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A Computerized Procedure for Estimating Chemical Changes in Thermal Processing Systems

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Abstract: Chemical changes caused by heating in a continuous flow, helically coiled tube indirect UHT process system were evaluated and compared to a non-flow, vat process system. On the basis of known formulas for evaluating bacterial destruction, a computerized procedure was developed to estimate the rates (R) and accumulated values (L_d) of chemical changes in the various stages of the UHT and vat thermal processes. Data were based on 149°C for 3.3 sec holding time in the continuous flow UHT process and compared to 82°C for 30 min holding time in the non-flow vat process system. The heat effect of the above heat treatments based on the 121°C reference temperature and a z-value of 7.2°C was approximately equal to 1.0 for the non-flow vat process and equal to 0.8 for the continuous UHT process. For UHT and vat processes that have L_d values equal to 1.0, the residence times in the holding sections were, 4.2 sec and 30 min, respectively. Approximately 10% of the overall chemical changes occurred during the heating period for both processes, 86.1% approximately during the holding periods and 1.5 and 6%, respectively in the UHT and vat processes during cooling.

Key words: UHT, vat thermal processing systems, chemical changes

INTRODUCTION

Food products are subjected to thermal processing to achieve certain heat effects. These effects can be classified into two groups: (1) those which lead to the destruction of spores and vegetative cells of microorganisms and (2) those which cause chemical and/or physicochemical changes resulting in quality degradation and nutrient losses. Both are temperature dependent and can be described by a z-value in the range from -5.5 to -11°C for bacterial spore inactivation and of 7.2 to 26.7°C for chemical changes affecting quality and nutritive values. The z-value indicates the temperature increase required for a ten fold change in the rate of chemical changes or microbial inactivation.

The difference in temperature requirement for chemical changes and microbial inactivation makes it possible to select process time-temperature parameters to optimize product quality retention (Lund, 1977).

Sahoo *et al.* (2002) designed and tested a laboratory model indirect type helical tube UHT milk sterilizer. The holding section was designed based on the Arrhenius model to reduce *B. stearothermophilus* microorganisms in the milk by 8 log cycles at a sterilization temperature of 150°C with a residence time of 2.64 sec. The helical double tube cooling section modeling and simulation was carried out to cool milk from 150 to 90°C.

Milk fouling is the main cause of progressive decline in the rate of heat transfer in a UHT milk sterilizer, which results in a drop in milk outlet temperature as the processing advances. Increasing

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steam temperature is one of the ways to overcome the drop in milk outlet temperature and prolong the operating time before the processing is stopped for cleaning of deposits in the heat exchanger. A computer model was developed by Nema and Datta (2005) for the accurate control of milk temperature as affected by fouling calculating accurately the increase in steam temperature required for maintaining the desired milk sterilization temperature.

A model for indirect thermal treatment of milk was implemented by Grijspeerdt *et al.* (2004) and applied to three commercial heat exchanger systems: two systems using tubular heat exchangers, albeit very different ones and a plate type heat exchanger system. The model emphasis was placed on fouling prediction and bacterial inactivation, but other heat induced reactions were also included. The model was able to reproduce the time-temperature profiles satisfactory in all three cases. Some optimisation strategies with respect to fouling minimization were simulated. For all cases, it was not possible to obtain major improvements using only the available degrees of freedom. However, the model predictions indicate that significant reductions in fouling are possible when applying minor redesigning to the systems. Especially the location of a preheating section proves to be of major importance.

Heat transfer during food processing plays important role for thermal process optimization (Ohlsson, 1980a). The microbial inactivation is evaluated at its minimum value, while the chemical changes are evaluated as volume average value (Ohlsson, 1980b). However, there are many empirical and theoretical procedures for evaluating the heat effects in food processing. Hayakawa and Timbers (1977) classified these procedures into two groups: group I, those based on the evaluation of heat energy applied at a specific location of a food product (Bigelow *et al.*, 1920; Ball, 1923; Hayakawa and Timbers, 1970; Stumbo, 1973) and group II, those based on the evaluation of heat energy applied to an average mass element of a food product (Ball and Olson, 1957; Gillepsy, 1951; Hayakawa and Timbers, 1969). Group II procedures are required for estimating quality factors or chemical destruction in processed foods, while procedures of both groups produce results in evaluating microbiologically safe processes (Hayakawa, 1977). However, the time-temperature distribution for the changes during thermal processing is necessary (Ohlsson, 1980b).

Hayakawa and Timbers (1977) showed the z-values for the color destruction of green vegetables upon thermal processing ranged to an average of 40 to 41°C. On the other hand, the z-values for organoleptic quality changes ranged from 27.8 to 32.2°C for different vegetables (Hayakawa *et al.*, 1977). A z-value of 7.2°C was reported by Karel *et al.* (1975) for browning reactions in milk processed at high temperatures.

This study presents a computerized procedure to evaluate the extent of chemical changes that take place during thermal processing. The procedure could also be used to determine the conditions necessary to optimize quality and/or nutrient retention.

MATERIALS AND METHODS

Rate of Chemical Changes

Thermal effects were calculated both for a continuous flow indirect UHT system (149°C for 3.3 sec) and for a non-flow vat system (82.2°C for 30 min). The criterion for estimating chemical heat effects of a thermal process is defined as the rate of chemical change. The heat effect on chemical changes was estimated on the basis of reported equations by Bigelow (1921) and others to define the effect of heat on thermal destruction of microorganisms. It is possible to get an accurate estimate of the heat effect on chemical changes in the same way as bacterial destruction is estimated by using the basic empirical equation defining the thermal death time curve (Bigelow, 1921) and using values taken from the process profile curves (Fig. 1, 2). This empirical equation can be written in this particular case as:

$$\log \frac{CCT_i}{CCT_j} = (-1/z) (T_i - T_j) = (T_j - T_i)/z \quad (1)$$

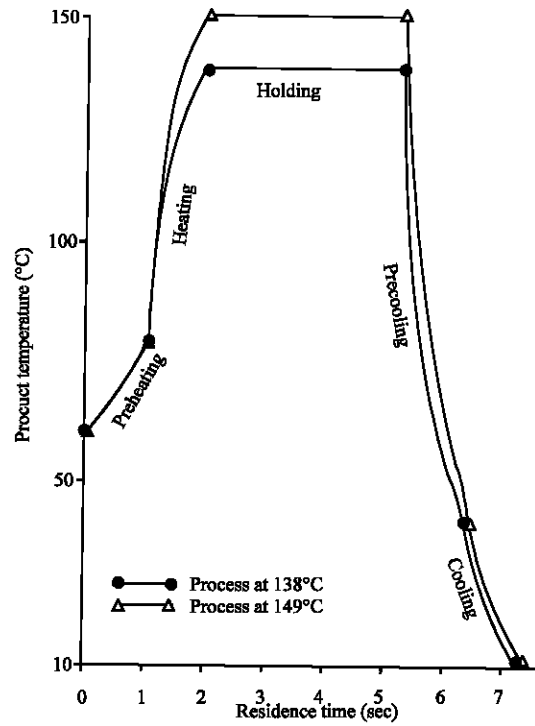


Fig. 1: Time-temperature distribution in the various stages of an indirect, helically coiled tube, UHT system at flow rate of 5 l min⁻¹

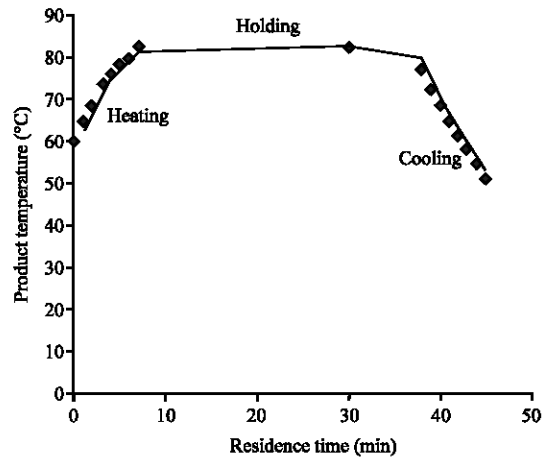


Fig. 2: Time-temperature distribution in the various stages of a conventional vat process system

where:

CCT_i = Chemical change time at temperature T_i ,

CCT_j = Chemical change time at reference temperature T_j ,

z = The temperature required for the log of CCT to decrease by one unit.

This equation can be written as

$$\log (CCT_j/CCT_i) = (T_i - 250)/z \quad (2)$$

or

$$1/CCT_i = 10^{(T_i - 250)/45} \quad (3)$$

by substituting the CCT_j notation as the thermal destruction time equivalent to 1 min at the convenience reference temperature of 121 °C and by using an average Q_{10} value equal to 2.5 for chemical reactions, which gives a z value equal to 45 ($z = 18/\log Q_{10}$, Karel *et al.* (1975). The term $1/CCT$ (Eq. 3) representing the rate of heat effect at temperature T_i can be called chemical change rate. It can be used for calculating accumulated chemical changes of the processes under consideration.

Accumulated Chemical Changes

The ratio (L_d) of the time, t , at a constant temperature to the CCT_i , at that process temperature might be defined as accumulated chemical changes,

$$L_d = t/CCT_i \quad (4)$$

Although the heat effect on chemical changes is defined for a constant temperature process, the definition can be applied to a variable temperature process by obtaining an equivalent constant temperature process that would produce the same heat effect on chemical changes. The rate of chemical changes was obtained by taking the derivative of Eq. 4 with respect to time,

$$dL_d/dt = 1/CCT_i \quad (5)$$

or

$$dL_d/dt = 10^{-(T_i - 250)/45} \quad (6)$$

Hence, according to Eq. 1 the rate of chemical changes is a function of only one variable, i.e., the process temperature. Integration of Eq. 6 over the processing time will give the heat effect on chemical changes of the process as follows,

$$L_{d_{tot}} = \int_0^t (dL_d / dt) dt \quad (7)$$

A computer program was written that simultaneously estimated the total heat effect of the process as a function of temperature, residence time, z -value and reference temperature according to Eq. 8:

$$L_{d_{tot}} = L_d + t \left[\left(\frac{1}{CCT_i} \right) + \left(\frac{1}{CCT_{i+1}} \right) \right] / 2 \quad (8)$$

where:

- $L_{d_{tot}}$ = Total accumulated chemical changes,
- L_d = Accumulated chemical changes for a specific time,
- t = Interval time from temperature T_i to T_{i+1} ,
- $1/CCT_{i, i+1}$ = Rate of chemical changes at temperature T_i and T_{i+1} .

A flow chart of this program is shown in Fig. 3.

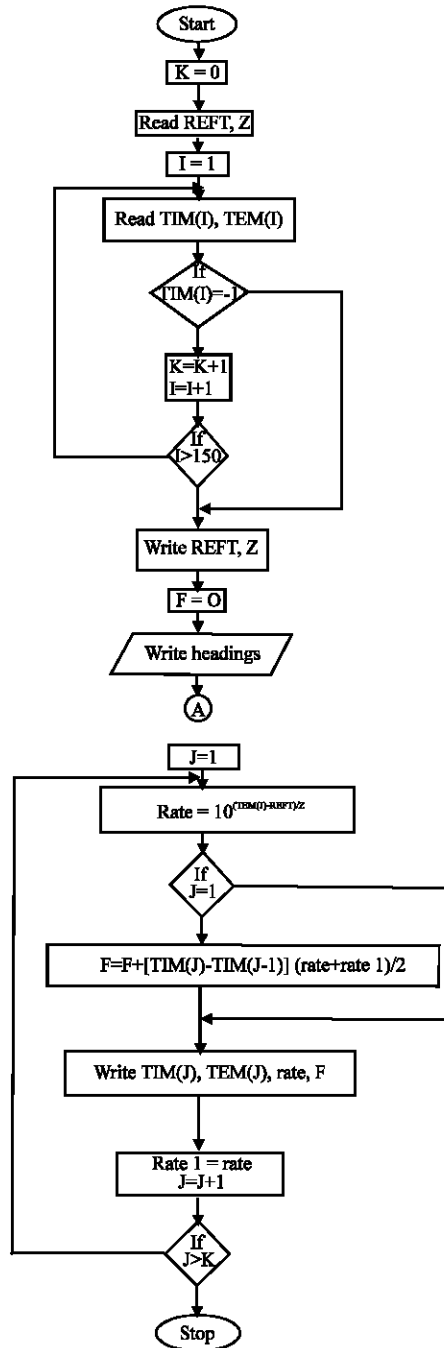


Fig. 3: Flow chart of a computerized process evaluation

Processing System Assumptions

To illustrate, assume that a fairly common fluid e.g., milk is to be processed in a helically coiled tube, indirect steam heated UHT heat exchange system. The spread of retention times among

constituents is considered negligible. The process is treated as if all of the fluid through the heat exchangers travels at an average velocity (slug flow) sufficient for turbulent flow. For comparison purposes, a non-flow vat process system was used. Temperature distribution for the UHT and vat thermal processes (Fig. 1, 2) (Labropoulos, 1980).

RESULTS AND DISCUSSION

When determining commercial sterilization processes for foods, the effect of the thermal treatment upon the food product quality should be considered. The activation energies characterizing the degradation of nutrients and quality factors are similar to those for chemical reactions (Karel *et al.*, 1975). A well documented fact is that the z-values for chemical reactions involving degradation of nutrients and of other quality factors are larger than those for bacterial spores. In this study, a z-value of 45 was adopted on the basis of the studies by Burton (1963) and Karel *et al.* (1975) on chemical and physicochemical changes of food constituents during heating. Also, for purposes of determining the effect of the diverse heat treatments on fluids such as milk, it was found convenient to express the heat effect in terms of chemical change values at some reference temperature. Obviously, 121°C was a convenient reference temperature to be assumed, since it is the most common used in studies of thermal process evaluations. In addition, 121°C is a convenient reference temperature for low acid food thermal processing. This approach establishes a value of chemical changes equal to 1.0 as the starting basis for the thermal process evaluation of UHT and vat processes. Equation 3 was utilized in order to express the heat effect on chemical changes at process temperature T_i in terms of the heat effect on chemical changes at the reference temperature 121°C. Using Eq. 7 for example, for the product temperature 149°C the accumulated heat effect on chemical changes was 12.9. This means that the heat effect on chemical changes of 1 min at temperature T_i is equivalent to 12.9 min at 121°C.

Since the rate of chemical changes, $1/CCT_i$, is only the function of product temperature and z-value, a series of chemical changes rate values was used as a basis for the thermal process evaluation. The results show that the accumulated heat effect on chemical changes obtained in the UHT process is comparable to that of vat process (Table 1). The heat effect on chemical changes and bacterial spore destruction for different total process residence times (Table 2). For UHT and vat processes that have L_d values equivalent to 1.0, the process holding times are, respectively, 4.2 sec and 30 min. For an L_d value equivalent to 0.8 for both processes, the process holding times are 3.3 sec and 23 min, respectively. On the other hand, for UHT and vat processes that have equivalent cumulative L_d values, the bacterial spore destruction values (F_0) are, respectively, 45 and 0 (Table 2). This means that the UHT process has an F_0 value that is much greater than that for a vat process with equivalent cumulative chemical change (L_d) values. The high accumulated chemical change values of the UHT process in relation to its processing time are obviously due to the rate of chemical changes per unit of time at the elevated temperatures and flow property characteristics.

Thus, for the UHT heat treatment, 9.8, 88.3 and 1.9% of the total accumulated chemical change values occurred, respectively during the heating, holding and cooling periods (Table 3). The major portion of the heat effect on chemical changes occurred during the process holding time for both UHT and vat processes. A very small portion of the heat effect on chemical changes was obtained during the cooling period for both heat treatments. According to Read *et al.* (1957) there are no reported data on the importance of bacterial destruction during the cooling period for evaluating straight tube turbulent flow systems. Burton (1958) claimed that the bacteriological destruction during the cooling period was insignificant in plate type systems. On the other hand, in commercial UHT processes, the bacteriological thermal destruction of heating and cooling periods are neglected when prescribing equivalent heat treatments (Hsu, 1970). This procedure could result in some degree of undesirable destruction of nutrients and in unnecessary organoleptic changes.

Table 1: Chemical change rates (R) and accumulated chemical change (L_a) values in coiled tube, UHT and conventional vat process systems

Section	UHT processing system				Vat processing system			
	Time (sec)	Temp. (°C)	(R × 10 ³)	(L_a × 10 ³)	Time (min)	Temp. (°C)	(R × 10 ³)	(L_a × 10 ³)
Heating	0.0	60.0	3.59	0.006	0.0	60.0	3.59	
	0.1	78.3	4.04	0.014	1.0	64.4	5.41	4.50
	0.2	62.7	4.59		2.0	68.3	7.74	11.08
	0.3	64.2	5.28	0.022	3.0	73.3	12.27	21.09
	0.4	65.8	6.12	0.031	4.0	75.6	15.06	34.75
	0.5	67.6	7.21	0.042	5.0	77.8	18.48	51.52
	0.6	69.4	8.58	0.056	6.0	79.4	21.54	71.73
	0.7	71.4	10.31	0.071	7.0	82.2	27.83	96.22
	0.8	73.7	12.65	0.090				
	0.9	76.1	15.77	0.114				
	1.0	78.6	19.95	0.144				
	1.1	79.4	21.54	0.178				
	1.2	97.1	109.09	0.287				
	1.3	110.5	376.32	0.692				
	1.4	120.8	974.74	1.818				
	1.5	128.7	2015.78	4.310				
	1.6	134.7	3503.04	8.090				
	1.7	139.4	5384.05	16.315				
	1.8	142.9	7432.07	26.995				
	1.9	145.6	9549.97	41.146				
	2.0	147.7	11540.44	58.722				
Holding	2.1	149.0	12915.48	79.102				
	3.3	149.0	12915.48	710.351	30.0	82.2	27.83	834.76
Cooling	5.5	129.0	2046.97	801.922	38.0	76.7	16.68	953.24
	5.6	112.2	444.01	803.995	39.0	72.2	11.08	967.12
	5.7	98.4	123.34	804.465	40.0	68.3	7.74	976.53
	5.8	86.9	42.77	804.604	41.0	64.4	5.41	983.10
	5.9	77.3	17.74	804.654	42.0	61.1	3.98	987.80
	6.0	69.3	8.49	804.676	43.0	57.8	2.93	991.26
	6.1	62.8	4.64	804.686	44.0	54.4	2.15	993.80
	6.2	57.3	2.80	804.692	45.0	51.1	1.58	995.67
	6.3	52.7	1.83	804.696				
	6.4	48.9	1.29	804.699				
Total	6.4			804.699	45.0			995.67

Table 2: Comparative chemical changes (L_a) and bacterial spore destruction values (F_0) for UHT and vat thermal processes at a reference temperature of 121°C

Process system	Process temp. (°C)	Holding residence time	Total residence time	(L_a) ^a	(F_0) ^b
UHT	149.0	4.2 sec	7.3 sec	1.0	45.0
UHT	137.8	1.0 sec	4.0 sec	0.1	1.0
UHT	149.0	0.1 sec	3.2 sec	0.1	3.6
VAT	82.2	30.0 min	45.0 min	1.0	0.0
VAT	82.2	125.0 h	125.0 h	209.0	1.0

^a: For z = 45, ^bFor z = 18

Table 3: Computed accumulated chemical change (L_a) values per stage of the UHT and vat processes

Processing stage	UHT system				Vat system			
	Accum. chem. changes				Accum. chem. changes			
	Residence time (sec)	Temp. range (°C)	(L_a) ^a	(%)	Residence time (min)	Temp. range (°C)	(L_a)	(%)
Heating	2.1	60-149	0.079	9.8	7.0	60-82.2	0.096	9.6
Holding	3.3	149	0.710	88.3	30.0	82.2	0.835	83.8
Cooling	1.0	49-149	0.015	1.9	8.0	49-82.2	0.065	6.5
Overall	6.4	49-149	0.804	100.0	45.0	49-82.2	0.996	100.0
Overall ^b	7.3	49-149	0.998		38.0	49-82.2	0.801	

^a: Chemical change values based on 121°C reference temperature. ^b: If 4.2 and 23 min process holding times are used, respectively in the UHT and vat systems

Since the accumulated chemical change values increased during the cooling process period as the process temperature increased, it indicates that the contributed heat effect on chemical changes during the cooling period must be taken into account, especially when high temperatures are used. Thus, for highly heat sensitive products it is necessary to take into account the heat effect on chemical changes during both the heating and cooling periods of the process.

Equivalent L_d values of chemical changes for the two mentioned processes were obtained by estimating the process holding time while keeping temperature constant. It could also be done by estimating the temperature while keeping time constant. A total accumulated L_d -value of 0.99 for chemical changes was obtained for both process systems by increasing the UHT holding time in to 4.2 sec at 149°C. A total accumulated L_d of 0.80 for chemical changes was the equivalence between the two systems by decreasing the vat process holding time to 23 min at 82.2°C.

The rates of chemical changes ($1/CCT_i$) already determined at regular intervals can be plotted against process residence time. The area under the resulting curve will give an approximation of the total heat effect on chemical changes which in essence has already been calculated.

CONCLUSIONS

A computerized procedure for evaluating the heat effect in variable temperature continuous flow UHT and non-flow vat thermal processes has been developed based on similar procedures used for calculating bacterial spore destruction by heat. The mathematical analysis provides a basis to evaluate and compare similar processes.

The three stages of the UHT system were evaluated by calculating the percentage of chemical changes in each stage. More than 80% of the accumulated chemical changes occurred during the process holding time, less than 10% during the process heating time and approximately 2% during the cooling period. Thus, the evaluation of heat effects on chemical changes for both continuous flow and non-flow processes could be based mainly on the process holding stages. However, for an accurate evaluation for a process, the total accumulated chemical change values in the three stages must be taken into account. An estimation of the heat effects on chemical changes could serve as a guide for evaluating quality and nutrient retention in heat sensitive products during thermal processing.

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