating temperature, °C

z = 10 deg C the increase in temperature necessary to obtain the same lethal effect in one tenth of the time

 $F_o = 1.0$ when product is heated one minute at 121.1°C

Expressed in equivalent minutes at a reference temperature of 250°F or 121.1°C.

Microbial Sterilization Index:

 Measure of the level of sterility or microbial destruction delivered by a thermal process or heat treatment.



Food Reaction Kinetic Models Cook Value Model

C (min.) =
$$\frac{t}{60} * 10^{(T-100)/z}$$

$$C = \left(\frac{1}{60}\right) * \int_{t=0}^{t} 10^{(T-100)/z} dt$$

Where

- t = heating time, seconds
- T = heating temperature, °C
- z = the increase in temperature necessary for obtaining the same temperature effect in one tenth of the time

Original z value proposed for Cook value calculations is 33°C



Thermal Processing Kinetics -

D and z Values for Thermal Degradation of Food & Bev Nutrients

Component	Medium	Z (°C)	D _{121°C} (min)
Vitamin B12	Liquid Multi-Vitamin	28	1.94 days
Vitamin C	Liquid Multi-Vitamin	28	1.12 days
Lysine	Soybean Meal	21	13.1 hrs
Thiamine	Carrot Puree	25	158
Chlorophyll	Spinach	51	13







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Example of Relation between Fo and C values with varying temperatures

Temperature (°C)	Min Res Time (sec)	Fo (minutes) z = 10°C
121	360	6.0
130	45	6.0
135	14	6.0
140	5	6.0
141	5	8.3



Reaction Kinetics – Reaction Rate Order and Rate Equations

Zero-order Reaction

- Rate does not vary with increasing nor decreasing reactants concentrations.
- Destruction rate of a component is equal to a rate constant, k, for that reaction.

First-order Reaction

- Proceeds at a rate that depends on (only) one reactant concentration.
- Destruction rate of a component is dependent on the concentration of the component.



$$Rate = -rac{d[A]}{dt} = k[A]^0 = k = constant$$

 $|A| = [A]_0 - kt$

 $Rate = -rac{d[A]}{\mu} = k[A]$







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Food Reaction Kinetic Models Arrhenius Model

The dependence of the Reaction rate constant, k, on temperature is given by the Arrhenius equation:

$k = k_o e^{-E_a/RT}$

Where:

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 k_o = a constant known as frequency factor (min⁻¹)

 E_a = Activation energy (cal/mole)

R = ideal gas law constant (1.98 cal/mol K)

T = absolute temperature (K)







Thermal Processing Kinetic Parameters with Arrhenius Constants

Data for Milk from NIZO Institute

Component	Concentra -tion in Raw Milk	Type of Reaction	Temperature Range (deg C)	ln k	E _a , Activation Energy (kJ/mol)	Reaction Order
Bacillus stearothermophilus spores	100cfu/ml	Destruction	100 – 140	101.15	345.4	1.0
Bovine serum albumin	0.4 g/l	Denaturation	70 - 98	83.91	268	1.0
Catalase	100%	Inactivation	60 - 80	180.72	529	1.0
Color (browning)	0	Formation	50 – 160	29.09	116.0	0
Phosphatase	100%	Inactivation	60 - 80	135.15	393	1.0
Furosin	0 µmol/liter	Formation	120 – 150	24.28	81.6	0
Hydroxy-methylfurfural	0 µmol/liter	Formation	130 – 160	39.69	139	0
Lipase	100%	Inactivation	60 – 90	53.7	160	1.0
Lysine	2880 mg/lt	Loss	130 – 160	15.68	109	2nd
Lysino-alanin	0 µmol/liter	Formation	110 - 130	27.76	101.4	0
Thiamin	0.4 mg/lt	Loss	120 – 150	22.87	100.8	2nd



Food Reaction Kinetic Models Q₁₀ Model

Q₁₀ is defined as the increase in Reaction Rate for 10 degree C increase in temperature

$$Q_{10} = \frac{Rate_{T+10^{\circ}}}{Rate_{T}}$$

The Q_{10} values for most biochemical and enzymatic reactions fall within the range of 2 - 3

The relationship between z and Q_{10} is:

$$z(^{o}C) = \frac{10^{o}C}{\log Q_{10}}$$

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*Q*₁₀ concept applied for the prediction of a product's *shelf life* under "real-*life*" conditions compared to "accelerated" storage tests conducted at higher temperatures.



Some Potentially Undesirable Effects of Thermal Treatment

Vitamin Degradation

Maillard Browning compounds

HMF – Hydroxymethyl-furfural Furans Lysino-alanin

Lysine Blockage

Acrylamide

Color Change

De-stabilization of Emulsions







Fouling

Cooked Flavors



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Vitamins - Comparison of Heat Treatment with Other Stressors

Qualitative Effects of Heat, Light, Oxygen and Metals on Vitamins

0 ! ★ - Stable $\star \star \star \star - Very$ Unstable From "Food Product **Development: From** concept to marketplace" ed. By Ernst Graf and Israel Sam Saguy, 1991 by Van Nostrand Reinhold

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Soluble

Water Soluble

Vitamin	Heat
Vitamin A and D	***
Vitamin E	**
Vitamin K	*
Ascorbic Acid (C)	***
Thiamine (B1)	****
Riboflavin (B2)	*
Niacin (B3)	*
Pyridoxine (B6)	*
Cyanocobalamin (B12)	*
Pantothenic Acid	***
Biotin	*
Folic Acid	*



Differences in Destruction Curves – Microbial Spores versus Quality Indicators



Source: H.G. Kessler

Medium = Milk

Dairy Engineering; Tetra Pak Dairy Handbook

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Nestle THERMOKINETICS – Published Internal Nestle Application

• What can THERMOKINETICS calculate?



- 1. Mainly based on Dairy Science and Technology
- 2. Limited raw materials mainly liquids and not powders
- 3. Considers thermal reactions...parallel reactions could also exist





• Once you are in...

	Documentation		
PRINT BUTTON IS FUNCTIONAL Published by Diego	to Larrain on 2021-07-02 09:04:38		
but the results table still need to be expanded coming very soon.	mysim training viceo	Thermokinetics/PREPROD Create Case Results Reference cases Manage Data -	
Significant updates now online! Published by Diego	go Larrain on 2021-06-24 15:42:13 Help / Feedback		
Improved view for the results Improved comparison view	- Topp - F - Goldmann	Assemble your data subsets to create a named case	Welcome back Ernest. ×
Have a try and feedback!		CREATE NEW CASE	SCHEMATIC
Copyright © 2023 Process Modelling Group	Powered by	Case Name ACME Dairy Fresh Milk Based Coffee Drinks Group Default Comments Time [s] Temperature [°C] 1 0 10 2 15 45 3 50 78 4 65 78 5 80 30 6 20 7	Data can be copy-pasted from Excel! $ \begin{array}{c} $



✿ADMIN

Buonaiorno Ernest

Whey Protein Denaturat	ion				
Thermokinetics - Reaction Selection	X	J			
Product 5002 Milk (skimmed, 0 % fat) SMU 141 Homogenized No	Customized	Microbial Dea	ith		
TS 9.00 % Temperature 2.0 °C Mass Flow 100000 kg/h Reaction Components	De Thermokinetics - Reaction Sel Product S002 Milk (s Homogenized No TS 9.00	lection skimmed, 0 % fat) SMU 141 %	Customized	Formation of Rxn	Compounds
Whey Protein Denaturation (Components)	Temperature 2.0	°C	Thermokinetics - Reaction Sele	ection	X
Components Medium Reference	Mass Flow 10000 Reaction Internal Death Kinetic Thermal Death Kinetic Ovirus type 2 (PCV2) high heat r Micrococc, luteus cells (WM) Clostridium botulinum spores, J Bacillus coagulans spores (WM) Bacillus coagulans spores (WM) Bacillus stearotherm. spores (WB) Bacillus stearotherm.spores (WD)	Components © Default Customized Medium Reference Medium Reference Medium Reference Medium Reference Medium Reference Operation Operation Medium Reference Reference Operation Medium Reference Operation Operation Operation Operation Operation Operation Operation Operation Operation Operation Medium Reference Description Operation Medium Reference Reference Operation Operation Operation Operation Operation Operation Operation Operation Operation Operation Operation Operation Operation Operation Operation Operation Operation	Product 5002 Milk (sl Homogenized No T5 9.00 Temperature 2.0 Mass Flow 100000 Reaction Formation	kimmed, 0 % fat) SMU 141 % °C D kg/h Components © Default © Customized	Customized Default
	Bacillus licheniformis spores, Al	ŭ <u>ko 27</u> ▼	Components Colour Furosine (WM) Hydroxymethylfurfural (WM) Lactulose (SM) Lactulose (VM) Lactulose (WM)	Medium Reference	2 Cancel

- 1. 1st Order and Zero order Reactions
- 2. 33 Total Reactions reported
- 3. Destruction and formation Rxns based on Ea and In(k) values
 - a) Exception is Fo calculation



<u>Case Study:</u>

Dairy Co-Man in India

- 1. Existing Fresh Milk (>82%) + sugar and coffee recipes
- 2. Existing FW Immersion Retort with high C values
- 3. New larger WS Retort Temp Dist and Heat Pen Study
- 4. Desired Fo Target > 18 minutes
- 5. Flavor match important
- 4. How much Eurosine and HiviE (ivialiard chemical markers) are formed?
- 5. How well is heat resistant protease dealt with?
- 6. How much Lysine is retained?
- 7. How much Thiamine is retained?

- HTST Treatment of Fresh Milk Based RTD Beverage
 90 deg C / 60 seconds
- 6 Basket Water Spray Retort Process
 □ 34 minute Come Up Time to 123°C
 □ 16 minute Sterilization Hold Step @ 122°C
 □ Cooling to RT < 35°C
- 2nd Scenario with Extended Hold to try to match existing retort process
 26 minute Sterilization Hold Step

Recommendation – Run 2 simulations in each scenario

- 1. Fo and Microbial Death Kinetics Cold Spot Temperature and minimum residence time
- 2. Average Temperature and flow velocities for other reactions



Simulation Output:



Tabular Comparison of 2 Different Thermal Processes with Different Sterilization Hold Times - 16 min vs 26 min @ 122 deg C

CUT (minutes)	Sterilization Step Time (minutes)	Total Fo (min)	Cook Value, C (min)	Log Rdxn Geobacillus stearothermophilus spores, FS 1518	Formation of Furosine (Micromol/liter)	Formation of HMF (Micromol/liter)	Inactivation of Pseudomonas heat-resistant protease (% Remain)	Loss of Lysine (Based on skim milk) % Remain	Loss of Thiamine (Based on skim milk) % Remain
34	16	19.8	121	7.5	807	190	0.06%	87.5%	58.8%
34	26	31.9	175	12.1	1150	285	0.003%	82.4%	46.1%



Conclusion

- Quick Review of 3 approaches to quantify thermal degradation
 Cook Value
 - Arrhenius equation
 - **Q**₁₀
- Compared Microbial death kinetics with thermal degradation kinetics

 A case study of a program we can use in Nestle R&D to calculate the effects of thermal process on various quality attributes using the approaches presented







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THANK YOU!



